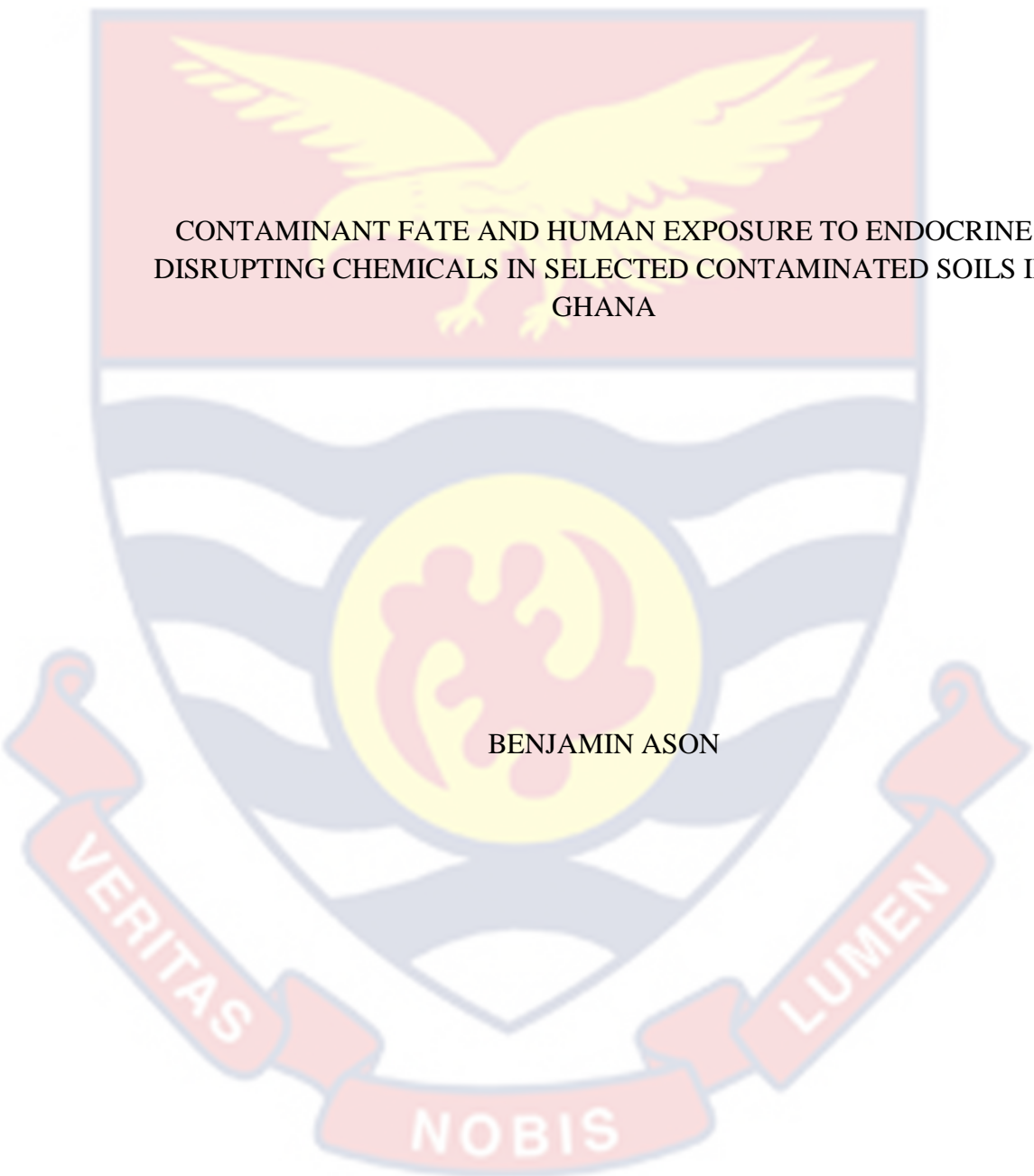


UNIVERSITY OF CAPE COAST



CONTAMINANT FATE AND HUMAN EXPOSURE TO ENDOCRINE
DISRUPTING CHEMICALS IN SELECTED CONTAMINATED SOILS IN
GHANA

BENJAMIN ASON

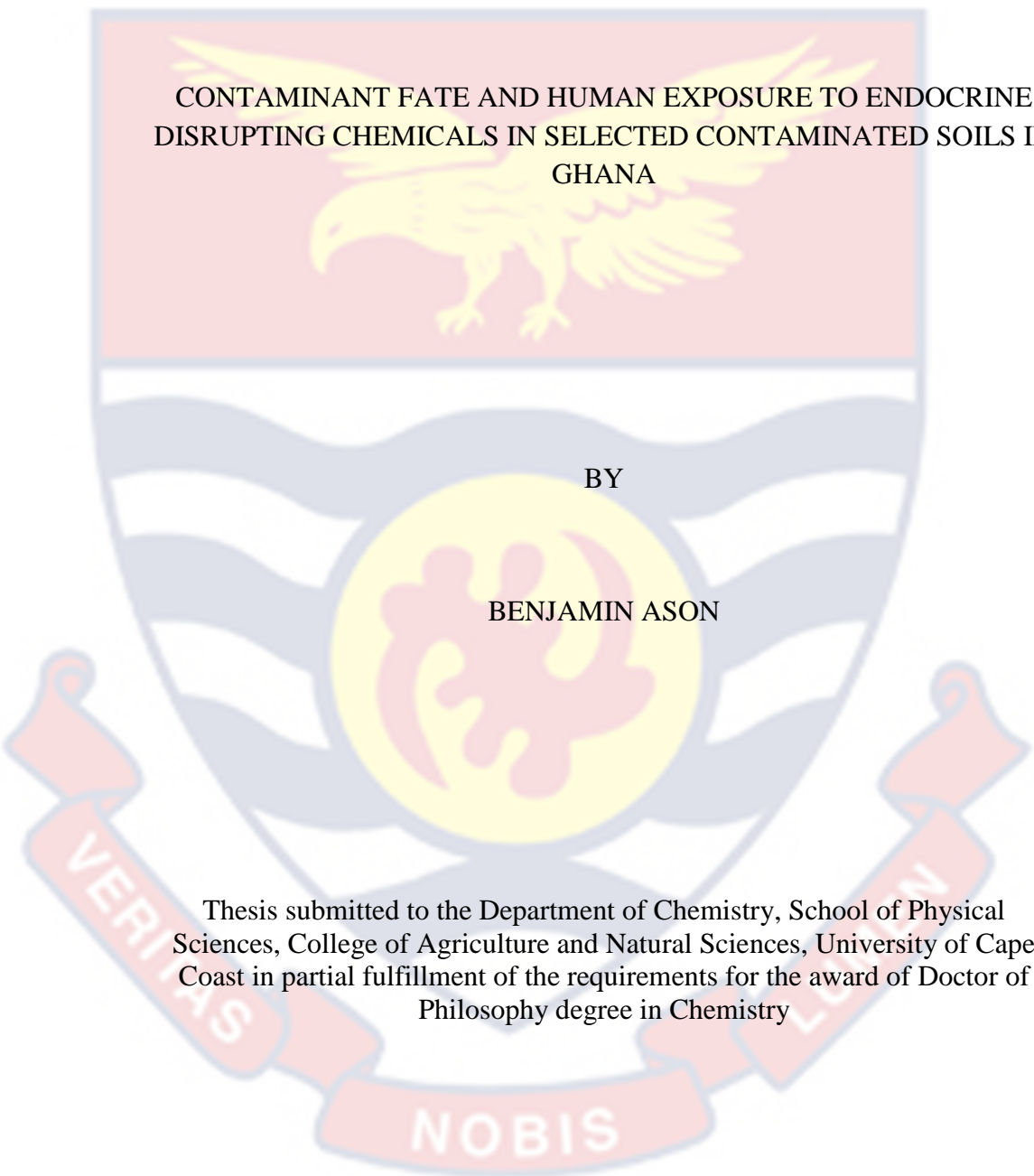
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CONTAMINANT FATE AND HUMAN EXPOSURE TO ENDOCRINE
DISRUPTING CHEMICALS IN SELECTED CONTAMINATED SOILS IN
GHANA

BY

BENJAMIN ASON

Thesis submitted to the Department of Chemistry, School of Physical
Sciences, College of Agriculture and Natural Sciences, University of Cape
Coast in partial fulfillment of the requirements for the award of Doctor of
Philosophy degree in Chemistry

DECEMBER 2022

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my original research and that no part of it has been presented for another degree in this university or elsewhere.

Candidate's Signature..... Date

Name: Benjamin Ason

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised following the guidelines on supervision of thesis laid down by the University of Cape Coast.

Principal Supervisor's Signature..... Date.....

Name: Professor David Kofi Essumang

Co-supervisor's Signature..... Date.....

Name: Professor Frederick Ato Armah

ABSTRACT

The study was based on quantitative methods. The quick, easy, cheap, effective, rugged, and safe (QuEChERS) analytical method was used for the extraction and cleanup to quantify endocrine disrupting chemicals (EDCs) in agricultural soils and female blood samples. Four composite soil samples were taken from Accra and Cape Coast to represent cultivated soils, industry, decommissioned waste dump and forest reserve at a depth of 30cm for the analysis of potentially Toxic elements (PTE) (Fe, Cd, As, Pb Ni, Co, Cu, Zn, Mn), Phthalates and Bisphenol A. Twelve composite samples were taken per site to determine soil quality. Menstrual blood, samples were collected on aluminum foil and transferred into a vacutainer tube. Also survey questionnaire administered to 300 respondents in selected communities was used to determine individual understanding of pesticide use and health effects of EDCs. Ordinary least squares regression and multivariate statistics were fitted to the data obtained. The study indicated low level of knowledge of health effects of EDCs among the three communities. The study also indicated that generally PTEs and EDCs in soils were within recommended thresholds except for arsenic (As) and bisphenol A (BPA). Similarly, carcinogenic exposure risks of Benzyl butyl phthalate (BBP) and Bis (2-ethylhexyl) phthalate (DEHP) via non-dietary routes were lower than 1×10^{-6} however; the ingestion cancer risk (CR) values of Cadmium (Cd), Arsenic (As) and Lead (Pb) exceeded the threshold value. Traces of Diethyl phthalates (DEP), Dibutyl phthalate (DBP) and Bis (2-ethylhexyl) phthalate (DEHP) were found in menstrual blood ahower, the carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} .

KEYWORDS

Endocrine disruptors

Knowledge

Menstrual blood

Soil

Toxic elements

Waste



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DEDICATION

To my wife Theresa, children Daniel, Miriam, Marian and entire Ason Family



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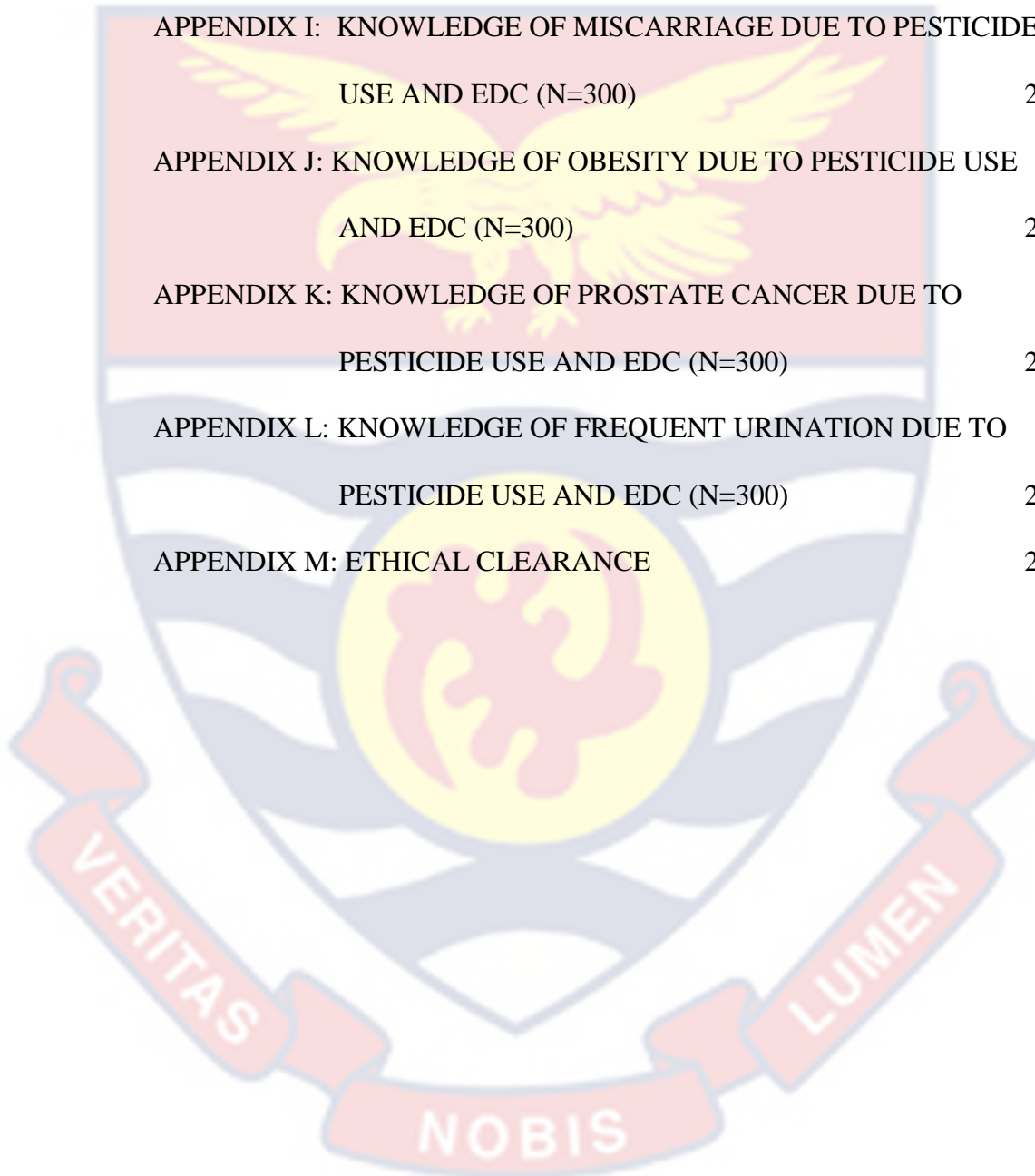
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LIST OF ABBREVIATIONS

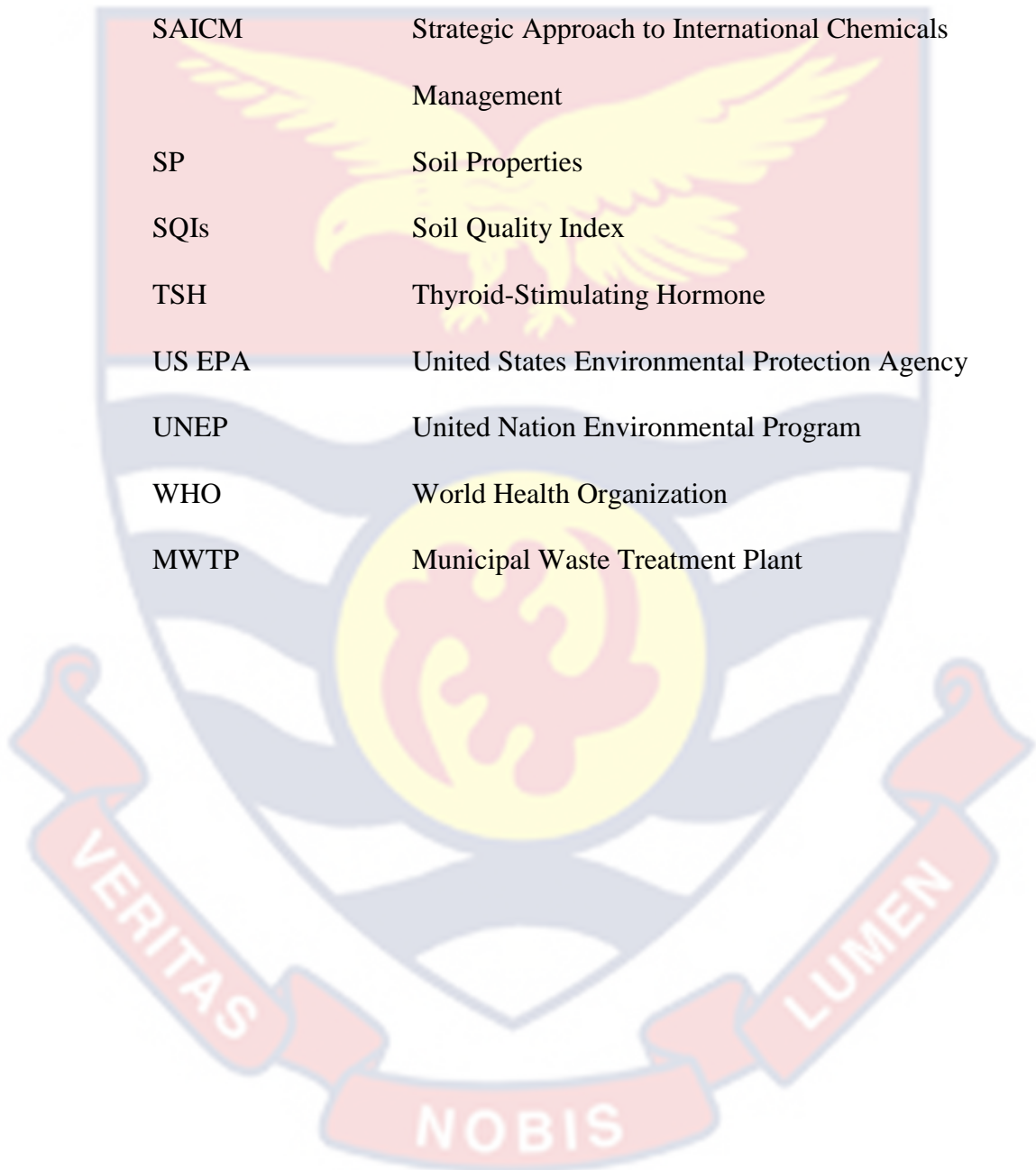
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AAS	Atomic adsorption spectrophotometer
ABS	Dermal Adsorption Fraction
ACTH	Adrenocorticotropic Hormone
ADD	Average Daily Dose
AF	Dermal Adherence Factor
AOP	Anthropogenic Organic Pollutants
AT	Average Lifetime
BBP	Benzyl Butyl Phthalate
BPA	Bisphenol A
BW	Body Weight
CA	Correlation Analysis
CEC	Council of the European Commission
CF	Conversion Factor
CSFo	Cancer Slope Factor
CSIR	Council for Scientific and Industrial Research
CR	Cancer Risk
DBP	Dibenzyl Phthalate
DDT	Dichlorodiphenyltrichloroethane
DEHA	Bis(2-ethylhexyl) Adipate
DEHP	Bis (2-ethylhexyl) Phthalate
DEP,	Diethyl Phthalate
DES	Diethylstilbestrol
DMP	Dimethyl Phthalate
DNOP	Di-n-octyl Phthalate

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ED	Exposure Duration
EDC	Endocrine Disrupting Chemicals
EF	Exposure Frequency
GC-MS	Gas Chromatography-Mass Spectrometer
GH	Growth Hormone
GSS	Ghana Statistical Service
HPAP	Health and Pollution Action Plan
IARC	International Agency for Research on Cancer
LOD	Limit of Detection
MEF	Ministry of the Environment Finland
MEP	Monoethyl phthalate
NHANES	National Health and Nutrition Examination Survey
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NYSDEC	New York State Department of Environmental Conservation
PAE	Phthalate Esters
PAH	Polynuclear Aromatic Hydrocarbons
PEF	Particle Emission Factor
PBBs	Polybrominated Biphenyls
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyls
PIRI	Pyrimidine
PROG	Progesterone
PTE	Potentially Toxic Elements

PSA	Primary Secondary Amine
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, Safe
RfDo	Reference Dose Value
SA	Dermal Exposure Area
SAICM	Strategic Approach to International Chemicals Management
SP	Soil Properties
SQIs	Soil Quality Index
TSH	Thyroid-Stimulating Hormone
US EPA	United States Environmental Protection Agency
UNEP	United Nation Environmental Program
WHO	World Health Organization
MWTP	Municipal Waste Treatment Plant



CHAPTER ONE

INTRODUCTION

Anthropogenic causes account for majority of the chemical pollution that occurs in soil, which is a complex and heterogeneous matrix (Vera et al., 2014). The ecosystem and human health are both seriously endangered by soil contamination. Panagos et al (2013) indicted that the main causes of soil pollution are industrial and commercial land usage, mining, waste land-fills, etc. Humans and the environment are put at risk by improper management of chemicals in industrial, agricultural, and domestic contexts as well as inadequate methods for disposing of hazardous waste. In Africa, and notably in Ghana, the generation of solid garbage has increased but the ability to manage it has not kept pace as reported by Lissah et al (2021). Poor waste management can have disastrous effects on people's health, depending on the type of trash exposed, the length of exposure, and the accessibility of solutions for those exposed (Ziraba et al., 2016). Although remediation has been thought of as the solution to restoring polluted soils, only portion of the pollutant can actually be removed. Once more, the high cost of remediation is a barrier, and only a small number of polluted soils may be remedied (Wuana & Okieimen, 2011).

Large parts of Ghana's agricultural soils have become contaminated, primarily as a result of artisanal gold mining, inadequate waste management, and subpar farming techniques as reported by Doso et al., (2015); Fianko et al., (2011). They indicated that intense vegetable production in Ghana already had some amounts of pesticide contamination in the water, sediment, crops, and bodily fluids. Similar to this, a number of studies have documented the

incorrect application of pesticides and the poor disposal of waste from chemicals that cause endocrine disruption (Amoako et al., 2012; Onwona et al., 2019; Oteng-Ababio, 2012). The fate of these contaminants is then a subject for inquiry.

Variety of contaminants, both organic and inorganic in nature, may be present in contaminated soil. These contaminants may interact with one another and have an impact on both people and the environment. Endocrine disrupting chemicals (EDCs) and heavy metals are two contaminants of particular concern (Lauretta et al., 2019). Metals, industrial chemicals, and natural compounds are among the environmental pollutants known as endocrine disrupting chemicals or endocrine disruptors. These substances have the ability to change the regular function of the endocrine systems in both persons and animals operate.

1.1 Background to the Study

Understanding of the health effects of Endocrine Disrupting Chemicals

Widespread pesticide usage and public consciousness of the health risks of EDC is important considering the changes in urban and peri-urban inhabitants' lives. The viewpoint of the community is crucial because it influences how people will behave in reaction to the harmful health impacts of pesticide exposure. Although the use of chemicals and personal care products cannot be completely eliminated, it is vital to ensure that they are used properly.

Three key factors—biosocial, sociocultural, and contextual factors are conceptualized as constituting the level of Knowledge of pesticide usage and health impacts of EDCs on people and the environment. Age and sex are two

biosocial characteristics that are inherently personal. These characteristics are inherited at birth and are not easily modifiable (Pol & Thomas, 2013). Again Pol & Thomas (2013) indicted that the second group of compositional elements, or sociocultural characteristics, reflects how people fit within the social system. These qualities are acquired rather than being given. Additionally, these features are intrinsically "cultural," meaning that those who are impacted adopt the traits that society assigns.

Furthermore, abnormalities in reproductive function and a high incidence of malignancies are linked to the health effects of EDC exposure in females (Buoso et al., 2020). EDCs may affect reproductive function at all stages of life, causing early puberty or elevating miscarriage and infertility rates (Diamanti-Kandarakis et al., 2009; Zama & Uzumcu, 2010). EDC exposure is also linked to alterations in immunity, neurodevelopmental delays, and aberrant growth patterns in children, as well as an increased risk of reproductive cancers, particularly breast, ovarian, and endometrial cancers (Crain et al., 2008; Gore et al., 2015; Kumar et al., 2020). The effect of EDCs on female health is crucial (La Merrill et al., 2020). These substances can induce estrogenic responses at extremely low concentrations, which could have an influence on pregnant women and their unborn children.

Human biological matrices used frequently to assess EDCs include blood, urine, or breast milk in epidemiologic studies. In addition, saliva, amniotic fluid, and hair have been employed in the analysis of EDC exposure in the laboratory. Regarding the possible use of menstrual blood in exposure analysis, however, not much is known. For the purposes of determining how pollutants affect people, monitoring of contaminants is then crucial and either

use of invasive or non-invasive matrix sampling techniques depending on the goal.

Additionally, regular biomonitoring is required to assess risk management choices and the efficacy of environmental and health policies (Smolders et al., 2009). Repeated exposure sampling for chemicals with short half-lives, such as agricultural pesticides or volatile organic compounds, can reveal more about the real makeup of these substances and their toxicological effects. Non-invasive methods of matrix collection are preferred in these circumstances, especially for the most vulnerable such as those who are chronically unwell. Menstrual discharge has not been widely used as a biomonitoring matrix, probably because of the stigma associated with it in Africa. Blood, vaginal secretions, and endometrial cells from the uterine wall are three different bodily fluids that make up menstrual discharge (Yang et al., 2012). With the advantage of early contamination detection prior to conception, it may therefore be appropriate for the monitoring of females who are of childbearing age.

Endocrine disrupting chemical

Hormones control how millions of specialized cells that make up the blood, bones, brain, and other tissues in each person are developed (Gore et al., 2015). The needs of each organ and tissue fluctuate during the life cycle, which is related to the changing hormonal requirements of each organ and necessitates the presence of specific hormones in specific amounts at specific times. Though they circulate in extremely low amounts, hormones are vital for reproductive function, appropriate body and brain development, and controlling how the body reacts to various nutritional demands (such as

hunger, starvation, obesity, etc). (Gore et al., 2015). The endocrine system as a whole serves as one of the body's key environmental interfaces and is crucial for growth, adaptability, and maintenance of bodily functions and good health. Hormones are absolutely necessary for survival, and they play vital roles in defining the quality of life. Given the endocrine system's critical function, deficiencies in any one of its components can result in illness or even death.

EDC exposure can therefore disrupt a number of activities by interfering with the body's endocrine systems (Gore et al., 2015).. The highly heterogeneous class of compounds known as "endocrine disruptors" that have the ability to change the normal operation of the endocrine systems in both humans and animals includes chemicals used as solvents or lubricants and their byproducts [polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), and dioxins], plastics [bisphenol A (BPA)], plasticizers (phthalates), insecticide and pharmaceutical agents (Choi et al., 2004 ; Foster, 2001). EDC is an exogenous substance that prevents the body's natural blood-borne hormones, which are necessary for homeostasis, reproduction, and development, from being produced, secreted, transported, metabolized, bound, or eliminated (Diamanti-Kandarakis et al., 2009; Zoeller et al., 2012). Numerous studies indicate the harmful effects of this group of chemicals are present in food, consumer products, and the environment. The impact of EDCs on human and animal health is sufficiently supported by the available data. There is no doubt about the harmful impact of EDCs on natural processes in the global environment, whether directly or indirectly due to anthropogenic or natural sources.

Knowledge and health effect of endocrine disrupting chemicals

There has been a growth in scientific evidence over the past two decades that explains how EDCs cause biological changes and how those changes may result in disease based on research (Street et al., 2018). But endocrinologists now think that a departure from conventional toxicity testing is required. The adage "the dose creates the poison" is generally used in chemical risk assessment. These testing procedures are predicated on the notion that dose and toxicity always follow a straightforward, linear relationship, with greater doses being more harmful and lower doses being less toxic. In order to define that chemical "safe," dose studies are carried out to establish that dose's safety threshold.

Concerns about endocrine-disrupting chemicals (EDCs) have increased in recent years among the scientific community due to significant improvements in research into these chemicals' health consequences. The release of scientific statement on EDCs in 2009 by the Endocrine Society makes it the first organization to publicly address the state of EDCs (Gore et al., 2015). At that time, the Society's members argued that there was enough data to draw the conclusion that EDCs are dangerous to public health. EDC awareness and comprehension were furthered by the Society's 2012 Statement of Principles on EDCs and Public Health Protection, letters to the European Commission (March 2013) and the Secretariat of the Strategic Approach to International Chemicals Management (Wania & Mackay, 1996), both of which urged science-based action on EDCs. The number of medical organisations around the world raising concerns about EDCs has increased since the Endocrine Society's original statement in 2009, growing in tandem

with the volume of research indicating harmful health impacts of these chemicals.

A policy calling for improved regulatory oversight of EDCs was adopted by the American Medical Association in November 2009 (D-135.982, Regulation of Endocrine-Disrupting Chemicals). This policy is based on "comprehensive data covering both low-level and high-level exposures." The American Public Health Association urged "a cautious approach to reduce American exposure to endocrine-disrupting chemicals". In the 2012-2015 policy statement on testing for endocrine disruption, the American Chemical Society suggested increased education and research, updated testing procedures, and creation of safer EDC substitutes.

Environmental influence and behavioral change

Activities that make Africa population and humanity as a whole vulnerable to EDCs put human health at risk and jeopardize the integrity of the ecosystem (Bornman et al., 2017b). African countries with 1.3 billion people are currently experiencing rapid urbanization, social, industrial, and economic development (Nweke & Sanders, 2009), which is encouraging young people to move from rural to urban areas in pursuit of employment and financial independence. Humans and the environment are at risk from improper management of chemicals used in industry, agriculture, and households as well as from inadequate methods for disposing of hazardous waste. According to research, pesticides are thought to contribute to acute poisoning deaths in underdeveloped nations with laxer health, safety, and environmental standards that results in about 99% of fatalities (Karunarathne et al., 2020; UN, 2017). The likelihood of human exposures is further increased by increased usage of

household pesticides, personal care items, fabrics, lubricants, and chemical products (WHO, 2018). The development of some of the most polluting economies seems to be drawn to developing nations, harming both the environment and human health (UNEP, 2018).

The number of anthropogenic pollutants and environmental degradation products released into water, air, and soil is rising as more people in Africa and other developing nations move to cities (Miller et al., 2016). The ability of around 800 substances to interfere with hormone receptors, hormone production, or hormone conversion is known or hypothesized to exist. However, studies able to detect overt endocrine effects in intact organisms have only been conducted on a limited scale of these substances (Arendrup et al, 2018).

Occupational influences on the soil resource

The agricultural industry is one of the major factors that have significantly boosted the usage of synthetic pesticides in most African nations. The majority of developing nations' economy continues to be supported by agriculture, which has increased pesticide use in an effort to boost food production and lower poverty. Synthetic agrochemicals are used primarily to manage pests since they are quick acting, provide temporary control, and are simple to use. It seems obvious that normal land use procedures have not been followed, which has led to issues for many communities. Maintaining soil quality is the best way to guarantee food security for supporting life (de la Guardia & Garrigues, 2012). However, poor soil fertility and excessive amounts of potentially harmful chemicals, heavy metals, and antibiotics pose a threat to these crucial resources. Soil is a significant source of nutrients for

food supply and plant-based medicines. Pests in the home can also be managed with pesticides.

According to Dinham (2003), 87% of Ghana's vegetable producers use chemical pesticides to control pests and diseases. There are signs that improper and excessive use of pesticides will have negative impacts on production, the environment, and human health (Gerken, A., J.-V. Suglo, 2001; Mattah, Mattah, & Futagbi, 2015) Aside from how these chemicals affect the environment and the health of farmers, consumers of improperly treated food products also experience health issues (Ntow et al, 2006; Owusu-Boateng et al, 2013) . Therefore, there is a chance that adverse health-related issues will affect every Ghanaian. Despite tremendous improvements in our understanding of EDCs, there are still information gaps that are too significant to ignore.

The advancement of improved societal and wildlife conservation is hampered by these knowledge gaps. To identify the function of EDCs in human and wildlife health, an international effort that is coordinated and integrated is required (Arendrup et al., 2018). There is again a gap in the knowledge transfer and translation of scientific findings to the general public. For instance, the effects of exposure to EDC on an adult may differ greatly from those on a developing foetus or newborn (Arendrup et al., 2018; Heindel et al., 2015). Similarly there is a delay between exposure, illness manifestation and developmental underpinnings of adult disease (Arendrup et al., 2018; Heindel et al., 2015). Due to changes in metabolism and body composition, distinct classes of EDCs may have additive or even synergistic effects. As a result, the half-life and persistence of EDCs, as well as their breakdown in

bodily fluids and tissue, are very variable (Bergman et al., 2012; Diamanti-Kandarakis et al., 2009).

Several EDC characteristics have generated debate given the incredibly low exposure levels necessary to have an impact. In fact, exposure at any level could result in endocrine or reproductive problems, especially if it happens during a crucial developmental period (Diamanti-Kandarakis E et al., 2009; Sisk, Lonstein, & Gore, 2016) As scientific knowledge and public health professionals' understanding of EDCs continue to grow as a result of study, the question of whether they have harmful effects is no longer relevant. In order to close the knowledge gap between professionals and non-experts, it is urgent to address the myriad environmental and human health difficulties of the entire globe, but especially the majority of developing countries

1.2 Problem Statement

Chemical risks posed to human and the environment are created by improper management in industry, agriculture, and households as well as inadequate hazardous waste disposal systems (Taherzadeh et al, 2019). Activities that make humanity sensitive to EDCs and consequently results in adverse health and compromised environmental integrity are extant (Bornman et al., 2017). Through population increase, urbanization, lifestyle changes and demographic changes primarily affect consumer demand for chemicals and goods that include endocrine disruptive substances. Inadequate investments in infrastructure, employment, education, health, and waste management systems are also caused by high rates of population expansion (Ganivet, 2020), which exacerbates the issues brought on by the rising usage of EDCs (WHO, 2018). The development of some of the most polluting economies appear to be drawn

to developing nations, harming both the environment and human health (UNEP, 2013). The number of anthropogenic pollutants and environmental degradation products released into water, air, and soil is rising as more people in Africa and other developing nations move to cities (Miller et al., 2016). The agricultural industry is one of the major sectors that have significantly boosted the usage of synthetic pesticides in majority of African nations.

Africa's population is expanding at a high rate, which is correlated with an increase in the volume and intensity of agricultural production (United Nations, 2019). The climate in Africa is conducive for pests to thrive that has resulted in increased use of pesticides in an effort to scale up food production, to meet the increased demand brought on by population growth, and to combat poverty. Urbanization, caused by a steady reduction in the amount of agricultural land through housing, industry, and the supply of other social amenities, has worsened this trend.

In several nations, detectable quantities of EDCs have been discovered in groundwater, surface waterways, sediments, wastewater, and even drinking water (Brueller et al., 2018; Gonsioroski et al., 2020). They may disrupt hormone synthesis by producing too many, too few, or causing a break in hormone production, all of which are detrimental to the body's ability to operate normally (Gupta et al., 2010). These hormones are necessary to control the body's growth in limited doses and at specific times. EDCs have been linked to altered reproductive function in males and females, as well as a high incidence of cancer.

They can again have complex effects on women's health, affecting reproductive processes throughout the life cycle, causing early puberty and

raising the risk of miscarriage and infertility (Diamanti-Kandarakis et al., 2009a; Zama & Uzumcu, 2010). Further triggering increased incidences of reproductive cancers, particularly breast, ovarian, and endometrial cancers, as well as delays in children's neurodevelopment and atypical growth patterns, as well as alterations in immunity, all have an impact on reproductive function (Crain et al., 2008; Gore et al., 2015; Kumar et al., 2020).

1.3 Research Questions

The research questions guiding the study are:

1. What is the level of understanding of the health effect of the use of pesticides and products that contain endocrine disrupting chemicals?
2. What are the concentration levels of endocrine disrupting chemicals and potentially toxic elements in selected contaminated soil sites and are the concentrations carcinogenic to humans?
3. How does the concentration level of potentially toxic elements in selected contaminated soils sites affect soil quality?
4. What are the level of concentration of endocrine disrupting chemicals in female menstrual blood and are the concentrations carcinogenic?

Study Objectives

The main objective of the thesis is to determine the level of knowledge of the health effect of endocrine disrupting chemicals and the extent to which human menstrual blood and soil are contaminated. However below are the four different but inter-related specific objectives that were formulated to guide this thesis based on the assumption that the higher the anthropogenic influence on the environment the more contaminated the environment becomes.

Objective 1

Assess general public understanding of the health effects of endocrine disrupting chemical and pesticide use in three communities in Ghana.

Objective 2

To characterize and assess health risk of EDCs and PTEs in four selected sites to represent agriculture, industry, decommissioned waste dump and forest reserve.

Objective 3

To analyze the physical and chemical properties of soils with different land uses to generate a soil quality index data.

Objective 4

Assess and quantify the health risk of EDCs in adult female menstrual blood.

General Hypotheses

H₁: Land use influences the type and levels of contaminants in environmental media and biota

H₁: Higher levels of knowledge influences the extent of behavioral change to pesticides use

H₁: Menstrual blood can be used as bio indicator to monitor environmental exposure.

1.4 Significance of the study

The following arguments support and make this thesis very important. The method employed in this thesis to calculate exposure and conduct biological monitoring yields data on commonly used chemicals present in the environment. It takes into account the subpopulations' cumulative exposure to phthalates, bisphenol A, and potentially hazardous substances through all

pathways (oral, dermal, and inhalation). Credible information is obtained by analyzing blood and soil samples for endocrine disruptors. We come into contact with a wide range of chemicals every day through consumer products including foam, electronics, plastics, and pesticides that end up in our food, water, and soil.

To embrace technology and boost food production, the usage of these chemicals has expanded. As a result of the effects of these chemicals, farmers and consumers experience health issues. The production, use, and importation of specific pesticides, flame retardants, plasticizers, and other chemicals that have been proved to behave as endocrine disruptors have been subject to regulation in the last ten years by governments. As a result, alternative chemicals are required to close market "gaps." This shows that every Ghanaian is at danger as a result of this, but the extent of our exposure to these substances is frequently unknown.

The thesis is important as it focuses first on determining the extent to which human blood and soil contain the chemicals such as phthalates and bisphenol A. It also determines if these EDCs are present in quantities deemed to be safe. The goal is to transform the knowledge that is acquired during this research into policy objectives and legal standards.

1.5 Delimitation

This study is delimited to assessing the level of knowledge of health effects endocrine disrupting chemicals of males and females between the ages of 18-50 years residing at Nmai Dzorn (urban community) in the Greater Accra region and also residents of Kakumdo and Essuekyir (peri-urban communities) in the Central region of Ghana. Again potentially toxic elements

Iron (Fe), Manganese (Mn), Cadmium (Cd), Lead (Pb), Nickel (Ni), Cobalt (Co), Copper (Cu), Zinc (Zn), Arsenic (As) and endocrine disrupting chemicals Bisphenol A (BPA). Diethyl phthalates (DEP), Di-n-octyl phthalate (DNOP), Dimethyl phthalate (DMP), Dibutyl phthalate (DBP) and Bis (2-ethylhexyl) phthalate (DEHP) Bis (2-ethylhexyl) adipate (DEHA) and Benzyl butyl phthalate (BBP) were studied. Ordinary least squares regression and multivariate (Principal Component Analysis, Cluster Analysis) statistical methods were used for the analysis.

1.6 Limitations

The advantage of questionnaires is that they are designed to collect specific items intended at measuring knowledge, attitudes, and perceptions. They are also quick, inexpensive, and simple to administer. The social desirability bias that exists in questionnaires is a clear limitation. Additionally, there is a chance that this study's responses were biased. Response bias, which happens when people provide self-assessed assessments of some event (Rosenman et al., 2011), in this case diseases linked to pesticide exposure, is a well-studied topic in behavioral and healthcare research that uses self-reported data.

Analytical procedures were also meticulously followed; however given the prevalence of endocrine disruptors, it was nearly impossible to completely exclude instruments that might contain some EDC during the experiment.

1.7 Definition of Terms

Potentially toxic elements (PTEs)

(PTEs) is a group of elements, which can be found naturally in soils, water and sediments. The potential toxicity is due to the possibility of those

elements to accumulate over time and above certain limits to be harmful to humans, animals and in general to the environment. This increment can be due to urbanization, agricultural activities, industry or mining. These elements include, Arsenic (As), Cadmium (Cd), Cobalt (Co), Copper (Cu), Lead (Pb), Iron (Fe), nickel (Ni), manganese (Mn) and zinc (Zn).

Endocrine disrupting chemicals (EDCs)

The EDCs are a group of chemical compounds with both natural and manufactured (anthropogenic) origins that are widely dispersed in the environment and are known to disrupt both animal and human endocrine systems by functioning as hormone-like substances inside the body (Godfray et al., 2019)

Soil quality index (SQI)

It is the integration of specific measured soil properties into a single parameter that could be used as an indicator of soil quality (Amacher, O'Neill, & Perry, 2007)

Ethical Clearance

Research Integrity embodies a range of good research practice and conduct which can include intellectual honesty, accuracy, fairness, and protection of human and animal subjects involved in the conduct of research. Ethical clearance is sought prior to any research work that involves the use of human or animal subjects

Endocrine system

Endocrine system is made up of several organs called glands. These glands, located all over the body, create and secrete hormones.

Hormones

Hormones are chemicals that coordinate different functions of the body by carrying messages through the blood to organs, skin, muscles and other tissues. These signals tell the body what to do and when to do it.

Physicochemical analysis

The physical and chemical laboratory analysis of soil samples for parameters of interest.

1.8 General methodology

In this study, quantitative methods were adopted based on the research design. Survey questionnaire were administered to three hundred (300) respondents in selected communities to gather data on knowledge of the health effect of EDCs of individuals. Individuals were chosen from three separate communities, which included both homogeneous and heterogeneous in terms of ethnic and cultural diversity. The three hundred (300) respondents surveyed include two hundred and eleven (211) females and eighty-nine (89) males. Due to the delicate nature of some of the questions, the questionnaire was piloted before it was administered with approval from the Ghana Medical Association's ethical clearance review committee. Based on how EDCs affect gender-specific health, a stratified sampling technique was employed to choose the ratio of male to female interviewees.

Informal and one-on-one interviews were carried out to sample interviewee's usage of pesticides and understanding of EDCs. Four theme data areas were the focus of the questionnaire: (1) personal information, (2) understanding of the consequences of EDCs by mentioning potential disorders, and (3) a change in lifestyle, including dietary habits, relationships,

and employment history; (4) potential reproductive anomalies. Using a 5-point Likert scale, knowledge of the specific harmful health effects linked to exposure to EDCs and pesticides was assessed. Other questions required respondents to choose "yes" or "no" as a response in combined closed-ended and open-ended questions in a multiple-choice format. Males and female respondents that were of sound mind between the ages of eighteen (18) and fifty (50) were used.

The quantitative method was adopted to enable characterization and quantification of contaminants in two main matrixes (soil and blood). Standard laboratory methods were used for pre-treatment of sampled matrix, extraction, clean ups and instrumental analysis. Modification of the original Quick, Easy, Cheap, Effective, Rugged, Safe (QuEChERS) procedure as described by Pinto et al (Pinto et al., 2010) were used for the determination of the organics while method described by Verloo and Demeyer 1997 were used for the extraction of heavy metals and metalloid.

Study locations

Soil samples were collected from the Greater Accra and Central regions of Ghana (Fig 1.1). Three of the sampling sites were in Greater Accra and one site in the Central region. The four (4) sites represent cultivated soil, industrial soil, decommission refuse dump in Greater Accra and forest reserve in Central region. The three sampling sites in Greater Accra are separated about 9 km apart and 140 km from the last location in Central region. The cultivated soils were taken from the environs of the Council for Scientific and Industrial Research (CSIR) head office within an urban setting. The area remains a major vegetable growing site all year round for over 50 years and

the continuous application of pesticides, organic and inorganic fertilizers. Soil from the dump was taken from the Adenta decommissioned refuse dump that had received all manner of solid waste from most part of the capital city for many decades. The industrial soils were taken from Accra North industrial area that has most of the companies that produce plastic products and the soils from forest reserve were taken from Kakum National park. Kakum National Park, is located in the coastal environs of the Central Region and covers an area of 375 square kilometres with tropical forest

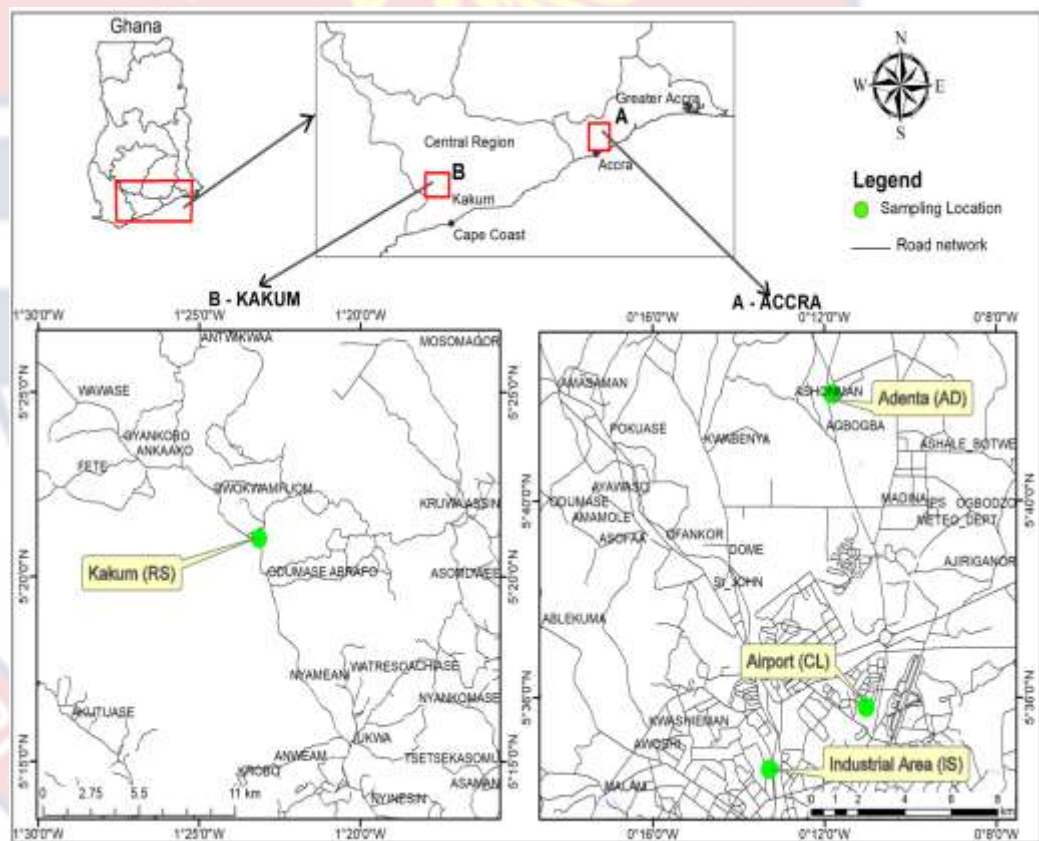


Figure 1.1 Map of geographical location of sampling areas

Collection of soil sample

Soils were randomly sampled with auger at a depth of 30 cm from the four (4) sites. Four (4) composite samples were taken per site from 12 different sampling points. Soil samples were initially stored in aluminum foil

and taken through preparatory procedures. The samples were air dried at room temperature, homogenized and sieved (2-mm mesh) before use. Portions were used to determine contaminants and the physicochemical characteristics of the soils.

Collection and storage of Menstrual blood samples

Menstrual blood samples were collected by volunteers for three consecutive days from the second day of flow within the monthly cycle. Twenty (20) females from Accra and Cape Coast between the ages of 25-45 years participated in the study. Participants refrained from sex during sample collection. Since there is no standard protocol for the collection of menstrual blood, samples were collected on aluminum foil and transferred into a vacutainer tube containing anticoagulant. The collected blood samples were stored in sealed sterile containers at $-10\text{ }^{\circ}\text{C}$ ($\pm 2\text{ }^{\circ}\text{C}$) until extraction. All subjects included in the study gave their consent to participate voluntarily. Ethical approval was granted by the Ghana Health Service Ethical Review Board

Physicochemical analysis of soil samples

Soil particle size analysis was carried out using the pipette method as described by Rowell (1994). Soil reaction (pH) and electrical conductivity (EC) were measured in 1:2.5 soil: water suspension. Total nitrogen was determined by the Kjeldahl method (Bremner, 1996) Available phosphorus and potassium contents in soils were extracted by Bray's P1 solution and measured on a spectrophotometer (Bray and Kurtz, 1945). Organic carbon was determined by the wet oxidation method of Walkley and Black (1934) as modified by Nelson and Sommers (1982). Analyses of the exchangeable bases

(Ca²⁺, Mg²⁺, K⁺ and Na⁺) were done by the method described by Rowell (1994). Heavy metals analysis was done using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique while Phthalates and Bisphenol A were determined using QuEChERS method.

Digestion of soil samples

Soil samples were digested using aqua regia according to (Verloo and Demeyer 1997) for the extraction of heavy metals and metalloid. Approximately 1.00 g of oven-dried, finely ground soil was weighed into a digestion flask and moistened with 2 mL deionized water. Then, 7.5 mL concentrated HCl and 2.5 mL HNO₃ were added. The reaction flask was covered and allowed to stand at room temperature overnight. The mixture was heated progressively under reflux and allowed to boil for 2 h. After cooling to room temperature, the reflux column was rinsed with 20 mL deionized water. Content of the digestion vessel were filtered into a 100 mL volumetric flask and rinsed with 10 mL 0.5 M HNO₃. The volume was made up to 100 mL with deionized water.

Extraction and clean-up of soil samples

Five gram (5 g) portion of the soil samples was weighed into 50 mL centrifuge tubes, and 5 mL of ultrapure water was added. 20 mL of acidified acetonitrile (1% acetic acid in acetonitrile) and 2 g of sodium chloride (NaCl) were added. The tube was sealed, and the ultrasonic extraction was performed for 5 min. and centrifuged for 5 min at 4000 rpm. 10 mL of the supernatant was transferred to a centrifuge tube containing 0.1 g of the clean-up materials (PSA). 2 g of magnesium sulfate (MgSO₄) was added, ultrasonicated for 2 min and centrifuged at 4000 rpm for 5 min. Supernatant was transferred into a

test tube using 5 mL and concentrated to almost drying by nitrogen sweeping; the sample was reconstitute with 1ml of acetonitrile and vortex for 2mins to dissolve all sample. 1.0 mL of the extract was transferred to an auto sampler vial for analysis by GC–MS.

Extraction and cleanup of blood samples

The modified method described by (Usui et al., 2012) was used for extraction and clean up. About 0.5 mL of blood serum was diluted with 1.5 mL of distilled water. Samples were placed in a 5mL centrifuge tube containing 6g of magnesium sulphate and 1.5 g sodium chloride with 1ml of 1% acetic acid in acetonitrile (v/v). The mixture was vigorously vortexed for 30 sec, shaken up and down for 5 min, vortexed again for 30 sec and centrifuged at 4400rpm for 15 min at 4⁰C. For sample clean up, 600 µL supernatant of each sample was transferred into a 1.5mL tube containing the solid phase extraction sorbent (25mg of primary secondary amine, 25mg of end-capped octadecylsilane (C18) and 150 mg of magnesium sulphate). The tube was mixed by hand (up and down) for 10 mins, vortexed for 30 sec and centrifuged at 4400 rpm for 10 min at 4⁰C. Supernatant were collected and filtered through 0.22 PTEF filter into vials. About 1µL of each sample was injected directly into GC-MS/MS system for analysis.

Analysis of EDCs

Endocrine disruptors in menstrual blood and soil were analysed with GC-MS QP 2020 Shimadzu equipped with RTS-5MS trace analysis column (30 m × 0.25 mm × 0.25 µm).. Helium gas of high purity (99.99 %) was used as the carrier gas at a flow rate was 1mL min⁻¹ at a pressure of 83.1kp. Sample

volume of 1 μL was injected in pulsed splitless mode with an inlet temperature of 265°C .

To quantify phthalates, the column temperature was programmed as follows: initial oven temperature was set at 70°C for 2 min, then increased to 200°C at $15^{\circ}\text{C}/\text{min}$. It was further ramped up at $6^{\circ}\text{C}/\text{min}$ to 310°C and held for 1 minute. The interface and ion source temperatures were set at 265°C and 220°C respectively. For bisphenol A, the column temperature program was as follows: 50°C for 1 min, ramped up at $15^{\circ}\text{C}/\text{min}$ to 180°C , further ramped up at $8^{\circ}\text{C}/\text{min}$ to 300°C and held for 1min. The interface and ion source temperatures were set to 270°C and 220°C , respectively. Quantifications were all carried out in the selected ion monitoring mode (SIM), selecting two characteristics fragments ions for each.

The heavy metals (Fe, Cd, As, Pb Ni, Co, Cu, Zn, Mn), were determined with Atomic adsorption spectrophotometer (AAS), Agilent Technologies 200 series 240FS AA and Graphite Tube Atomizer 240ZAA after extraction.

Quality control

All glasswares used were thoroughly washed with hexane and acetonitrile, then heated at 140°C for 1 h to ensure that contamination of glassware was reduced. The EDC extraction solvent and matrix adsorbent were studied using blank samples spiked with standards. The blank values of the analytical procedure were determined by extracting the spiked sample by the same method as the real blood sample with recovery of spiked sample in the range of 86%–116%. The estimation of the limit of detection (LOD) for the EDCs in the blood samples was conducted based on U.S. EPA guidelines

(USEPA, 1995) with a confidence level of 95%. An LOD of $3\times$ (detection peak/blank peak + standard deviation) was observed. Instrumental detection limits were calculated by a signal-to-noise ratio of 3 times the sample concentration and ranged from 100 to $310 \mu\text{g l}^{-1}$. Method detection limits of the EDCs including DMP, DEP, BBP, DEHP, DBP, DnOP, DEHA and BPA were 5, 7, 10, 5, 15, 10, 7 and $40 \mu\text{g l}^{-1}$ respectively. Surrogate standards and internal standards concentrations of $20 \mu\text{l}$ of 5 ppm and $50 \mu\text{l}$ of 20 ppm in 1 ml, respectively, were added to all the samples to monitor the matrix effects, calibration and quantification. A calibration curve was made by serial dilutions of calibration standards with at least five concentrations for each EDC compound monitored. Linear regression with coefficient of $(R^2) > 0.99$ was accepted.

Evaluation of human exposure and health risks

The US EPA's guidance for cancer and non-cancer risks evaluation was used to calculate the chosen endocrine disrupting substances and PTEs. The formulas with amendment from the US EPA, (U.S. EPA, 2015) which have been generally used in earlier studies (Başaran et al., 2020; Li et al., 2021; Wang et al., 2018; Zhu et al., 2019) were used to evaluate the average daily dosage (ADD, $\text{mg}\cdot\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$) of EDCs and PTEs via different exposure pathways, namely ingestion (ADDing), dermal absorption (ADDder) and inhalation (ADDinh)

1.9 Linkage of Articles

Paper 1: Ason, B., Essumang, D.K. (2022) Increasing pesticide use and knowledge of the health effect of endocrine disrupting chemicals in the environment: a study of three communities in Ghana. *Population and*

Sustainability vol. 6, No 2. <https://www.whp-journals.co.uk/JPS/article/view/722>

Paper 2: Ason, B., Armah, F. A., Essumang, D.K. (2023) Risks of toxic elements and endocrine disruptors in some soils in Ghana. *International Journal of Environmental Studies*, <https://doi.org/10.1080/00207233.2023.2192617>

Paper 3: Ason, B., Kofi Essumang, D., Armah, F. A, & Obiri, S. (2022). Soil Quality Index of land impacted by anthropogenic activities in coastal Ghana. *EQA - International Journal of Environmental Quality*, 47, 31–39. <https://eqa.unibo.it/article/view/14197>

Paper 4: Ason, B., Kofi Essumang, D., Ato Armah, F. (2022). Characterization and Quantification of Endocrine Disruptors in Female Blood Samples *Toxicology Reports* 9, 1877–1882 <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9764248/>

1.10 Organization of the Study

This thesis considers the effect of contaminants (including fate) on human in agricultural soils of three coastal towns of Ghana. It is organized and given a quick outline in Chapter One. It also highlights pertinent research on heavy metals and endocrine disrupting substances, as well as the connections between people's awareness of endocrine disruptive substances and their effects.; behavioral change and how people adapt to the environment and occupational influence on the environment. The chapter also explains how the thesis is situated within the broader human-environment interaction and followed by the study objectives. It concludes with an outline of the linkages among the various chapters in this thesis.

CHAPTER TWO

LITERATURE REVIEW

Introduction

This chapter gives an overview of the previously scholarly works relating to the use of chemicals especially potentially toxic elements (PTE) and endocrine disrupting chemicals (EDCs) within the environment especially in agricultural soils and the impact of poor waste disposal systems.

2.1 Health risks of chemical use and wastes disposal systems

Chemicals, such as pesticides, PCBs, PAHs, phthalates, phytoestrogens, and others, are estrogenic in in-vitro tests (Carpenter et al., 2002). According to Murray & Lopez (1996), environmental pollution (chemicals, radiation, and tobacco smoke combined) is to blame for about 80% of all malignancies. Again Smith et al. (1999), indicated that environmental factors account for 25–33% of the total global burden of disease, and children are particularly susceptible to these factors. This estimate takes into account illnesses brought on by contagious agents spread through the environment. Evidence suggests the involvement of environmental chemicals in a number of diseases that were not previously thought of has surfaced in recent years. This is particularly accurate for the several chronic diseases, including diabetes and cardiovascular disease (Henriksen et al, 1997; Vaarala et al, 1999), as well as bone, joint, and intervertebral disk disease all of which are included in the basic categories of illnesses that are thought to fall under the category of endocrine disruption (Guo et al, 1999). Many farmers, according to Onwona et al (2019), are not adequately informed on the risks involved in handling and using pesticides, which poses a serious risk to

their health. Poor chemical waste disposal practices have major environmental and human health effects (Fazzo et al., 2017).

It is known that depositing garbage on soils raises pollutant concentrations (Ali et al, 2014). Indications are that organic and inorganic pollutants are the two types of soil contaminants according to Webber & Singh (1995). Agricultural pesticides and non-pesticide substances like phthalate esters and bisphenol A are among the organic contaminants of industrial origin that are of the most concern; in contrast, the majority of inorganic contaminants are metals that come from industrial processes (Adeniyi et al, 2008; Navarro et al, 1991). According to reports, substantial environmental and public health issues are caused by improper waste disposal in cities all over the world (Mazhindu, Gumbo, & Gondo, 2012; Omang, John, Inah, & Bisong, 2021). Planners working in both the rural and urban sectors are now concerned about this. According to Yoada et al, (2014) majority of open dumps are currently located close to residential areas due to rising populations, urbanization, and spatial growth, especially in Africa . Through pollutant leaching and runoffs, the open dumps seriously jeopardize the quality of the air, soil, ground water, and surface water (Ali et al, 2014). Studies by Rutherford et al (2000); Webber & Singh, (1995) indicted that species living in polluted soils absorb contaminants, which can bioaccumulate in the intricate food chain. Even now, open dumps are still sometimes the only option for disposing of municipal solid trash in developing nations as reported by Arimah (2003). Many urban managers are concerned about the rising expenses of trash disposal as well as the potential risks to water supply and air quality,

and this lack of space for depositing solid waste has become a problem (Omang et al., 2021).

Dialkyl or alkyl aryl esters of 1, 2-benzenedicarboxylic acid, sometimes known as phthalate esters and bisphenol A, are widely used in industry and are widely recognized as environmental pollutants. Over 8 billion tonnes of phthalate esters are used annually throughout the world, mostly as industrial solvents, additions to PVC plastics, and parts of numerous consumer items (Adeniyi et al., 2008) . According to Wang & Qian,'s (2021) research has it that, phthalates may cause human cancer and birth defects. The most significant issue, has been the potential for phthalates and bisphenol A to function as endocrine disruptors in humans (Darbre, 2020). Metals like cadmium and lead have a detrimental effect on both people and wildlife. Humans don't even need very modest levels of this class of metals (Tchounwou et al, 2012). Similar findings have been made about high levels of critical metals like zinc, manganese, and iron (Tchounwou et al, 2012).

A major factor making solid waste management a top concern for the environment and public health is the fact that solid waste has effects on health. Despite the fact that a number of causal relationships between trash exposure and certain waste-related health effects have been identified, some are either unresolved or not given as much importance as public health concerns. The whole burden of ill health related to exposure may not be recognized in situations where the causative linkages are not known. Establishing causal links can be difficult since it might be difficult to determine the kind, dose, and duration of exposure without any doubt (Ziraba et al., 2016). The difficulty in excluding alternative factors when it comes to health outcomes is

due to the possibility that other environmental exposures could also result in the same effects.

In addition, some clinical effects, such as malignancies and other types of degenerative illnesses, take a long time to appear after exposure, and it might be difficult to follow up with exposed people (Ziraba et al., 2016). The primary contributor to the current global environmental and climatic changes that have a direct impact on health and welfare is now understood to be human activities and their products (McMichael et al., 2008). Similar to this, several human activities at the local municipal level produce garbage, which is a major contributor to environmental problems and health issues like respiratory problems, injuries, and infectious diseases like cholera, and dysentery (Fadhullah et al., 2022). Increased demand for solid waste management services, which are in many African countries the single largest budgetary item for local governments, stems from an increase in solid waste (Awunyo-Vitor et al., 2013). Most of Africa's urbanization has not coincided with the rise of social amenities and economic possibilities; as a result, many cities struggle to meet the needs of an expanding, primarily impoverished urban population by providing basic services like shelter, water, and environmental upkeep (Arimah, 2003).

According to Miezah et al (2015), the average rate of garbage generation in Ghana's ten regional capitals was 0.51 kg/person/day. The garbage creation rate in the Kumasi metropolis is 0.75 kg per person per day, which is somewhat more than Accra, the nation's capital, at 0.74 kg per person per day. The average daily waste production in Accra, Kumasi, Takoradi, and

Cape Coast is 0.72 kg/person. More solid waste is generated in cities, which has a greater negative impact on the environment and human health.

2.2 Public knowledge of health effects of endocrine disrupting chemical

It has been established that all vertebrates have an endocrine system that controls vital biological processes like metabolism, development, reproduction, and behavior (Colborn et al., 1993).

Concerns about the impact of endocrine disrupting pollutants on human health and the environment have emerged since the endocrine disrupting contaminants hypothesis was first proposed (Street et al., 2018). Endocrine disrupting chemicals (EDCs) are thought to have a major impact on both wildlife and human health, according to data from ecological research, animal models, clinical findings in people, and epidemiological investigations (Street et al., 2018). Early experimental work was motivated by ecological studies that revealed a connection between a complex mixture of xenobiotic pollutants and endocrine disruption of reproduction and development in fish, reptiles, birds, and mammals, as well as behavior that ranges from subtle changes to permanent alterations, such as disturbed sex differentiation with feminized or masculinized sex organs, changed sexual behavior, and altered immune function (Crisp et al., 1998; Street et al., 2018).

Data gathered over the past few decades show that purposeful or unintentional environmental releases of EDCs as well as their incorporation into consumer products have significantly contaminated the environment worldwide. The vertebrate neuroendocrine system is an obvious illustration of the evolutionary homology principle in this context, as its development and organization are mostly preserved and similar throughout the many classes. In

fact, it is hardly unexpected that wildlife has served as a sentinel for human health for generations (Woodruff et al., 2010). According to reports, nearly 1000 chemicals have the potential to disrupt the endocrine system. Additionally, every year, new chemicals are introduced to the market, and the vast majority of these chemicals are developed using subpar or inappropriate toxicological testing to identify potential endocrine disruption (Yilmaz et al., 2020). Exogenous compounds known as EDCs affect hormone action, raising the likelihood of undesirable health outcomes such as obesity, cancer, reproductive and cognitive problems. In fact, it's crucial to emphasize that similar to natural hormones, prenatal and early postnatal exposure to EDCs during the most susceptible times of life can have profound impacts on development at very low dose levels of exposure (La Merrill et al., 2020)

Recent research has demonstrated that even very low dosages of EDCs (parts per billion and parts per trillion) can have an impact on animal behavior similarly, multiple studies have demonstrated both gene activation and gene suppression in this context (Sachs, 1999). Low quantities of hormones have a significant impact on a wide range of phenotypes, as demonstrated by studies on intrauterine placement of foetuses in rodents and other animals. In addition to increased risk of endocrine malignancies, exposure to endocrine disrupting chemicals (EDCs) is linked to dysfunctions of metabolism, energy balance, thyroid function, and reproduction. Through molecular epigenetic alterations brought on by early exposure to EDCs, these multifactorial illnesses can be "programmed," even if their expression might not become apparent until adulthood. EDCs can sometimes have negative impacts on later generations, suggesting that disease-predisposition features may be handed down through

nongenomic inheritance (Walker & Gore, 2011). A new paradigm for non-communicable disease was developed as a result of the evidence demonstrating these effects: the developmental roots of health and disease (Heindel et al., 2015).

Neurobehavioral reactions, immunological, endocrine, and respiratory system responses are examples of possible affects that may be partially mediated by epigenetic mechanisms. These responses may be directly on the infant or indirectly when mediated by placental transfer or breastfeeding. Children are more at risk of excessive exposure because they consume more air, food, and liquids relative to body weight, exhibit crawling activities, and are smaller in stature (Mastorci et al., 2021).

Numerous animal studies demonstrate direct causal links between fetal exposure to chemicals and illness outcomes. In some cases, the unfavorable impacts can be passed down through transgenerational epigenetic inheritance to succeeding generations (Crews et al., 2007). In fact, a number of substances, including some EDCs, have the ability to alter the epigenetic makeup of the offspring of exposed persons, leading to adverse health impacts. Therefore, if we continue to permit exposure of humans to substances with endocrine action, it may have an impact on the viability of both the animals and the human population. EDCs are one of the key things that can seriously jeopardize the sustainability of our environment (Colborn et al., 1993). As a result, caution demands that we act now rather than waiting for "conclusive" proof that harm is being done to human populations. To encourage science-based decision making, better communication between scientists, business executives, government officials and politicians is needed.

According to Wang et al (2021) there is a connection between developmental exposure to environmental contaminants and an increase in the prevalence of neurodegenerative disorders like Alzheimer's and Parkinson's diseases. There is substantial evidence that one of the most common EDCs, BPA, can impair sexual differentiation in animal models by disrupting neuroendocrine function in addition to its other negative effects (Marlatt et al., 2022). Recent studies on the relationship between maternal EDC exposure and the neurodevelopmental outcomes of children have demonstrated a strong link between gestational levels of BPA or phthalates and changes in children's emotional behavior, aggressive behavior, cognitive impairment, and ADHD (Palanza et al., 2016)

Welch & Mulligan (2022) indicated that animal studies conducted over the course of more than 20 years of experimentation have demonstrated that maternal exposure to BPA during pregnancy and/or lactation causes long-term changes in offspring behavior, primarily in three behavioral categories: anxiety and exploration; learning and memory; and socio-sexual behaviors in all mammalian species. Data can be contradictory even though experimental animal models show that chemical contaminants have a significant impact on adipocyte physiology and glucose metabolism (Street et al., 2018). The differences are complex and likely the result of a variety of factors, such as the inherent characteristics of each EDC, the variability of how widely distributed they are in the environment, the different ways that these chemicals act depending on when they are exposed as children, and concurrent exposure to a variety of chemicals, which is likely to have a synergistic effect (Magueresse-Battistoni et al., 2017). Because of this intricacy, it is challenging to develop a

solid epidemiological model for researching the human mechanisms of action of EDC and comprehending the true clinical effects of each EDC. The most common conclusion in recent research on a variety of mammals, including humans, is that sex is a key factor in determining how BPA affects behavior.

Numerous studies have shown demonstrated that BPA and other EDCs can alter the natural steroid programming of the developing brain in rodents, causing sex-specific effects even at extremely low doses (Masuo & Ishido, 2011).

Without access to reliable, trustworthy information regarding the scientific evidence proving negative health effects following exposure to endocrine disruptors, people cannot make fully informed decisions. In order to bridge the gap between expert and non-expert information for the general public through two-way, interactive communication, knowledge translation and transfer of scientific studies are required (Kelly et al., 2020). Consumers routinely undervalue the benefits of pesticides used to clean water or improve agricultural quality and yields, according to public perception of chemicals (Tyshenko et al., 2008). According to Raats & Shepherd (1996), the general public perceives endocrine-disrupting chemicals as posing a higher risk than other chemicals released into the environment. Differences between expert and non-expert perceptions of chemical risks are thought to have their roots in a lack of understanding and familiarity with science and technology (Slovic et al., 1995). Similar to this, non-experts who have learned something about endocrine disrupting substances frequently get their information from non-expert sources. Once an initial impression has been created, this influences and distorts how following new evidence is interpreted and integrated

(Tyshenko et al., 2008). Secondly, while deciding whether to accept or reject a risk, people tend to think broadly and ultimately make a binary choice. Since oversimplification eases cognitive strain and anxiety, people use it to make decisions from otherwise complex situations (Loewenstein et al., 2001). Once more, according to (Van Ravenswaay (1995) rational people might be emotionally impacted and have false judgments of the hazards they are exposed to. For instance, repeated deaths, illness, and suffering can cause strong feelings of dread. Since the public experiences a variety of unfavorable health impacts that go beyond those that are generally addressed by professionals, effective knowledge translation and transfer of risk information must be based on a broad context.

The Ministry of Food and Agriculture report (2011) shows that the use and importation of pesticides in Ghana has steadily increased. This includes the quantity and number of chemicals that have been registered and recorded by the appropriate authorities and regulators, including the Ghana Standards Authority (GSA), Ghana Environmental Protection Agency (EPA), and Food and Drugs Authority Onwona et al., (2019). Since the adoption of the pesticide registration process, the state and several non-state organizations have arranged a number of interventions, however, not much is known about how and to what extent the effective implementation of pesticide registration, distribution, and use is carried out in Ghana. It is also unclear whether the registration authorities' activities have resulted in the essential advancements in pesticide use and control. Many farmers, according to Onwona et al. (2019), are not adequately informed on the risks associated with the handling and use of pesticides that pose a health risk.

2.3 Health risk of organic pollutant and PTEs in soils

Loffredo & Senesi (2006) held that any organic substance that is alien to the natural ecosystem and has the potential to negatively impact the physical, chemical, and biological equilibria is referred to as an organic pollutant (OP). There are a number of organic molecules of both natural and human origin that are widely dispersed in the environment and that are either known or believed to interfere with the normal endocrine activities of both humans and animals by acting as hormone-like substances in the body (Lintelmann et al., 2003).

The developing world is experiencing unprecedented health problems as a result of the expanding worldwide market for electronic and electrical gadgets, lower device life expectancies, and rapid device disposal (Needhidasan et al., 2014). These expose people to potentially harmful e-waste compounds, some of which are endocrine disruptors. Only 17.4% of the 53.6 million tonnes of manufactured e-waste in 2019 were disposed of or recycled through formal processes. The remaining materials were either recycled locally, by unofficial employees, or through primitive recycling techniques (WHO, 2021). Lack of personal safety precautions and protection puts workers and those who live close to e-waste sites at great risk of serious environmental contamination. Hazardous compounds may evaporate from contaminated soil or leach into the soil and water (Palansooriya et al., 2020). Agbogbloshie e-waste site near Accra, Ghana, a significant destination for European e-waste, is one example of a site that has grown into a whole community within a town or city in Ghana (Daum et al., 2017).

These chemicals may also include natural and synthetic estrogens, various classes of herbicides, fungicides, insecticides, and nematicides. These chemicals may also include various industrial chemicals like PCBs, PAEs, and dioxins, as well as various products and byproducts of paper, paint, and plastic industries (Daum et al., 2017). Current agricultural methods, as well as the application, discharge, and disposal of industrial and urban wastes, all have the potential to introduce these compounds into the soil (Aqeel et al., 2014). Little is known about the impact and fate of EDCs that end up in the soil (Street et al., 2018). An accurate assessment and measurement of the soil response to these chemicals are necessary for the risk assessment of potential environmental risks linked to the presence of EDCs in soil as well as the design of suitable remediation solutions (Kumar et al., 2020).

The distribution and speciation of EDCs in the various soil phases generally influence how soil reacts to environmental impact of EDCs (Senesi & Loffredo, 2009). It is extensively and securely attached to the solid soil components, where they are likely transported to deeper soil horizons and groundwater (Loffredo & Senesi, 2006). Therefore, determining the pace and extent of EDCs' adsorption and desorption processes onto and from various soil strata is crucial for understanding their behavior, performance and fate in soil as well as determining how much of an influence they may have on the environment (Loffredo & Senesi, 2006). Pesticides of all kinds (herbicides, insecticides, fungicides, etc.) and other organic chemicals that are currently utilized in agricultural activities and as agricultural product preservation are examples of potential organic pollutants (Ops) that can reach the soil by purpose ((Tudi et al., 2021).

Additional ways that OPs can enter the soil incidentally include soil amendment, discharge of municipal and industrial waste, atmospheric deposition of volatile chemicals from a variety of sources, such as waste incineration and industrial emissions (Loffredo & Senesi, 2006). These OPs include chemical compounds with a wide range of classes and characteristics, including: polynuclear aromatic hydrocarbons (PAHs), which are found in waste streams resulting from a variety of industrial processes, including the combustion of fossil fuels, chemical manufacturing and petroleum refining (Lawal, 2017).

Phthalic acid diesters (PAEs) are mostly employed as plasticizers but are also used as insecticides and pesticide transporters in dyes, cosmetics and lubricants. OPs may volatilize, photodegrade, or be carried to surface waters via soil runoff. Sunlight, in particular, causes the photochemical breakdown of OPs and can do so either directly or indirectly (Sawhney & Brown, 2015). The parent OPs, as well as perhaps the photodecomposition byproducts, gets to the soil and are influenced by a number of variables, including the OP's physical and chemical properties, hydrological status, composition, and nature, as well as the type and extent of interactions between the OP and the different soil constituents. One of the main elements influencing the destiny of OPs in soil is biodegradation carried out by soil microorganisms (Dean, 1999). The most significant microbial processes that OPs may go through in soil include ring cleavage. Intracellular and extracellular enzymes, including hydrolases, esterases, amidases, phosphatases, proteases, lyases, different phenoloxidases, monooxygenases, and numerous mixed function oxidases, mediate all of these processes (Killham, 2003). The OPs with chemical structure like that of

natural organic compounds are usually prone to biodegradation than those having little structural sameness to natural organic matter (Hickey, 1999).

2.4 Soil quality with regards to agricultural activities and solid waste dumps

According to Stamatiadis et al., (1999) agricultural soil quality refers to the state of the land and its potential for production, conservation, and environmental management, including its soil and biological characteristics. The capacity of soil to act within ecosystem limits in order to sustain biological productivity, preserve environmental quality, and advance plant and animal health as was defined by Doran & Jones (2015). Human activities have a positive and negative impact on soil quality; the level of both relies on ecosystem resilience and disturbance feedback (Franzluebbers & Stuedemann, 2006). On the other hand, improper human activities like irrigation of sewage sludge and excessive use of chemical and inorganic fertilizers degrade soil quality (Datta & Jong, 2002). Ecosystem sustainability is becoming more and more dependent on how human activities, rising populations, and the rapid expansion of the global economy affect natural ecosystems (Dumanski & Pieri, 2000). Human activities have had a significant impact on modern agricultural soil quality, which is directly related to soil productivity and humans' ability to feed themselves (Huang et al., 2007).

The creation of high-yield crop varieties, as well as growing usage of chemical fertilizers, pesticides, irrigation, and mechanization, have all contributed to an increase in crop yields over the past three decades (Bindraban et al., 2000). According to research, good agricultural techniques like tillage, applying lime, and incorporating crop residues into the soil have

enhanced soil quality (Huang et al., 2007) Both directly and indirectly, these variables are hastening changes in soil characteristics to the point that, according to recent trends, human-induced variation in soil characteristics has surpassed natural variation (Ward et al., 2001). There are numerous ways to assess soil quality, including integrated soil quality indexes (SQIs) (Doran & Parkin, 2015), multi-variable indicator kriging (Diodato & Ceccarelli, 2004) and soil quality dynamics, but no single, consistent approach has been widely adopted. The most popular techniques for evaluating soil quality are integrated SQIs. The three most crucial factors in SQI approaches are the indicators, their weights, and how the quality indices are calculated (Wang & Gong, 1998).

Soil quality (SQ) tackles both sustainability and productivity issues at once, which is why it has presently become so crucial for developing nations. Many rapidly urbanizing areas face a rising difficulty with solid waste management. According to current estimates, the growth of urban solid waste is outpacing urbanization.

According to predictions, there will be 4.3 billion urban dwellers worldwide by 2025, who will produce 1.42 kg of waste day on average (D. Hoornweg, 2012). By 2050, 56% of the population in Africa and around 66% of the entire world's population would reside in urban regions. The primary contributor to the current global environmental and climatic changes that have a direct impact on health and welfare is now understood to be human activities and their products (Whitmee et al., 2015). Due to the limited soil resources available, solid waste sorting at any level is difficult because it might include human, industrial, and medical trash as well as electronic and medical garbage

that is thrown on the same open spaces as all other municipal waste (Needhidasan et al., 2014).

The two main categories of municipal solid waste are frequently separated into organic and inorganic trash. Fast-decomposing goods like food are putrescible wastes. While non-fermentable wastes have a tendency to resist decomposition and as a result, breakdown very slowly (Ziraba et al., 2016). Items like metals, polymers, and other non-biodegradable elements are included in inorganic solid waste. Wastes, such as pesticides, medical waste, electrical trash, herbicides, fertilizers, and paints, are deemed hazardous in terms of toxicity and are advised to be disposed of in special methods rather than being combined with regular municipal rubbish (Ziraba et al., 2016). Solid waste from poor nations is regarded as a soil amendment because it often contains more organic matter than waste from industrialized nations. The addition of these materials to soils can be seen as having two functions: (1) removing solid waste from municipal and agricultural operations; and (2) enhancing the chemical and physical characteristics of the soil, which in turn encourages improved crop yields. Excessive waste in the soil may raise the concentration of heavy metals there, having negative consequences on the land, crops, and people's health (Jiwan & Ajay, 2011).

Food crops grown on these polluted soils may be harmed by some of the pollutants for a long time because it is difficult and expensive to clean up soils because of the adsorptive and buffering qualities of soils (Olowoyo & Mugivhisa, 2019).

The chemical characteristics of the waste material may significantly affect how well crops perform (Olowoyo & Mugivhisa, 2019). Additionally,

waste has been demonstrated to have an effect on soil properties such as pH, electrical conductivity, water retention capacity, and accessible phosphorus (Almendo-Candel et al., 2018).

Once more, the application of compost generated an increase in a number of soil microbial processes, such as substrate-driven respiration, nitrogen mineralization, and enzyme activity (Zhen et al., 2014). However, there is a chance that waste additions will have negative effects, particularly because of the presence of heavy metals (Agbeshie et al., 2020).

Furthermore, studies indicate that the presence of microplastics in soils may affect plant maturity, microbial activity, and soil physico-chemical properties. Microplastics may enter soils as a result of numerous factors, including irrigation, plastic mulching, soil supplements, flooding, and urban runoff (Agbeshie et al., 2020; Majewsky et al., 2016). Through the use of soil management techniques, microplastic particles can subsequently intersperse themselves throughout the soil (Steinmetz et al., 2016). Studies show that the presence of microplastics in terrestrial ecosystems may harm plant performance, microbial activities, and soil characteristics. Additionally, the decomposition of microplastics in soil aggregates can change the soil's pH and physicochemical properties, including its ability to hold water and its bulk density (Machado et al., 2018).

2.5 Background of human endocrine system

The body's endocrine system is made up of numerous glands that are dispersed all throughout. Hormones can be produced by any gland (Hiller-Sturmhöfel & Bartke, 1998). Hormones are organic molecules that are created in glandular cells and released into the bloodstream, where they circulate until

they reach a particular tissue or organ. Depending on the particular hormone and its target, they attach to those receptors and cause a response such as the generation of another hormone, a change in metabolism, a behavioral response, or other responses (Gore et al., 2014). Each gland and hormone has a specific part in a person's health and well-being, making the endocrine systems and functions complicated and diverse. They are critically essential to maintaining human health (Diamanti-Kandarakis et al., 2009). Endocrine glands and the hormones they generate aid in reproductive function, appropriate body and brain growth, and adaptation to environmental change. They also permit metabolic changes in response to various dietary needs (such as hunger, famine, obesity, etc) (Lam & Ravussin, 2016). As a result, the endocrine system functions as one of the body's primary environmental interfaces, enabling the development, adaptation, and maintenance of bodily functions and good health. Infertility, development irregularities, sleep issues, and a variety of other chronic and acute ailments are other examples of hormonal dysfunctions. To permit a healthy life, endocrine hormones must be produced in the proper quantities and endocrine glands must be able to modify hormone release in reaction to the changing environment.

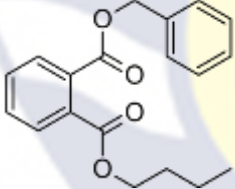
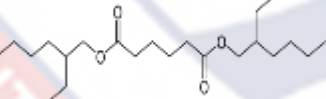
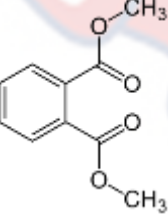
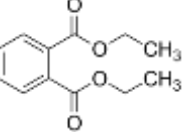
2.6 Endocrine disrupting chemicals (EDCs)

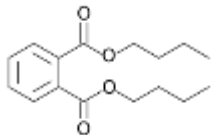
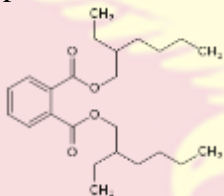
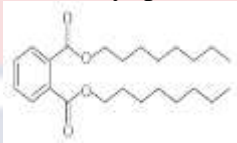
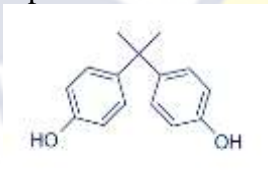
The EDCs are a group of chemical compounds with both natural and manufactured (anthropogenic) origins that are widely dispersed in the environment and are known to disrupt both animal and human endocrine systems by functioning as hormone-like substances inside the body (Godfray et al., 2019). Many industrial chemicals, such as bisphenol A, phthalic acid esters (PAEs), dioxins, and various products and byproducts of the paper,

paint, and plastic industries; some pharmaceutical products, such as estrogenic compounds; various classes of pesticides (Frye et al., 2012a). These substances may be applied to, discharged into, or disposed of from urban and industrial wastes, as well as through agricultural methods (Aqeel et al., 2014).

EDCs are currently defined as "an exogenous [non-natural] chemical, or mixture of chemicals, that interferes with any aspect of hormone action" by the Endocrine Society (endocrine.org), the largest international group of scientists and physicians working and practicing in the field of endocrinology (Bornman et al., 2017). Over 85,000 manmade compounds are produced, thousands of which could be EDCs. A list of representative EDCs and their physical properties is provided in Table 2.1.

Table 2.1 Physical properties of phthalates and BPA

Compound	Properties	Detail
 Benzyl butyl Phthalate	Molecular Formula Melting Point Boiling Point Solubility Information Formula Weight	$C_{19}H_{20}O_4$ $-35\text{ }^{\circ}\text{C}$ $370\text{ }^{\circ}\text{C}$ Slightly soluble 312.37 g/mol
 Bis(2-ethylhexyl) adipate	Molecular Formula Melting Point Boiling Point Solubility Information Formula Weight	$C_{22}H_{42}O_4$ $-67\text{ }^{\circ}\text{C}$ $417^{\circ}\text{C}(783^{\circ}\text{F};690\text{ K})$ Negligible in water 370.57 g/mol
 Dimethyl phthalate	Molecular Formula Melting Point Boiling Point Solubility Information Formula Weight	$C_{10}H_{10}O_4$ $2\text{ }^{\circ}\text{C}(36\text{ }^{\circ}\text{F};275\text{ K})$ $283\text{ }^{\circ}\text{C}$ $0.4\%(20^{\circ}\text{C})$ 194.18 g/mol
 Diethyl phthalate	Molecular Formula Melting Point Boiling Point Solubility Information	$C_{12}H_{14}O_4$ oily liquid $302\text{ }^{\circ}\text{C}$ $1080\text{ mg/L at }25\text{ }^{\circ}\text{C}$, insoluble in

		water
	Formula Weight	222.24 g/mol
Dibutyl phthalate	Molecular Formula	$C_6H_4(CO_2C_4H_9)_2$
	Melting Point	-35 °C
	Boiling Point	340 °C
	Solubility Information	13 mg/L (25 °C), colorless oil
	Formula Weight	278.34 g/mol
Bis(2-ethylhexyl) phthalate	Molecular Formula	$C_6H_4(CO_2C_8H_{17})_2$
	Melting Point	-50 °C
	Boiling Point	385 °C
	Solubility Information	Not soluble 0.00003% (23.8°C)
	Formula Weight	390.564 g·mol ⁻¹
Di-n-octyl phthalate	Molecular Formula	$C_{24}H_{38}O_4$
	Melting Point	-25°C
	Boiling Point	390°C
	Solubility Information	3.0×10^{-3} g/L (25°C)
	Formula Weight	390.56 g·mol ⁻¹
Bisphenol A: 4,4'-(propane-2,2-diyl)diphenol	Molecular Formula	$C_{15}H_{16}O_2$
	Melting Point	158 °C
	Boiling Point	360 °C
	Solubility Information	Poorly soluble colourless solid
	Formula Weight	228.29 g/mol

Dionisio et al., 2018

2.7 Sources and Uses of BPA

Chemically speaking, bisphenol A is one of the most straightforward and well-known members of the bisphenol family. It is created by condensing phenol with acetone in the presence of a catalyst, an extremely acidic ion-exchange resin. BPA is a xenoestrogen that is created as an intermediary during the production of polycarbonates and epoxy resins. It is also used in the production of adhesives, building materials, compact discs, electrical and electronic components, as well as fungicide in agriculture. Plastics, paints and lacquers, binding materials, and filling-in materials all use bisphenol A as an intermediary (binding, plasticizing, hardening).

BPA can enter the environment either directly from chemicals or indirectly through plastic, paper and metal trash in landfills, or even directly from foundries that employ it in casting sand.

Despite not being present in nature, bisphenol A has spread across the environment due to high levels of production, consumption, and subsequent environmental introduction (Tsai, 2006). Pre- and post-consumer items can be categorized as environmental sources of BPA. Pre-consumer sources consist of those connected to the production of BPA and BPA-containing goods. BPA's pre-consumer release can also occur during the transportation, processing, and manufacturing of BPA-containing items (Flint et al., 2012). Postconsumer sources include those related to waste disposal or disposal of trash, such as effluent discharge from municipal wastewater treatment plants (MWTP), leaching from landfills, burning of household waste, and environmental degradation of plastics (Fu & Kawamura, 2010). In a factory in southern Austria, Fürhacker et al. reported in 2000 that 90% of BPA was removed during wastewater treatment; comparable findings were reported in the United States. However, despite efforts to remediate BPA, reports of its discovery in the environment persist (Musolff et al., 2010; Xu et al., 2014). For instance, leachates from Japan's hazardous waste landfills were found to contain BPA at levels as high as 17.2 mg/L (Yamamoto et al., 2001) and 12 g/L in American effluents as reported by Kolpin et al (2002). In addition to being a natural occurrence, contact with heat and acidic or basic conditions speeds up the hydrolysis of the ester bonds between BPA molecules. As a result, heating to sterilize acidic or basic food or beverages in cans or polycarbonate plastic, and repeatedly heating and washing these products

exposes people and domesticated animals to BPA (Howdeshell et al., 2003; Vandenberg et al., 2007).

2.8 Sources and Uses of Phthalate

Phthalate esters (PAEs), (Fig 2.1) are a group of organic compounds that do not occur naturally within the environment but are synthesized.

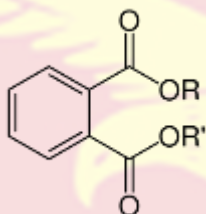


Figure 2.1 Phthalate esters

Phthalates are utilized in a wide range of items, including lubricants, gelling agents, film formers, stabilizers, dispersants, medicinal tablets, nutritional supplements, emulsifying agents, and suspending agents (Manayi et al., 2014). End-use items include children's toys, waxes, paints, printing inks and coatings, pharmaceuticals, culinary products, textiles, personal care products, building materials, medical devices, detergents and surfactants (Covaci et al., 2012). In addition, phthalates are widely utilized in sex toys made of so-called "jelly rubber," caulk, paint pigments, and soft plastic fishing lures. Many household products, including shower curtains, vinyl furniture, adhesives, floor tiles, food wrap film, and cleaning products, contain phthalates (Koger et al., 2005). Perfume, eye makeup, moisturizer, nail polish, liquid soap, and hair spray are examples of personal care products that has phthalates (Parlett et al., 2013). They are also found in medical products like catheters and blood transfusion equipment.

Benzyl-butyl phthalate

Vinyl tiles, vehicle upholstery, and adhesives are made mostly from benzyl-butyl phthalate (BBP), which is frequently metabolized into monobutyl phthalate (MBP). In-utero exposure to BBP in rats causes post implantation embryo loss, decreased blood progesterone levels, and decreased uterine and ovarian weights. In addition, rats exposed to BBP or MBP had a higher probability of losing an embryo after implantation (Barakat & Ko, 2018). Fetal exposure of rats to BBP lowered the weight of living foetuses, increased the prevalence of skeletal deformities, and increased embryonic death (Piersma et al., 2000). After BBP administration, uterine weights and progesterone levels fell; this decreased decidualization in pregnant rats was explained by the lower progesterone serum concentrations (Barakat & Ko, 2018). After being exposed to BBP in utero, a study found that the number of alveolar buds and terminal ducts increased (Harris & Sumpter, 2006). In Sprague-Dawley rats, BBP intake through diet from GD15 to PND21 led to a tendency for a delayed initiation of vaginal opening. In rats, exposure to BBP has been demonstrated to reduce pregnancy weight gain, fetal weight, and food intake while increasing the probability of miscarriage.

Di (2-ethylhexyl) adipate

Di(2-ethylhexyl) adipate, also known as bis(2-ethylhexyl) adipate (DEHA), is a possible plasticizer that greatly improves the flexibility of polymeric products Xu et al (2019). It is employed in the production of a variety of goods, including paints, flooring, lacquers, toys, faux leather, and medical equipment (Malarvannan et al., 2019). Di(2-ethylhexyl) phthalate (DEHP) is sometimes substituted with DEHA due to DEHP's endocrine

disruption and harmful effects on the reproductive system. Numerous nations throughout the world, including the European Union (EU) and the United States (US), have approved the use of DEHA in goods that come into contact with food (Rauh, 2019). Due to its release into the environment via its synthesis, distribution, and consumer use of finished plastic items, it is widely present in the environment. Nehring et al (2019) estimated that DEHA emissions from crib mattress covers are predicted to be 1.05 g/m³ in indoor air (Liang & Xu, 2014). DEHA was recently discovered in all indoor dust from 63 daycare centers in Germany at an average concentration of 80 g/g (Fromme et al., 2016).

DEHA is very frequently found in the aquatic environment. Similarly, due to food contact products, the oral route has been recognized as a significant source of DEHA exposure in numerous investigations (Fromme et al., 2016). For instance, plastics made from different polymers such as high-density polyethylene, polyethylene terephthalate, polycarbonate, polystyrene, and polypropylene contain plasticizers like DEHA to increase the flexibility of the polymers. Significantly, it is thought that the primary elements regulating the movement of DEHA are the storage conditions (time and temperature) and the amount of fat in the food (Petersen & Naamansen, 1998). analyzed the high levels of DEHA found in various food products, ranging from 151 mg/kg in fresh beef to 429 mg/kg in cheese covered in PVC film. Therefore, it is highly probable that the general population will be exposed to DEHA given that it is used in consumer goods and food contact materials. DEHA is regarded as a secure substitute plasticizer. However, DEHA had a negative impact on health at high exposure levels (Silva et al., 2013).

Dimethyl phthalate

Commercial production of dimethyl phthalate is accomplished by esterification of phthalic anhydride and methanol with the aid of a strong acid like sulfuric acid. Dimethyl phthalate (DMP) is infrequently employed as a plasticizer for PVC, in contrast to the majority of other phthalate esters. It is said to be too volatile and produces a lot of fumes while processing PVC (Verlag, 1991). Dimethyl phthalate is a chemical that is utilized in many goods, but it is most frequently employed as an ectoparasiticide for mosquitoes and flies in livestock (Niazi et al., 2001). Additionally, the short-chain or low-molecular-weight phthalate is often used in consumer goods like plastics, ink, soap, cosmetics, household cleaning products, and ink (Giuliani et al., 2020). For the cellulose acetate phthalate used to create enteric coatings for pharmaceuticals, it serves as a plasticizer. Although it is not as frequently used as DEP, it also has other cosmetic functions, such as serving as a fixative for perfumes. Due of its ability to dissolve nitrocellulose, dimethyl phthalate has historically played a significant role in several automobile coatings and paints. Dimethyl phthalate (DMP) is one of the PAEs with the highest solubility in water, reaching 4500 mg L⁻¹ at 25°C; hence, it might build up in aquatic systems (Zhang et al., 2016). Although DMP only has a modest level of toxicity, its metabolic intermediate mono-methylphthalate (MMP) is not only poisonous but also an endocrine disruptor. By lowering testosterone production and sperm counts, MMP may affect the development and reproductive system of animals and even humans. MMP can then be further broken down into phthalic acid (PA), then carbon dioxide (CO₂), water (H₂O), and other compounds.

Diethyl phthalate

Diethyl phthalate (DEP) is a synthetic liquid that is colorless, has a faint fragrant odour, and tastes harsh and unpleasant. Diethyl phthalate is produced for a variety of purposes. It is frequently used to increase the flexibility of plastics. Diethyl phthalate can be easily liberated from these items because it is not a component of the chemical chain (polymers) that makes up the plastics.

Diethyl phthalates are easily discharged into the environment since they are not covalently attached to items and can thus be ingested, inhaled, or absorbed via the skin (Clark et al., 2011).

Products including toothbrushes, vehicle parts, tools, toys, and food packaging contain these compounds. In addition to being used in aspirin and insecticides, diethyl phthalate is also utilized in cosmetics. DEP is mostly found in the kidneys and liver in rats after oral exposure, then deposits in fat (Weaver et al., 2020). The active metabolite monoethyl phthalate (MEP), which is eventually eliminated in urine and acts as a biomarker of DEP exposure, is rapidly formed from DEP. During each survey cycle between 2001 and 2010, MEP was found in the urine of at least 98% of individuals in the US general population, according to exposure assessment data from the National Health and Nutrition Examination Survey (NHANES); Urine MEP concentrations decreased significantly during that time, with an adult and adolescent tendency toward decreased urinary MEP being more prominent than that of children, possibly reflecting a trend toward less DEP use in personal care products (Zota et al., 2014). Despite this pattern, MEP levels in

urine across age groups in the study tended to continue to be greater than other phthalate metabolites (Zota et al., 2014).

In line with other assessments of biomonitoring data, DEP exposure among women of reproductive age is among the greatest, with personal care products being a key source. Diethyl phthalate may enter the environment through a variety of routes, including industrial waste streams, landfill leaks, consumer products, burning of plastics, and evaporation into the atmosphere from disposal sites. Diethyl phthalate can decompose into different substances when exposed to air. Rainwater may also deposit it on the ground or in bodies of water. Another way that diethyl phthalate might enter the environment is via adhering to dust particles. Diethyl phthalate can travel long distances in quickly flowing rivers if released into the water. In waterways that are moving more slowly, some of the diethyl phthalate may be converted into harmless substances by microorganisms in the water or sediment. Diethyl phthalate in waste waters may be broken down by sewage microbes from industrial facilities. Diethyl phthalate may cling to particles in soils containing organic matter (stuff rich in carbon), where it may finally decompose. Diethyl phthalate may penetrate the soil and reach the groundwater if there is minimal organic matter present. The chemical diethyl phthalate can be broken down by a variety of microbes into innocuous chemicals like carbon dioxide. Fish and oysters are two examples of aquatic creatures that can accumulate small levels of diethyl phthalate.

Dibutyl Phthalate

Dibutyl phthalate (DBP) is a phthalate ester that is created through the formal condensation of two molecules of butan-1-ol with the carboxy groups of phthalic acid. Despite being widely utilized as a plasticizer, it is a pervasive environmental pollutant that endangers people. It functions as a plasticizer, teratogen, metabolite, inhibitor, and environmental pollutant. Flexible plastics are produced using dibutyl phthalate and can be found in many consumer goods. It appears to be only mildly harmful. Di butyl phthalate (DBP) is incredibly pervasive and simple to find in many water bodies. The DBP concentration has frequently been found to greatly exceed the permissible limits established by national and international standards. DBP is used in industry as a plasticizer, a solvent, and is frequently added to inks and adhesives. Its main uses are in the production of plastics, textiles, paints, toys, and pharmaceutical product packaging.

It is well known that exposure to DBP can cause weight loss, endocrine system disturbance, inhibition of testicular enzyme activity, and reproductive tract deformity in both humans and animals. DBP has been observed to promote prostatic hyperplasia and an inflammatory response in mice after prolonged exposure (Scarano et al., 2009). DBP alters thyroid system function, which has a negative impact on human and animal brain development. It can also diminish organisms' ability to detoxify superoxide dismutase, which has very negative consequences (Scarano et al., 2009). Recent biological monitoring investigations have shown DBP in human bodily fluids, including saliva, breast milk, serum, and urine (Wang, Zhu, & Kannan, 2019). Concern over DBP has resulted in limitations on its usage in the

production of toys and a ban on its use in cosmetics. Despite the fact that DBP has been isolated from microorganisms and plants, it is challenging to determine whether the substance came from the environment or from the secondary metabolites of these plants given that DBP is already present in air and surface waters.

Bis (2-ethylhexyl) phthalate

Most prevalent phthalate is bis (2-ethylhexyl) phthalate (DEHP), which is widely used in a variety of products as a plasticizer, including medical devices, consumer goods such as food packages, toys etc., building and furniture products and personal products (Rowdhwal & Chen, 2018). DEHP is used extensively and is therefore present in food and the environment. Recent research revealed the presence of DEHP in particulate matter and microplastics (Deng et al., 2020). Through eating, inhalation, cutaneous absorption, medicinal injection, and parenteral administration, human DEHP exposure occurs across all age groups. The well-known EDC may have an impact on male reproductive function by acting as an androgen antagonist and altering thyroid levels (Parks et al., 2000).

Obesity and developmental abnormalities are brought on by the endocrine disturbance brought on by exposure to DEHP (Kim & Park, 2014; Zhao et al., 2018). Additionally, DEHP is linked to neurobehavioral problems like depression and causes cardiotoxicity, hepatotoxicity, and neurotoxicity. In both the old and young populations, there is a strong correlation between urine metabolites of DEHP and depressed symptoms, according to (Lee et al. (2018). Xu et al., 2020 indicated that studies on mice that were exposed to DEHP during perinatal development revealed that the chemical causes

neurobehavioral abnormalities, including anxiety and cognitive defects, and suggested that the abnormal behaviors were linked to oxidative stress and a disruption in the metabolism of sexual hormones (Barakat & Ko, 2018). In a different study, mice that were intragastrically intubated with DEHP for 10 days displayed cognitive impairment and depressed behavior, which was attributed to oxidative stress (Tang et al., 2015).

Di-n-octylphthalate

Di-n-octylphthalate (DNOP), commonly referred to as dioctyl phthalate, is a liquid that is greasy and odourless. It is difficult to evaporate. There is no proof that it is naturally occurring substance in the environment. It is produced for a variety of purposes and frequently serves as a plasticizer. Products like carpetback coating, packing films, medical tubing and blood storage bags, floor tile, wire, cables, and adhesives all contain these polymers in addition to being used in insecticides and cosmetics (NICNAS, 2008). Di-n-octylphthalate can enter the environment through evaporation from plastics, burning of plastic items, and leakage from landfills into groundwater or soil. It can also enter through air emissions, industrial waste streams.

When di-n-octylphthalate is discharged into the environment, it is anticipated to adhere firmly to soil, silt, and dust particles. The chemical may be deposited on the ground or into surface water if it is discharged into the atmosphere as rain or dust particles (Orecchio et al., 2013) Small concentrations of the substance can accumulate in aquatic species like fish and oysters. The chemical degrades into various compounds mostly as a result of microbial activity. Di-n-octyl phthalate can also change into other substances by interactions with water, sunshine, and other atmospheric molecules, as well

as through the breakdown of the chemical. Eating foods contaminated with the substance exposes people to di-n-octyl phthalate also exposure may happen during medical procedures like blood transfusions (NICNAS, 2008).

2.9 Effects of heavy metals

Humans are exposed to heavy metals through a variety of pathways since they are frequently found in the environment due to both anthropogenic and natural activity (Briffa et al., 2020). Wastewater irrigation, solid waste disposal, sludge applications, vehicle exhaust, and industrial operations are the main causes of heavy metal contamination of soil.

Food plants cultivated on these soils frequently have increased metal uptake. (Haron et al 2019). Large levels of both hazardous heavy metals and useful nutrients are typically present in wastewater, which presents both opportunities and challenges for agricultural development (Chaoua et al, 2019). The excessive buildup of heavy metals in agricultural soils caused by wastewater irrigation may also contaminate the soil. Food crops cultivated in soil contaminated with metals can absorb and collect metals in amounts high enough to have an impact on the quality and safety of the food (Emurotu & Onianwa, 2017). Heavy metals are absorbed by vegetables grown in wastewater-irrigated soils in significant amounts that pose a risk to consumer health. Humans are adversely affected by chronic level ingestion of hazardous metals, and the accompanying negative effects are only noticeable after several years of exposure (Boamponsem, G, A., Kumi, M. 2012) The most common method of human exposure to metals is through food (Rather et al, 2017). However, eating foods contaminated with heavy metals can contribute to decreased immune system function brought on by malnutrition, and a high

prevalence of upper gastrointestinal cancer rates. (Rai et al., 2019; Türkdoğan et al., 2003)

Sources and Uses of Heavy Metals

Natural elements with high atomic weight and a density at least five times greater than that of water are known as heavy metals (Tchounwou et al., 2012). Their wide distribution in the environment is a result of their numerous industrial, domestic effluents, agricultural, pharmaceutical, and technological applications as well as geogenic sources (Ali et al, 2019). Although Cd, Hg, As, and Pb were the focus of the majority of studies to evaluate the role of metals as EDCs, researchers have also turned their attention to additional metals, particularly manganese (Mn) and zinc (Zn), to examine the potential impacts that these metals may have on the endocrine system.

Heavy metals (HMs) can be generically divided into essential and nonessential heavy metals. Living things need essential HMs to carry out their basic functions, including growth, metabolism, and the formation of various organs. Heavy metals that are unnecessary for life have no recognized biological function in living things. Mn, Fe, Cu, Co, Ni, and Zn are examples of heavy metals that are biologically necessary, but Cd, Pb, and Hg are poisonous and are thought to be nonessential heavy metals (Ramírez, 2013; Zhuang et al., 2008). Mn, Fe, Co, Ni, Cu, Zn, and Mo are trace elements or micronutrients for plants and they are necessary for the manufacture and operation of various biomolecules, including carbohydrates, chlorophyll, nucleic acids, growth, and stress resistance (Appenroth, 2010)

Cadmium

Heavy metal that is commonly present in many environmental matrices is cadmium (Cd). Emissions from polluted sources are the cause of the elevated amounts of this metal in soils (Järup et al., 1998; Tchounwou et al., 2001). The primary occupational exposure sources for cadmium are the extraction, foundry, metallurgical, and electroplating industries. In contrast, exposure in the general population is caused by consumption of contaminated foods (meat, fish, and fruit) or contact with consumer goods (batteries, paints, and plastic products) (Järup et al., 1998). Human exposure to cadmium is associated with a number of health issues, such as an increased risk of renal diseases, osteoporosis, and hypertension, as well as the development of lung cancer (Koyama et al., 2002). The International Agency for Research on Cancer (IARC) classified this metal and its derivatives as carcinogenic to humans by placing them in Group 1. IARC, (2011). Studies have shown that this metal has an impact on hormones. Lafuente et al (2003) demonstrated that Cd had varied effects on the pituitary hormones gonadotropin, prolactin, ACTH, GH, and TSH in terms of their secretory patterns.

In actuality, greater dosages (25 or 50 ppm) of Cd lowered hormone levels while the lower dose of Cd increased plasma prolactin levels of rat. It has been demonstrated that gestational exposure to Cd²⁺ is linked to smaller neonatal birth weights, an increase in spontaneous abortions, and preterm deliveries. (Nishijo et al., 2002) found that mothers with higher urine Cd levels (2 nmol/mmol creatinine) had a higher rate of premature births than those with lower urinary Cd levels (2 nmol/mmol creatinine). However, these reductions were attributed to early delivery brought on by Cd. The height and

weight of newborns of mothers with greater urine Cd were considerably lower than those of newborn infants of mothers with lower urinary Cd. Similar findings were also established in a study that involved 102 mothers and their newborns and how low levels of Cd affected birth weight (Fréry et al., 1993).

Arsenic

Metalloid arsenic is commonly found in the ecosystem of the earth and is regarded as a concern to health worldwide. In essence, arsenic accumulates in the earth's crust and bedrocks and slowly seeps into drinking water (Vahter, 2008). Arsenic is a metalloid that can take on a variety of allotropic forms, including elemental, sulfide, and carbonate forms (Henke, 2009). The source of arsenic's biggest threat to public health is tainted groundwater. Many countries' groundwater naturally contains significant amounts of inorganic arsenic. Human health is seriously impacted by inorganic arsenic exposure, which occurs when people consume polluted food, drink, or air or are exposed to it at work.

Arsenicosis is a word used to describe a variety of medical issues caused by low dosages and prolonged exposure. Exposure to arsenic can result from manmade or natural sources. Arsenic enters the human body through a number of important ways, including ingestion, inhalation, and skin absorption. The gastrointestinal system quickly and extensively absorbs pentavalent and trivalent arsenic compounds. Moreover, inorganic tetravalent arsenic is weakly absorbed, whereas sodium arsenate absorption is higher. But among the arsenic compounds with the lowest rate of oral absorption are arsenic trisulfide and lead arsenate (Usman, et al., 2021). Arsenic sulfide and lead arsenate had higher rates of inhalational absorption than sodium arsenite,

sodium arsenate, and arsenic trioxide. Trivalent compounds are more hazardous in nature because they are more water soluble than pentavalent arsenic compounds. Arsenic can be absorbed and deposited in tissues and bodily fluids in its reduced (trivalent As (III)) and oxidized (pentavalent As(V)) forms (Zia et al., 2022). Although arsenic is widely dispersed in some organs, such as the skin, its distribution within the body is generally stable.

The skin typically exhibits the first signs of long-term exposure to high amounts of inorganic arsenic, such as pigmentation changes, skin lesions, and hard patches on the palms and soles of the feet and also lung, skin and bladder cancers. The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans. Long-term consumption of inorganic arsenic has been linked to harmful health effects, such as cardiovascular disease, diabetes, lung disease, and developmental impacts. Particularly in cases of arsenic-induced myocardial infarction, death can increase significantly. Arsenic exposure in utero and in early childhood has been connected to increases in mortality in young people due to numerous malignancies, lung illness, heart attacks, and renal failure. It is also associated with poor pregnancy outcomes and infant mortality, with implications on child health.

Lead

The majority of the lead (Pb) that is found in environmental matrices is produced by human activity. Lead was used in gasoline products as well as the manufacture of batteries, wires, pigments, and chemical additives (Dignam et al., 2019). The primary sources of Pb pollution in the environment are waste disposal facilities, refineries, the mining and foundry sectors, and the Pb

recycling sector (Dignam et al., 2019). Motor vehicle traffic is the primary cause of air pollution in nations that continue to use leaded gasoline because of Pb emissions. Pb exposure occurs in the general public when contaminated food, water, and air are consumed or inhaled (Dignam et al., 2019). Numerous harmful impacts of lead exposure on human health include anemia, mental problems, peripheral neuropathy, nephropathy, and stomach colic (Sanders et al., 2009).

Children with neurobehavioral issues and significantly lower cognitive function as a result of poorer levels of attention, focus, and memory were found to have blood Pb levels between 5 and 10 g/dl (Sanders et al., 2009; Téllez-Rojo et al., 2006). Pb exposure has also been related to impacts on the male and female reproductive systems, including changes in pregnancy and morphological changes in spermatozoa and sperm count (Rameshbhai et al., 2019). Due to this metal's impact on the endocrine system, it is one of the primary causes of Pb-related reproductive damage. In reality, there are a ton of research in the literature looking at the connection between hormone physiological activity and exposure to Pb (Kumar, 2018). Numerous investigations found different reproductive system anomalies in men who had been exposed to Pb. According to Gennart et al. (1992), Pb exposure caused asthenospermia, oligospermia, or terratospermia in workers at a battery plant if their blood Pb levels were 61 g/dl or between 41 and 75 g/dl, respectively.

Manganese

Manganese (Mn) exist in both organic and inorganic forms with the inorganic form being more prevalent in nature (Santamaria et al., 2007). It is used in the creation of potassium permanganate, dry-cell batteries, iron, and

steel production, among other things. Other Mn-containing substances are employed as oxidants in the production of hydroquinone, glassmaking, textile bleaching, electrode coating for welding rods, matches and fireworks, and leather tanning (Milatovic et al., 2011). Manganese causes neurotoxicity, and this toxicity has mostly been seen in work settings including Mn mining and smelting, battery production, and steel production (Santamaria et al., 2007). The first time that neurological problems related to exposure to Mn had been documented was in 1837 by John Couper who reported symptoms similar to Parkinson's disease known as "manganism," however there is strong evidence that Mn preferentially harms other parts of the brain from those damaged by Parkinson's disease (Calne et al., 1994). According to research conducted on animals, exposure to Mn may have an impact on how the endocrine system normally functions, particularly how sexual hormones are produced and secreted (Pine et al., 2005).

Zinc

Zinc (Zn) is a chalcophilic element and a minor component of most rocks. Zinc is rarely found in its metallic form in nature, however numerous minerals include Zn as a significant component, making the metal economically recoverable (Zhang et al., 2020). Zinc is used in dye casting, the building industry, and other alloys. This metal is a popular catalyst, and its inorganic compounds are utilized in a variety of products, including organ pipes, storage and dry-cell batteries, and automobile parts. Additionally, Zn chloride, sulfide, and sulfate have uses in dentistry, medicine, and the home. In comparison to other metal ions with comparable chemical characteristics, zinc is quite safe. Toxic effects only appear after exposure to high

concentrations or by a lack of copper (Plum et al., 2010). The relationship between sperm quality and sperm Zn concentration was investigated in epidemiologic research. Data indicated that Zn increased male fertility by positively affecting spermatogenesis. In actuality, oligospermic and azospermic patients have significantly lower Zn levels in their sperm than fertile men (Hasan et al., 2007). This metal's protective function, favorable impact on spermatogenesis, and capacity to preserve sperm viability by blocking DNAases are likely all a result of its antioxidant and membrane-stabilizing properties (Aitken & Clarkson, 1987). In fact, after ejaculation, excessive superoxide anions created by faulty spermatozoa and/or leukocytes in human semen appear to be effectively scavenged by Zn. Therefore, it appears that seminal plasma exerts protective, antioxidant-like activity adequate to counteract the excessive amount of superoxide anions due to its high Zn content (Gavella & Lipovac, 1998).

Copper

Despite being a necessary element, copper has the potential to be hazardous in certain doses. Although excess Cu negatively impacts plant metabolic processes like photosynthesis, respiration, and enzyme activity, it is nevertheless a necessary micronutrient for plants (Yruela, 2005). Copper is vital because it is a component of numerous proteins necessary for life. Copper deficiency has been linked to osteoporosis in adults and has been linked to bone deformity during development (Heller et al., 1978). (Conlan et al., 1990). Additionally, it has been linked to weakened immune defenses and a rise in infection rates (O'Connor et al., 2002). Marginal copper deficiency has been linked to changes in cholesterol metabolism and increased

cardiovascular risk (Uriu-Adams & Keen, 2005). Since copper metabolism is closely linked to that of other microminerals, it is well recognized that a copper deficiency can hinder the mobilization of iron and lead to a secondary iron insufficiency. The most common side effects of copper are acute nausea, vomiting, and diarrhea, but very high doses of copper have been known to cause multiple organ failure, shock, and even death in some people. The stomach is where early acute responses start; copper ions excite receptors, which in turn stimulate the vagus nerve, causing a reflex response of nausea. When the copper dose is somewhat higher, in addition to the vagal response, the hypothalamic vomit center is directly stimulated, causing nausea and vomiting (Horn et al., 2014). Health authorities and regulators have recently become concerned about the prospect that low copper concentrations (such those found in drinking water) could have immediate negative effects on humans (Simonsen, Harbak, & Bennekou, 2012)

Cobalt

Cobalt compounds primarily exist in two valence states: cobaltous (Co^{2+}) and cobaltic (Co^{3+}), with the former being the most readily available in terms of commerce and the environment (Huang et al., 2018). The immune system and regulation of gene expression are all aided by cobalt metal ions, which are trace elements that are widely distributed in nature and necessary for normal physiological function (González-Montaña et al., 2020). However, cobalt may be toxic when exposed in higher doses (Simonsen et al., 2012). Exposure might come from work-related, environmental, nutritional, and medical factors. Because it occurs frequently, humans are regularly exposed to different cobalt molecules (Leysens et al., 2017). The general public is mostly

exposed via breathing in ambient air and consuming food and water that contain Co compounds. The manufacture of hard metals, grinding, mining, and paint are just a few of the industries that use cobalt, making occupational exposure to it another reasonably common occurrence (Leysens et al., 2017).

Additionally, cobalt is or has been utilized for a variety of medical applications, some of which have been discontinued over time (Bhattacharya & Flora, 2015). The metal industry is thought to be the primary source of occupational Co exposure, as well as cement workers are considered to be the most frequent sources of irritant and allergic contact dermatitis. Because cobalt (Co) is frequently used in the manufacture and processing of hard metals, workers in the recycling of e-waste may be exposed to high levels of cobalt. In this context, Grant et al. (2013) identified three primary exposure pathways: inhalation, skin contact, and oral intake and depending on whether formal or informal recycling processes are used the exposure rate will vary. Cobalt is frequently used as a siccative in some paints or inks to speed up the drying process and in cobalt blue dyes for porcelain and pottery painting (Prescott et al., 1992).

The main exposure methods are coming into contact with skin and breathing in paint fumes or particles. In nature, various cobalt compounds are extensively distributed, usually in low amounts. At unpolluted locations, atmospheric Co concentrations are typically less than 2.0 ng/m³. An important illustration of a polluting activity is the incineration of combustible municipal solid waste. The residual bottom ash contains heavy metals (such as Co) that can seep into the ground and soil and provide long-term environmental

hazards (Huang et al., 2018). The recycling of e-waste could contaminate the environment nearby in the context of trash processing.

2.10 Exposure Effects of EDCs

Chemicals that have been developed have multiplied exponentially since 1940, some of which have been leaked into the environment (intentionally or unintentionally). This chemical revolution has permanently altered ecosystems, with negative effects on both animal and human health. Prior to a few years ago, it was believed that the placenta served as a barrier, shielding the growing foetus from any exposure to certain chemicals and drugs. This perspective was altered and ultimately refuted by two terrible clinical occurrences. The first was the discovery that some infants born to pregnant women who took thalidomide during the first trimester to treat morning sickness had serious abnormalities. Clearly, the mother's medications left the foetus susceptible. Diethylstilbestrol (DES), which is administered to pregnant women to prevent miscarriage, was the second ground-breaking discovery. DES shares characteristics with natural estrogen hormones. Girls exposed to DES in the womb frequently experienced reproductive system malformations, and some of them later on in adolescence got rare reproductive cancers that are typically only found in postmenopausal women. It is now widely acknowledged that some EDC substances can penetrate the placenta to affect the foetus and alter the normal function of the human endocrine system (Fig 2.2)

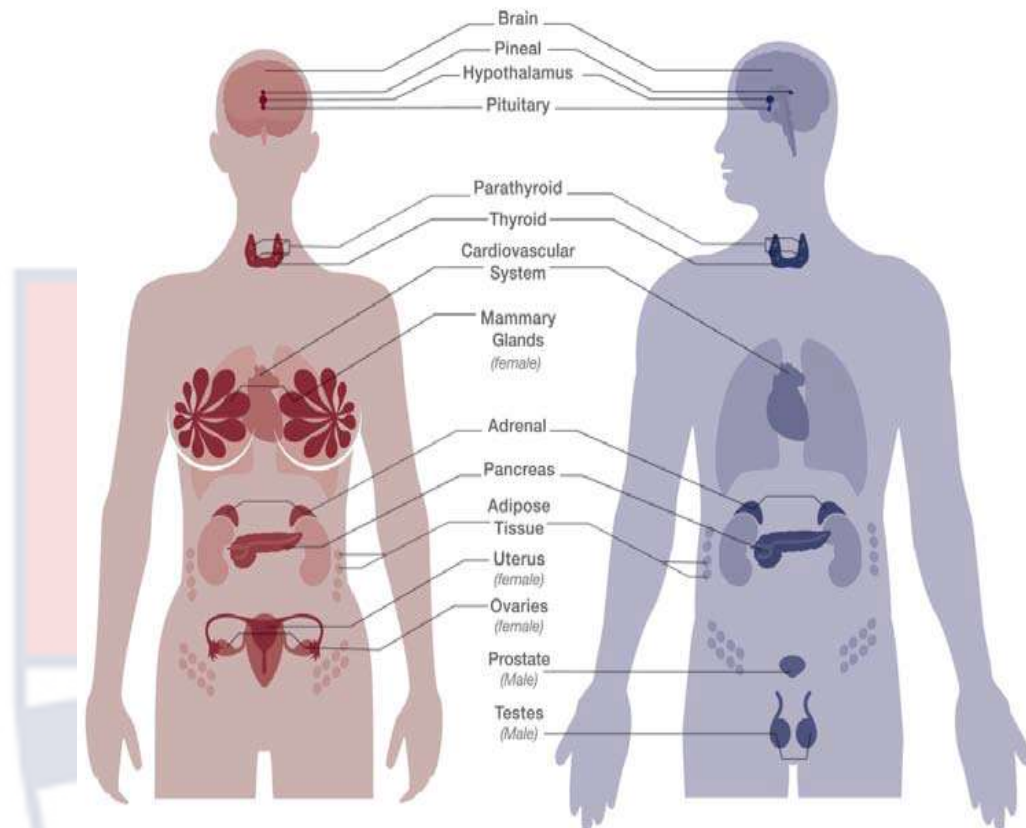


Figure 2.2 Organs of the endocrine system (Gore et al., 2014)

2.11 EDCs Effect on Soil

Soils play a significant role in maintaining life in addition to sustaining biological activity, immobilizing, detoxifying organic and inorganic materials, storing and cycling nutrients and protecting archaeological treasures (Drenning, 2021). According to studies, soil provides a variety of ecological functions, including a base for the production of biomass, a water filter or buffer, and a carbon storage facility. Additionally, soil acts as both a source and a sink of various types of pollution, having a significant impact on all plants and other living things (Banwart et al., 2015). Heavy metals' toxicity is evident in their adverse effects on human and animal health as well as the growth and development of plants (Jaishankar, Tseten, Anbalagan, Mathew, & Beeregowda, 2014). Changes in a variety of chlorophyll a fluorescence metrics are indicative of the fact that HM ions hinder numerous metabolic

pathways in plants (Zurek et al., 2014). Whether those effects are good or bad, direct or indirect, soil has a significant impact on human health. The nutrients in our food supply and pharmaceuticals like antibiotics come from the soil (Brevik et al., 2020). On the other hand, nutritional imbalances and the existence of human diseases in the soil's biological population can have a detrimental impact on health (Oliver & Gregory, 2015). Due to anthropogenic activity or natural conditions, numerous areas have dangerous quantities of certain elements or chemical compounds in soil (Steffan et al., 2018).

Numerous factors can contribute to soil contamination, including leaking oil tanks, chemicals that have leaked into the environment or fallen as dust, accidents involving the handling of hazardous goods, leaking sewers, and urban trash (Aqeel et al., 2014). In other words, industry, increased agricultural activity, conflicts, and human waste are the main causes of worldwide soil contamination. The fact that polluted soil may come into touch with both surface and subsurface waters increases the threat.

2.12 Fate of EDCs in Soil

Various pesticides and other organic compounds that are currently employed in agricultural activities are examples of EDCs that can enter the soil by purpose. Additionally, they can enter the soil incidentally through the discharge of municipal and industrial waste, soil amendment, atmospheric deposition of volatile chemicals originating from industrial emissions and solid waste incineration. Also chemicals such as: (a) polynuclear aromatic hydrocarbons (PAHs), which are found in waste streams, including the combustion of fossil fuels, petroleum refining, and metallurgical processes; (b) phthalic acid diesters (PAEs), used as plasticizer but also serve as pesticide

carriers and insect repellents. They could be carried to surface waters by soil runoff, erosion, volatilization, or photodecomposition after reaching the soil surface (Loffredo & Senesi, 2006). According to Loffredo & Senesi (2006), anthropogenic organic pollutants (AOPs) in soil may get immobilized or accumulate by surface and interlayer adsorption.



CHAPTER THREE

INCREASING PESTICIDE USE AND KNOWLEDGE OF THE HEALTH EFFECTS OF ENDOCRINE DISRUPTING CHEMICALS IN THE ENVIRONMENT: A STUDY OF THREE COMMUNITIES IN GHANA

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ABSTRACT

Population growth and urbanisation are contributing to the growth of the use of pesticides in Africa. However, poor understanding of the health and environmental effects of these chemicals represents a significant risk to both human health and ecosystems. Knowledge of health effects of pesticides use and endocrine disrupting chemicals (EDCs) was assessed using 300 respondents in three communities of Ghana. The data were fitted to bivariate and multivariate ordinary least squares regression models. About 76 per cent of the respondents used pesticides while 82 per cent had no knowledge of human diseases associated with EDCs and pesticides use. At the bivariate level, individuals who used pesticides had less knowledge of health effects of EDCs and pesticides use compared to their counterparts who did not use pesticides. Urban residents had more knowledge compared to rural dwellers and this robust relationship persisted at the multivariate level. Females of all ages had more knowledge of pesticides and EDCs effects than their male counterparts. Formal and informal education is required to improve knowledge on appropriate chemical use.

Keywords

Knowledge; endocrine disruptors; pesticides; environment; urbanisation; population growth.

3.1 Introduction

Hormone mimicking substances referred to as endocrine disrupting chemicals (EDCs) comprise a wide variety of environmental contaminants including pesticides, pharmaceuticals, metals, industrial chemicals and natural compounds (Foster, 2001, Choi et al., 2004). EDCs interfere with metabolic function that are responsible for homeostasis, reproduction, and developmental processes (Zoeller et al., 2012; Diamanti-Kandarakis et al., 2009).

Studies indicate an adverse effects of this group of substances when found in food, consumer products and the environment (Frye et al., 2012; Kumar et al., 2020; Yilmaz et al., 2020). As early as the 1930's, the ability of both natural and synthetic chemicals to interact with endogenous hormone receptors was already well established (Marty et al., 2011) however most individuals are unaware of the health risks. EDCs have such subtle effects that they may be extremely difficult to detect instantly and yet have significant impacts on human health over an extended time period where they remain 'out of sight out of mind'.

Despite significant advances in understanding of EDCs, knowledge gaps required to protect humans still exist that cannot be overlooked. For example, exposure of an adult to EDC may have very different consequences compared to exposure of a developing foetus or infant. Similarly, there is a lag between the time of exposure and the manifestation of a disorder (Heindel & Vandenberg, 2015; Arendrup et al., 2018). Effects of EDCs may also be additive or even synergistic (Diamanti-Kandarakis et al., 2009; Bergman et al., 2012). Indeed, any level may cause endocrine or reproductive abnormalities, if exposed during a critical developmental period (Sisk et al., 2016; Diamanti-

Kandarakis et al., 2009). Humanity as a whole, and Africa in particular, is faced with activities that make it susceptible to the effects of EDCs (Bornman et al., 2017). Lack of sound management of chemicals as well as poor hazardous wastes disposal systems pose risks to human health (Taherzadeh et al., 2019).

Africa is faced with rural to urban migration by its youths in search of jobs due to rapid population growth (Lomoro et al., 2017; Mutandwa et al., 2011), with accompanying shift in lifestyle and consumption patterns (Cockx et al., 2018). Increased use of household products which contain EDCs further increases the likelihood of human exposures (WHO, 2018). Developing countries seem to attract the development of economic sectors that are among the most polluting (UNEP 2013). The shift to urban living in Africa and other developing countries continues to increase the amount of contaminants and EDCs released into water, air, and soil (Miller and Marty, 2016).

Demographic changes have considerable influence on consumption patterns through population growth, urbanisation, as well as lifestyle changes. These factors principally influence the demand for chemicals and products that contain EDCs. High rates of population growth also results in inadequate investment in human capital: education, health, employment, infrastructure and poor waste disposal systems (Ganivet, 2020) which exacerbate the problems associated with the increased use of EDCs.

Africa has the fastest-growing rate of population which is directly related to the growth in size and intensity of agricultural production (United Nations, 2019). The use of pesticides has increased in an attempt to increase food production in response to increased demand from population growth

whilst reducing poverty. This trend is exacerbated by urbanisation which leads to a continuous decline in the size of agricultural land through housing, fully-fledged industry, cottage industry and the provision of other social amenities.

In Ghana, pesticides applied in agriculture for pest control constitute a widely used category of EDCs (Mattah et al. 2015; Denkyirah et al., 2016; Ginger et al 2005). Dinham (2003) estimated that 87 per cent of Ghana's vegetable farmers use chemical pesticides for pest and disease control. There are also indications of adverse effects on productivity, environment and human health due to overuse and misuse of pesticide in Ghana (Gerken et al., 2001; Amoako et al., 2012; Mattah et al., 2015). Farmers and consumers are also faced with health problems from the effect of these chemicals (Owusu-Boateng & Amuzu, 2013; Ntow et al., 2006). This puts every Ghanaian at risk and thus the need to properly regulate use.

The Government of Ghana ensured that standards are enacted to regulate imports of pesticides and ensure their proper use, however the use of pesticides by individuals remains difficult to control (Onwona Kwakye et al., 2019). Illiteracy and apathy of farmers about the health risks and environmental implications results in greater reliance on chemically-synthesised pesticides and increased use of cheap, mislabelled and adulterated pesticides in Ghana (Onwona et al., 2019; Imoro et al., 2019). Furthermore, rural poor who are employed to work as farm hands and also small holder farmers fail to wear protective equipment and observe good agricultural practices (Wumbei et al., 2019).

Despite the reported adverse health effects of pesticides and EDCs on humans, public awareness is low in Ghana. In 2019, the Government of Ghana

launched the Health and Pollution Action Plan (HPAP) that seeks to regulate EDCs and other types of pollutants that affect human health in an effort to sensitise the public and regulate the use of EDCs.

Despite advances made only few studies exist on exposure and perception of communities. Community perception is important as it underpins behavioural responses to the adverse health effects of exposure to pesticides. This study looks at general pesticide use and public understanding of health effects of EDCs in three communities in Ghana in the context of the changes in lifestyles of urban and peri-urban dwellers. Although the use of pesticides, personal care products and other chemicals cannot be done away with entirely, it is imperative to ensure their proper use. Pesticides use within three communities of Ghana and knowledge of the health effects of EDCs on human and the environment is conceptualised as a composition of three main factors - biosocial, sociocultural and contextual factors as shown in Fig. 1. Biosocial factors (age and sex) are intrinsically personal. These personal attributes are ascribed at birth and not easily amenable to change (Pol & Thomas, 2013). The second set of compositional factors, namely sociocultural attributes reflects the position of individuals within the social structure. These attributes are achieved rather than ascribed. Further, these attributes are inherently 'cultural', in that those affected take on characteristics assigned by society (Pol & Thomas, 2013). Some cultural and nature-based practices that protected rural people from excessive exposure to EDCs are being phased out through urbanisation. For instance, in the rural setting, food was cooked and served in earthenware bowls, however with rural-urban drift and increased

population, food is mostly served in plastic packs that may contain chemicals that are endocrine disrupting.

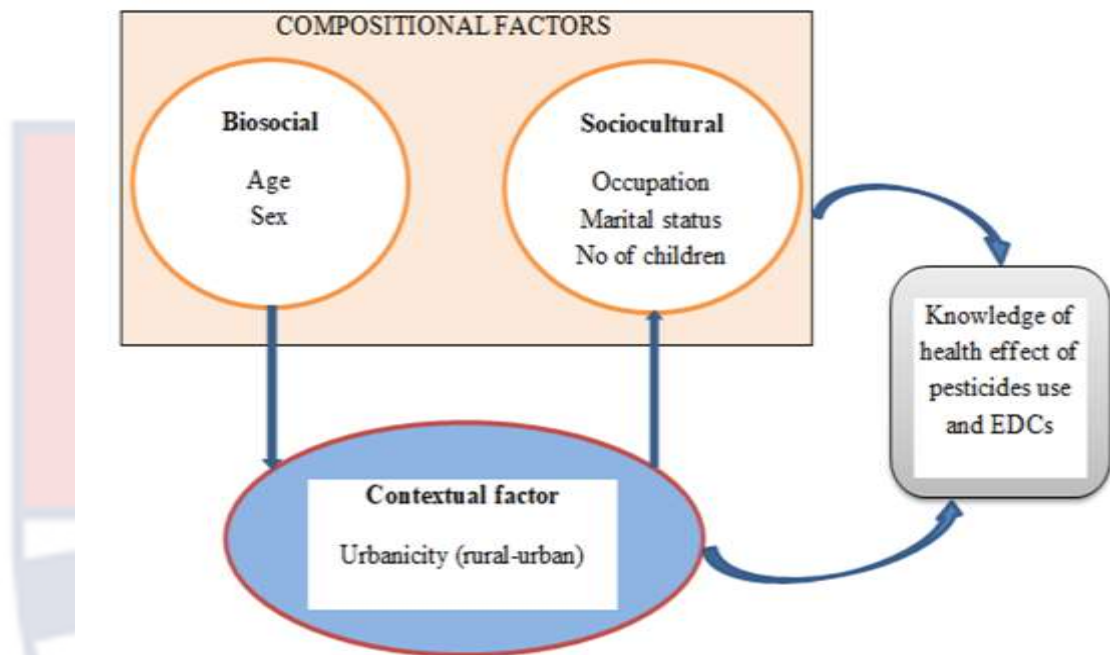


Figure 3.1 Conceptualisation of the relationship between Knowledge of health effect of EDCs and compositional and contextual factors

3.2 Materials and methods

Study area

This study was conducted in three communities in two different regions of Ghana. Two communities, Kakumdo and Essuekyir are in the Central Region and the third, Nmai Dzorn in Greater Accra Region. Kakumdo and Essuekyir are adjoining communities within the Cape Coast metropolis with Cape Coast as the regional capital. The Cape Coast Metropolitan area is one of the oldest districts in Ghana and is bounded to the South by the Gulf of Guinea. It occupies an area of approximately 122 square kilometres, with the farthest point at Brabedze located about 17 kilometres from the regional capital (Ghana Statistical Service 2010). The population of the Cape Coast Metropolis, according to the 2010 Population and Housing Census, is 169,894

representing 7.7 per cent of the region’s total population. Males constitute 48.7 per cent and females 51.3 per cent (GSS 2010).

The metropolis has a few rivers and streams including the Kakum, a major stream in the Metropolis. It serves as the main source of water for domestic and industrial purposes. Kakumdo and Essuekyir take their names from the river Kakum that separates the communities. Kakumdo means ‘on’ the Kakum and Essuekyir means ‘behind the river’ in the local Fante dialect and indicates their location. They are at outskirts of the regional capital about 8 kilometres from the Cape Coast castle and close to one of the forest reserves of Ghana (Kakum National Park). These communities are mainly residential and can be classified as peri-urban. The inhabitants are mostly traders, artisans and peasant farmers.

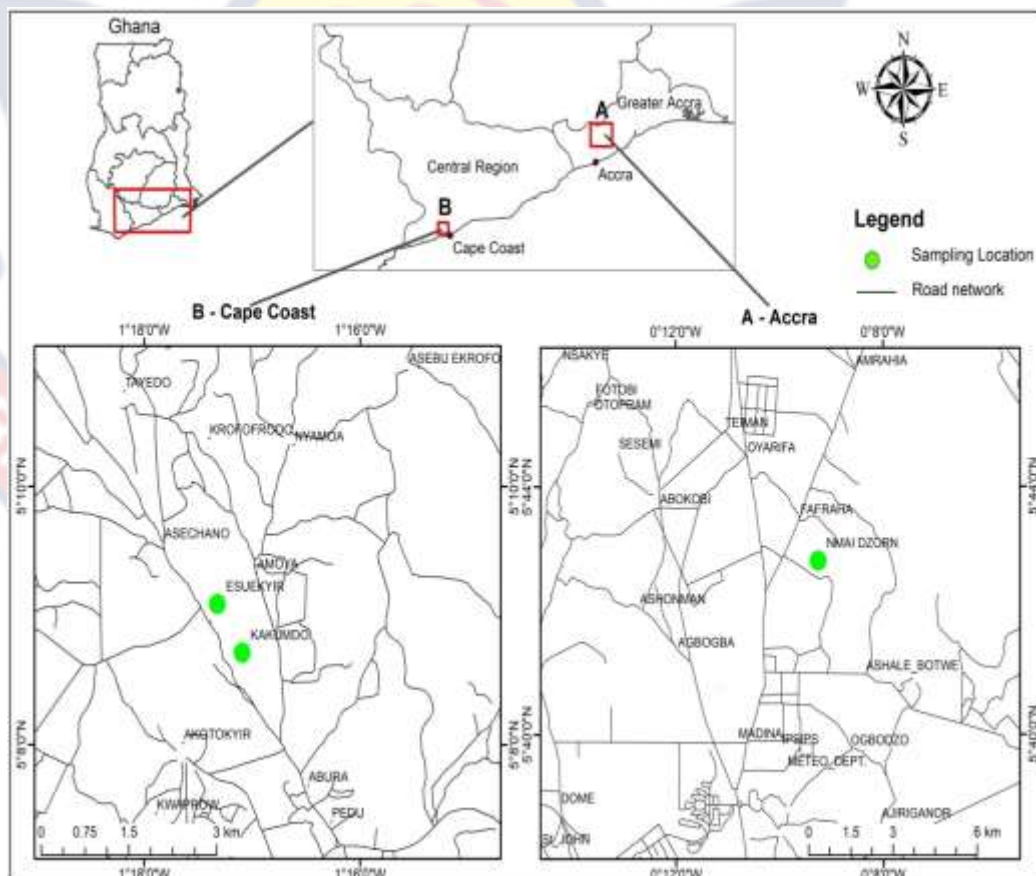


Figure 3.2 Map of Ghana showing regions, districts and study area

Our third study area, Nmai Dzorn is an urban community within the Adentan Municipality. The population of Adentan Municipality, according to the 2010 Population and Housing Census, is 78,215. Males constitute 50.3 percent and females 49.7 percent. The Total Fertility Rate (TFR) for the metropolis, at 2.2, is the lowest in the Greater Accra Region. The Adentan Municipal Assembly with Adentan as the Central Business District lies 10 kilometres to the Northeast of Accra and it is specifically located on latitude 5' 43" north and longitude 0' 09" west. The Municipality has a land area of about 928.4 sq. km. (GSS 2010). It is mainly a residential area with few commercial activities. These communities were selected to represent the lifestyles of individuals in urban and peri-urban setting.

Data collection

Respondents who volunteered and participated in the study were drawn from three different communities made up of homogeneous and heterogeneous localities in terms of ethnic and cultural diversity. Residents who were of sound mind, either household heads or their wards, were selected to participate in the study. Respondents who migrated to their current location in less than a year were classified based on their former place of residence. In all, three hundred (300) participants were selected randomly and interviewed. The sample consisted of two hundred and eleven (211) females and eighty nine (89) males between the ages of eighteen (18) and fifty (50). Modified Cochran formula for sample size calculation at 95% confidence level was used (Bartlett et al., 2001), as shown in equations (1) and (2).

$$n = \frac{n_0}{1 + \frac{(n_0-1)}{N}} \quad (1)$$

Where n_0 is Cochran's sample size recommendation,

N is the population size, N= 1350

n is the new, adjusted sample size.

n_0 is Cochran's sample size recommendation, $n_0 = 385$

Considering the target population of 1350 households, equation (2) was used to determine sample size.

$$385 / (1 + (384 / 1350)) = 300 \quad (2)$$

The questionnaire was tested before it was administered after approval from the ethical clearance review committee of the Ghana Medical Association due to the sensitive nature of some of the questions.

Stratified surveys, informal interviews, and individual interviews were used to gather information about the prevalence of pesticide use and the level of awareness of EDCs. Stratified sampling was used to select the proportion of male to female interviewees based on the health impact of EDCs on gender. Informal and individual interviews dealt with the interviewee's pesticide use and level of awareness of EDCs. The questionnaire focused on four thematic data areas: (1) personal information, (2) knowledge of the effects of EDCs by listing possible diseases, (3) lifestyle change, i.e. nutrition, social life and work history, and (4) possible reproductive irregularities (though it was not used as an indication of possible EDC effect).

Knowledge on the specific adverse health effects associated with exposure to EDCs and pesticides was measured using a 5-point Likert scale. Responses to the questions were: strongly disagree; disagree; neutral; agree; and strongly agree. A Likert scale is composed of a series of four or more Likert-type items that represent similar questions (adverse health outcomes) combined into a single composite score/variable. Likert scale data can be

analysed as interval data, i.e. the mean is the best measure of central tendency (Sullivan & Artino, 2013).

Other questions were a combination of closed and open-ended questions in a multiple choice format so that respondents had to select 'yes' or 'no' as an answer. However, some questions demanded explanation to the answer. The questionnaire was administered to the general public by the principal investigator at various locations, including homes, churches/mosques and schools. The objectives of the study were explained to the respondents and their consent to participate in the study was obtained. Respondents were at liberty to withdraw from the study any time they felt they could not respond to sensitive question(s). In instances where respondents were not English language literate the questions were translated into a local language that is understood by the interviewee without altering their original meaning. In situations where the principal investigator could not speak the preferred local language of the respondent it was done through an interpreter. The identities of respondents were coded and data recorded manually. Respondents' knowledge of human health effects of pesticide use and EDCs were gathered based on whether they agree, unaware or disagree with indicated human related diseases.

Statistical analysis

Data collected were first cleaned to eliminate double entries, missing values and other irregularities. Inferential and multivariate techniques were applied to examine the relationship between knowledge of the health effects of EDCs and pesticides use while controlling for theoretically relevant sociocultural and biosocial variables using STATA 13SE software. The

ordinary least square technique was employed for the analysis. Analyses were preceded by diagnostic tests to establish whether variables met the assumptions of the regression model. Univariate analysis of the predictors on each of the questions that measure knowledge of health effect of EDCs was operationalised using Pearson's Chi-square statistics. Bivariate analysis was initially performed to examine zero-order relationships between the dependent variable and theoretically relevant independent variables. A further three models were employed for the data analysis. Model 1 is Bivariate and biosocial factors, model 2 comprises of Bivariate, biosocial and sociocultural factors and model 3 is Bivariate, biosocial, sociocultural and contextual factors. The analysis has a hierarchical structure with respondents nested within survey clusters, which could potentially bias the standard errors. STATA 13 SE (Stata Corp, College Station, TX, USA), which has the capacity to address this problem, is used by imposing on our models a 'cluster' variable, that is, the identification numbers of respondents at the cluster level. This in turn adjusts the standard errors (SE) producing statistically robust parameter estimates. Multivariate models were estimated to explore the net effects of the predictor variables using the stepwise selection approach. For analytical purposes, the unstandardised regression coefficients were estimated. Positive coefficients for any of the predictors indicate higher levels of knowledge of the health effects of EDCs and pesticide use while negative coefficients show lower levels of knowledge of the health effects of EDCs and pesticides use.

3.3 Results

Relationship between knowledge of health effects of pesticides and EDCs and demographic attributes

The distribution of the responses on knowledge of health diseases associated with the use of pesticide and EDCs are shown in the appendices. Pesticide use is widespread in the communities; 76 per cent of the respondents surveyed used pesticides, though there were differences in the way the pesticides were actually employed. The majority of the respondents (82 per cent) had no knowledge of the health effects of pesticides use and EDCs. The remaining 18 per cent demonstrated they had some knowledge relating to one or more human diseases, mostly cancers. Different age groups of respondents showed varied levels of knowledge with respect to cancers while respondents who are married also demonstrated more knowledge of health effects of EDC with respect to cancer. The results show that higher percentages of males (48 per cent) know that pesticide use and EDCs could lead to prostate cancer and other forms of cancers than their female (22 per cent) counterparts. Only 1 per cent of males and 4 per cent of females know that pesticides and EDCs could lead to behaviour disorders. A few individuals, 11 per cent of the 82 per cent with no knowledge, had doubts about possible adverse health effects and disagreed with the notion that pesticides use and EDCs could cause diseases.

Table 3.1 shows zero-order relationships between the explanatory variables and knowledge of health effects of endocrine disruptors and pesticides use. Individuals who use pesticides had less knowledge of the health effects of EDCs and pesticides compared to their counterparts who did not use pesticides. There were differences in the knowledge that pesticide use could disrupt the function of the endocrine system based on age groups. The

younger respondents had greater knowledge of health risks than the older counterparts. Individuals above 45 years were less knowledgeable about the health effects of EDCs than respondents in the 15–25 age groups. Similarly, females had more knowledge of the health effects than their male counterparts.

The evidence demonstrates that urban dwellers have greater knowledge of the health effects than respondents in rural communities. Unmarried individuals were also more aware than married respondents as indicated in table 1. Robust standard errors used accounted for heteroskedasticity in the model's unexplained variation.

Table 3.1: Bivariate OLS regression model of the relationship between knowledge of health effects of Endocrine disruptors and pesticide use, and compositional and contextual factors

Variables	Coef.	Std. Error	p-value	[95% Conf. Interval]	
Pesticide use (ref: No)					
Yes	-0.338	0.135	0.013	-0.602	-0.073
Age (ref:15-25 years)					
26-35 years	0.003	0.153	0.982	-0.299	0.306
36-45 years	0.080	0.155	0.606	-0.229	0.385
Above 45 years	-0.350	0.173	0.043	-0.690	-0.010
Gender (ref: male)					
Female	0.621	0.121	0.000	0.3817	0.860
Marital Status (ref: not married)					
married	-0.459	0.113	0.000	-0.681	-0.238
Children (ref: No Child)					
1-3 children	0.134	0.130	0.302	-0.121	0.390
4-5 children	-0.115	0.175	0.511	-0.460	0.229
Above 5 children	-0.449	0.240	0.058	-0.913	0.016
Occupation (ref: unemployed)					
Self employed	-0.149	0.133	0.263	-0.410	0.112
formally employed	0.052	0.190	0.786	-0.323	0.427
Residence (ref: Rural)					
Urban	0.369	0.148	0.013	0.078	0.660

The multivariate model (Table 3.2) showed that gender was a significant predictor of knowledge of the health effects of EDCs even when socioeconomic and contextual factors were taken into account. However, the relationship between pesticides use and knowledge was not robust and disappeared, indicating that biosocial and contextual factors completely mediated the relationship. Females of all ages had greater knowledge of the effects of pesticide use and EDCs than their male counterparts. Unmarried women demonstrated more knowledge of health effects of pesticides and EDCs than their counterparts who are married and remained statistically significant, however, it was not robust when contextual factors were taken into account. The age group of 36-45 years was significant in model 2, though it was not significant in model 1, signifying a suppressed relationship between biosocial factors and knowledge of health effects of pesticides. Suppression occurred when the relationship between an independent variable and the dependent variable was increased following the statistical removal of variance associated with a third variable.

The place of residence of respondents was significant when all factors were considered indicating that it fully mediates the relationship between compositional variables and knowledge of the health effects of pesticides. This shows the effect that the independent variable has on the dependent variable via its association with a third variable. Urban residents had higher levels of knowledge of health effects of EDCs and pesticides use compared to rural dwellers and this robust relationship persisted when sociocultural and biosocial variables were introduced.

Table 3.2: Multivariate regression model of the relationship between knowledge of health effects of endocrine disruptors and pesticide use, compositional and contextual factors

Variables	model 1 (pesticide use + biosocial factors)					model 1+ socioeconomic					model 2 + contextual				
	Coef.	Std. Error	p-value	[95% Conf. Interval]		Coef.	Std. Error	p-value	[95% Conf. Interval]		Coef.	Std. Error	p-value	[95% Conf. Interval]	
Pesticide use (ref: No)															
Yes	-0.197	0.134	0.141	-0.461	0.066	-0.161	0.133	0.225	-0.422	0.100	0.131	0.130	0.316	-0.388	0.126
Age (ref:15-25 years)															
26-35 years	0.111	0.150	0.458	-0.184	0.406	0.161	0.176	0.363	-0.186	0.507	-0.011	0.180	0.952	-0.365	0.34357
36-45 years	0.269	0.155	0.083	-0.035	0.573	0.407	0.203	0.046	0.008	0.807	0.239	0.205	0.246	-0.165	0.643
Above 45 years	0.299	0.185	0.871	-0.334	0.394	0.278	0.250	0.267	-0.214	0.769	0.089	0.251	0.724	-0.406	0.583
Gender (ref: male)															
Female	0.602	0.139	0.000	0.329	0.875	0.487	0.147	0.001	0.198	0.776	0.542	0.145	0.000	0.256	0.828
Marital Status (ref: not married)															
married						-0.496	0.151	0.001	-0.792	-0.200	-0.473	0.148	0.002	-0.764	-0.182
Children (ref: No Child)															
1-3 children						0.328	0.160	0.042	0.012	0.643	0.243	0.160	0.129	-0.070	0.556
4-5 children						0.974	0.219	0.656	-0.333	0.528	0.088	0.215	0.683	-0.335	0.511
Above 5 children						-0.075	0.280	0.790	-0.625	0.476	-0.098	0.275	0.722	-0.638	0.443
Occupation (ref: unemployed)															
Self employed						-0.019	0.165	0.907	-0.344	0.306	-0.053	0.162	0.743	-0.373	0.266
formally employed						0.097	0.203	0.635	-0.303	0.496	0.042	0.200	0.834	-0.351	0.435
Residence (ref: Rural)															
Urban											0.559	0.162	0.001	0.239	0.879

Source: Researcher 2022

3.4 Discussion

General public understanding of the health effects of endocrine disrupting chemicals and pesticide use in three communities in Ghana were studied. The vast majority of the respondents (82 per cent) were ignorant of the diseases associated with pesticides use and EDCs, which is comparable to a similar study conducted by Hui et al., (2017). This is attributed mainly to poor information dissemination and regulatory policy. Our research shows that people who knew more about pesticide toxicology were less likely to use pesticides. Other studies, such as Dasgupta & Meisner (2005), Gesesew et al., (2016) and Sabran & Abas (2021), also support our observation. We also found that besides the relationship between pesticide knowledge and use behaviour, there were other individuals who do not use pesticides simply because they could not afford them and/or they preferred natural methods of pest control.

There is no coordinated plan to evaluate and disseminate information on health and environmental effects of chemicals that are endocrine disrupting in nature. The government, in a bid to address this challenge, launched the Health and Pollution Action Plan (HPAP) that seeks to regulate EDCs and other types of pollutants affecting human health with the aim of sensitising individuals to the effects of EDCs. Dinham (2003), indicated that low level of knowledge and how pesticides are handled hinders the overarching goal of protecting human health and the environment from the adverse effects of EDCs. Knowledge gaps that exist are too important to overlook considering the low dose effect and time lapse between exposures and development of disease later in life. The current 76.3 per cent prevalence of synthetic

pesticides use is partly attributed to ignorance of health effect as well as urbanisation and its associated problems. Several studies conducted have reported improper use of pesticides and disposal of waste from chemicals of endocrine disruptors (Amoako et al., 2014; Onwona Kwakye et al., 2019; Oteng-Ababio, 2012; Wumbei et al., 2019) For example, spraying of household pests when food and cooking utensils are not properly covered, spraying of pest without proper Personal Protective Equipment (PPE) and individuals not properly washing themselves after use of pesticides are some of the behaviours that predisposes individual to the various health effects. There is lack of sound management of chemicals for industrial, agricultural and household use as well as poor hazardous waste disposal systems. This results in high levels of pesticides residues within the environment thereby posing a risk to humans and the environment.

The finding that females of all ages are more knowledgeable about the effects of pesticides use and EDCs than their male counterparts was difficult to assign a specific reason. Females are generally provided with information on EDCs and pesticides during pregnancy as part of health education during antenatal care. Antenatal care is one of the three most important forms of welfare provided to women during pregnancy (Choi et al., 2004) to keep mother and the unborn child safe. Pregnancy is a sensitive window for toxicant exposure and EDCs are of particular significance to pregnant women, since foetal development is sensitive to maternal nutritional, chemical, and environmental stressors. EDCs may disrupt the maternal immune system, which may lead to poor pregnancy outcomes (Kelley et al., 2019). In Ghana, two-thirds of women who utilise antenatal care received information about the

danger signs of pregnancy complications (Wang et al., 2011) and hospitals and health centres have served as one of the main sources of information on the adverse health effects of EDCs and pesticides use. Again, health care facilities and the provision of services are improved in the urban centres than the rural areas. It therefore, showed that individual female respondents who lived in the urban centres have more knowledge than their counterparts in the rural areas as a result of the better provision of healthcare and likewise of antenatal care in the urban centres than the rural areas. This is supported by studies that revealed the existence of urban – rural differences and regional disparities among the providers of antenatal care services (Afulani, 2015; Abor et al., 2011).

3.5 Study Limitations

Questionnaires have the advantage of quick, cheap, and easy administration and can be crafted to capture specific items aimed at evaluating knowledge, attitudes and perceptions. One obvious limitation of questionnaires is that they are subject to social desirability bias. There is also the likelihood of response bias in this study. Response bias is a widely discussed phenomenon in behavioural and healthcare research where self-reported data are used; it occurs when individuals offer self-assessed measures of some phenomenon (Rosenman et al., 2011), in this case diseases associated with pesticide exposure. Educational attainment of the respondents was not included in this study.

3.6 Conclusion

The level of awareness of the health effects of endocrine disrupting chemical and pesticide use in three communities in Ghana were influenced by demographic, sociocultural and contextual factors.

Demographic changes in the form of population growth, rural to urban migration as well as changes in lifestyles have had a considerable influence on the consumption of pesticides and EDCs. In particular, population growth and urbanisation have influenced the increase in the use of these chemicals in agriculture in order to increase yields. As the population becomes increasingly urban, some cultural and nature-based practices that protected rural people from excessive exposure to EDCs are being lost. Furthermore, unsustainable population growth has exacerbated the effects of insufficient investment in education, health, employment, infrastructure and poor waste disposal systems increasing the vulnerability of people and ecosystems to the effects of pesticides and EDCs.

This study revealed low level of knowledge of the health effects of endocrine disrupting chemicals among the three communities, especially amongst those in rural areas where pesticides are widely used. Indeed, it showed that some individuals are dismissive of any possible adverse health effects. Considering the low dose effect and time lapse between exposures and development of disease later in life, these knowledge gaps cannot be overlooked.

3.7 Recommendation

Practical and effective measures are needed to reverse this disturbing trend among populace. A coordinated plan is required to evaluate and disseminate information on health and the environmental effects of chemicals that are endocrine disrupting in nature. The Ghanaian government's Health and Pollution Action Plan (HPAP) seeks to regulate EDCs and other types of pollutant that affect human health, however there is also the need for an integrated and coordinated effort to define the role of pesticides and other EDCs in human health. Health institutions should be encouraged to scale up the education on the adverse health effects of pesticides and other endocrine disrupting chemicals that has become part of everyday life



CHAPTER FOUR

RISKS OF TOXIC ELEMENTS AND ENDOCRINE DISRUPTORS IN SOME SOILS IN GHANA

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Abstract

Endocrine disrupting chemicals (EDCs) and potentially toxic elements (PTEs) may pose risks to humans and the ecosystem. Characterization and possible human risk of EDCs and PTEs were assessed in four land use classes. Four composite soil samples were taken per site and used for the analysis of heavy metals, and EDCs. The results generally indicated that PTEs and EDCs are within recommended thresholds except for arsenic (As) and bisphenol A (BPA). The dump site was most influenced by heavy metals, BPA, diethyl phthalates (DEP) and Di-n-octyl phthalate (DNOP). The industrial site had the highest level of Cd, Dimethyl phthalate (DMP), Dibutyl phthalate (DBP) and Bis (2-ethylhexyl) phthalate (DEHP) whereas the forest reserve had the highest level of Fe, Bis (2-ethylhexyl) adipate (DEHA) and Benzyl butyl phthalate (BBP). Arsenic had the highest variability with a minimum and maximum value of 2.58 and 2455.75 mg kg⁻¹, respectively. Overall, there are significant variations ($p < 0.05$) in PTEs and EDCs between sites except for DMP, DEP, BBP and DEHA. No single EDC non-cancer risk via non-dietary routes exceeded the allowable level ($HQ > 1$) for DMP, DEP, BPA, BBP, DEHP and DnOP. Similarly, carcinogenic exposure risks of BBP and DEHP via non-dietary routes were lower than 1×10^{-6} however, the ingestion cancer risk (CR) values of Cd, As and Pb exceeded the threshold value of 1×10^{-4} which indicates potential lifetime carcinogenic risk.

Key words

Risk, Toxic Elements, Endocrine disrupting chemical, Soils, Ghana

4.1 Introduction

The growing concern of possible health threat posed by organic compounds that are endocrine disrupting in nature is an important issue globally. These substances are found within the environment which interferes with hormone biosynthesis and metabolism. The World Health Organization (WHO) defined endocrine-disrupting chemicals (EDCs) as “an exogenous substance or mixture that alters functions of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations” (Damstra, Barlow, Bergman, Kavlock, & Van Der Kraak, 2002; WHO, 2018). Countless chemical substances found in industrial and domestic products have endocrine disrupting properties and also several heavy metals that are potential toxic elements (PTEs) (Choi, Yoo, & Lee, 2004; De Coster & Van Larebeke, 2012; Gregoraszczuk & Kovacevic, 2013; Kunz & Fent, 2006; Tseng, Scholz, Schöner, & Hotchkiss, 2003). Despite the adverse health effects, these chemical substances are widely used as a result of their application in industrial and domestic products. These chemicals enter the terrestrial environment through various pathways and adversely affect living organisms. Anthropogenic activities such as industrial activity and spillage, agricultural production and waste disposal remain the major source of soil pollution which acts as a sink (Aqeel et al., 2014). Most of these pollutants remain in the terrestrial environment for long periods and adversely affect human health and proper functioning of the soil, which is critical in ensuring food security and safety globally (Kong, Macleod, Hung, & Cousins, 2014).

Contributing to pollution is urbanization which is on the increase worldwide. The gradual shift of human settlement from rural to urban areas, coupled with the overall growth of the world's population could add another 2.5 billion people to urban areas by 2050 mostly in Asia and Africa (United Nations, 2019). The rural-urban drift comes with accompanying economic growth, increased use of chemicals for industrial, agricultural and household and its associated waste generation. Considering the current trend of population growth in Africa, it is estimated that Africa's population that lives in urban areas is expected to increase to about 59% by 2050 (United Nations, 2019). Waste management is a major challenge in most countries with less than 30% of urban waste in developing countries collected and disposed appropriately. Urban centers are prone to substantial burden of ill-health attributable to poor waste management (Ziraba et al., 2016b). Lack of sound management of chemicals in industrial, agricultural and household settings as well as poor disposal systems for hazardous wastes pose a threat to humans and the environment. The increasing generation of solid waste in Africa has not been accompanied by corresponding capacity to manage it. The ramifications of poorly managed waste on health of individuals can be dire and depend on the nature of the exposed waste, duration of exposure and availability of interventions for those exposed (Ziraba et al., 2016b).

Ghana is also experiencing problems associated with population growth, urbanization and economic growth. Residual waste from industry, agriculture and household is not adequately managed. Approximately, only 44% of the total solid waste generated is collected and managed properly; leaving a backlog of 56%, which are either burned by household or disposed

of through other inappropriate means (Abalo, Peprah, Nyonyo, Ampomah-Sarpong, & Agyemang-Duah, 2018). The substantial quantity of waste generated and left unattended to end up in the environment and pose health threat to life. The presence of potential toxic elements in soil can severely inhibit the biodegradation of organic contaminants. Similarly, contamination of soil with EDCs may pose risks to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain and drinking of contaminated ground water (Encarnação et al., 2019). EDCs may also reduce food quality, reduction in land suitability for agricultural production and causing food insecurity.

Limited information on EDCs in soil exists in Africa concerning the potential human health risks. There is also little knowledge of ways in which EDCs belonging to different classes may interact to produce synergetic effects or otherwise (Kortenkamp, 2007). In view of foregoing, this study aims to characterize and assess health risks of EDCs and PTEs in four selected sites that represent agriculture, industry, decommissioned waste dump and forest reserve.

4.2 Materials and methods

Study locations

Soil sampling was conducted in four sites within Greater Accra and Central Regions of Ghana as indicated in fig 1. Samples were taken in April prior to the main rainy season. Three of the sampling sites are in the Greater Accra and one site in the Central Region. The sampling sites represent four land use classes—agriculture, industry, waste dump and forest reserve that depict different anthropogenic effect in urban and rural settings.

The sites in Accra are within an urban area and separated about 9km apart and 140km from the last location in the Central Region. The site in Central Region is located in less influenced rural area. Agricultural soils were sampled from the environs of the Council for Scientific and Industrial Research (CSIR) head office within an urban setting. The area remains a major vegetable growing site all year for over 50 years and the continuous application of pesticides, organic and inorganic fertilizer. Soil from the dump was taken within 200m from the Adenta decommissioned dump that received all manner of solid waste (Metal-Tins/Cans, Food, plastics, Textile etc.) from most part of the capital for many decades. The industrial soils were taken from Accra North industrial area that has most of the companies that produce plastic products and samples from the forest reserve were taken from Kakum National Park, in the Central Region. The Kakum National Park is located in the rural coastal environs of Central Region and covers an area of 375 square kilometres with tropical forest. Soils taken from the forest reserve served as control.

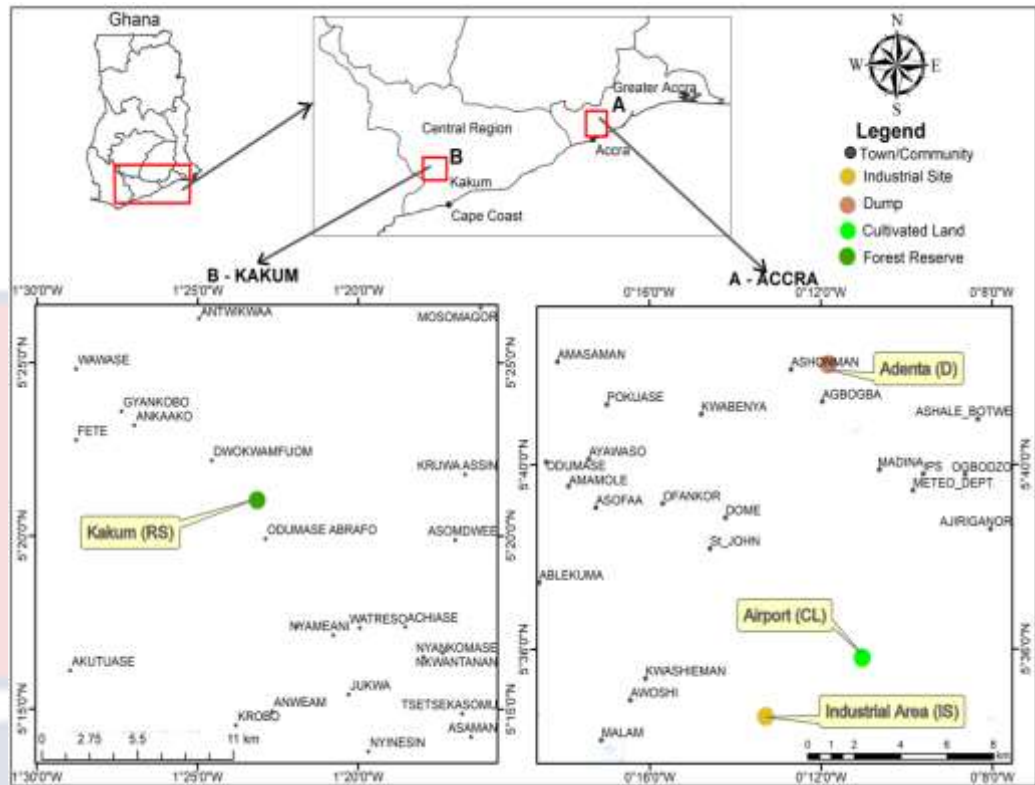


Figure 4.1 Map showing the geographical location of sampling sites

Sample collection

Soils were randomly sampled with auger at a depth of 30 cm from the four (4) sites. Four (4) composite samples were taken per site from 12 different sampling points. Soil samples were initially stored in aluminum foil and taken through preparatory procedures. The samples were air dried at room temperature, homogenized and sieved (2mm mesh) before use. Portions were used to determine the physicochemical characteristics of the soils, PTEs (Fe, Mn, Cd, Pb, Ni, Co, Cu, Zn, As) and EDCs (BPA, DMP, DEP, DBP, BBP, DEHA, DEHP, DNOP)

Physicochemical analyses of the soil samples

Soil particle size analysis was carried out using the pipette method (Rowell, 1994). Soil reaction pH and electrical conductivity (EC) were measured in 1:2.5 soil: water suspension. Total nitrogen was determined by the Kjeldahl method (Sparks et al., 1996). Available phosphorus contents in

soils were extracted by Bray's P1 solution and measured on Genesys 20 spectrophotometer (Bray & Kurtz, 1945). Organic carbon was determined by the wet oxidation method (Walkley & Black, 1934). Analyses of the exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ and Na^+) were done by the method described by Rowell (Rowell, 1994) and determined with Jenway PFP7 flame photometer.

Extraction of EDCs and PTEs

Soil samples were digested using aqua regia according to (Verloo and Demeyer 1997) for the extraction of heavy metals and metalloid. Approximately 1.00 g of oven-dried, finely ground soil was weighed into a digestion flask and moistened with 2 mL deionized water. Then, 7.5 mL concentrated HCl and 2.5 mL HNO_3 were added. The reaction flask was covered and allowed to stand at room temperature overnight. The mixture was heated progressively under reflux and allowed to boil for 2 h. After cooling to room temperature, the reflux column was rinsed with 20 mL deionized water. Content of the digestion vessel were filtered into a 100 mL volumetric flask and rinsed with 10 mL 0.5 M HNO_3 . The volume was made up to 100 mL with deionized water.

Phthalates and Bisphenol A were extracted using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method. A modified version of the original QuEChERS procedure (Pinto et al., 2010) was applied. Approximately 5g portion of the soil samples was weighed into 50 ml centrifuge tubes, and 5 ml of deionized water was added. Then 20 ml of acidified acetonitrile (1% acetic acid in acetonitrile) and 2g of sodium chloride (NaCl) were added. The tube was sealed, and shaken for 5 min. and then

centrifuged for 5 min. at 4000 rpm. Approximately 10mls of the supernatant was transferred to a centrifuge tube containing 0.1g of primary secondary amine (PSA), 2g of magnesium sulfate (MgSO_4) and then shaken for 2 mins and centrifuged at 4000 rpm for 5 min. Approximately 5ml portion of the supernatant was transferred into a test tube and concentrated to almost drying by evaporation under nitrogen flow; the sample was reconstituted with 1ml of acetonitrile and vortexed for 2 mins to dissolve all samples. The extract was then transferred to an auto sampler vial for GC–MS analysis.

Sample analysis

The soil samples were analyzed for PTE using Agilent 240FS AA and Agilent 240Z AA (200Series AA) with GTA 120. EDCs analyses were performed with GC-MS QP 2020 Shimadzu equipped with RTS-5MS trace analysis column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The carrier gas was helium of high purity (99.99 %), The flow rate was 1 mL min^{-1} at a pressure of 83.1kp. Sample volume of $1\text{ }\mu\text{L}$ was injected in pulsed splitless mode with an inlet temperature of 265°C . To quantify Phthalates, the column temperature was programmed as follows: the initial oven temperature was set at 70°C for 2 min, increased to 200°C at 15°C /min . It was further ramped at 6°C/min to 310°C and held for 1 minute. The interface and ion source temperatures were set at 265°C and 220°C respectively. Also for bisphenol A, the column temperature program was as follows: 50°C for 1 min. ramped at 15°C /min . to 180°C and further ramped at 8°C/ min . to 300°C and held for 1min. The interface and ion source temperatures were set at 270°C and 220°C respectively. Quantifications were all carried out in the selected ion monitoring mode (SIM) selecting two characteristics fragments ions for each.

The heavy metals and metalloid were determined with Atomic adsorption spectrophotometer (AAS), Agilent Technologies 200 series 240FS AA and Graphite Tube Atomizer 240ZAA.

Quality control

Soil samples were analyzed in triplicate and after every 10 samples, a certified standard and a blank solution were run to check for contamination and drift. The detection limits for Fe, Mn, Cd, Pb, Ni, Co, Cu, Zn and As were 0.010, 0.005, 0.002, 0.005, 0.010, 0.010, 0.010, 0.005 and 0.001 mg kg⁻¹, respectively.

The EDC extraction solvent and matrix adsorbent were studied using blank soil samples spiked with standards. The blank values of the analytical procedure were determined by extracting the spiked sample by the same method as the real soil sample with recovery of spiked sample in the range of 86%–116%. The estimation of the limit of detection (LOD) for the EDCs in the soil samples was conducted based on U.S. EPA guidelines (USEPA, 1995) with a confidence level of 95%. An LOD of 3× (detection peak/blank peak + standard deviation) was observed. Instrumental detection limits were calculated by a signal-to-noise ratio of 3 times the sample concentration and ranged from 0.10 to 0.31 mg L⁻¹. Method detection limits of the EDCs were 0.005, 0.007, 0.01, 0.005, 0.015, 0.01, 0.007 and 0.4 mg kg⁻¹ for DMP, DEP, BBP, DEHP, DBP, DnOP, DEHA and BPA, respectively. Surrogate standards and internal standards concentration of 20µl of 5ppm and 50µl of 20ppm in 1ml respectively were added to all the samples to monitor the matrix effects, calibration and quantification. A calibration curve was made by serial dilutions of calibration standards with at least five concentrations for each

EDC compound monitored. Linear regression with coefficient of (R^2) > 0.99 was accepted.

Human exposure and health risk assessment

The potential risks of EDC and PTE to the environment and human health cannot be overlooked. The cancer and non-cancer risks of the selected endocrine disrupting chemicals and PTE in soils were estimated according to the US EPA recommendation. Residents close to the decommissioned dump and human scavengers for metal scraps are exposed to risks via non-dietary pathways. Similarly farmers, workers of the industrial and reserved soils and residents within the catchment areas are also exposed. The formulas with modification from the US EPA, (U.S. EPA, 2015) which have been widely employed in previous studies (Başaran et al., 2020; Li et al., 2021; Wang et al., 2018; Zhu et al., 2019) were used to assess the average daily dosage (ADD, $\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$) of EDCs and PTEs via different exposure pathways, namely ingestion (ADD_{ing}), dermal absorption (ADD_{der}) and inhalation (ADD_{inh}) as Equations. (1–7). The cancer slope factor (CSF) values of As, Cd and Pb are 1.5, 6.3 and 0.0085 ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)⁻¹ respectively (Jia, Li, & Wang, 2018)

$$ADD_{ing} = \frac{C_S \times I_S \times EF \times ED}{BW \times AT} \times CF \quad (1)$$

$$ADD_{der} = \frac{C_S \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (2)$$

$$ADD_{inh} = \frac{C_S \times I_i \times EF \times ED}{PEF \times AT \times BW} \quad (3)$$

$$HQ_i = \left(\frac{ADD_i}{RfD} \right) \quad (4)$$

$$HI = \sum HQ_i \quad (5)$$

$$CR = \sum (ADD_j \times CFS) \quad (6)$$

Where C_s is the individual concentration of EDCs measured in soil ($\text{mg}\cdot\text{kg}^{-1}$). I is the daily intake rate; (I_s) is the soil ingestion rate ($\text{mg}\cdot\text{d}^{-1}$). (I_i) is the inhalation rate ($\text{m}^3\cdot\text{d}^{-1}$). SA is the dermal exposure area (cm^2). ABS is the dermal adsorption fraction. AF is the dermal adherence factor for soil ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$). BW is the body weight (kg). AT is the averaging time (Days): for non-cancer risks, $AT = ED \times 365$; for carcinogens risks, $AT = \text{average lifetime} \times 365$. ED is the exposure duration. EF is the exposure frequency ($\text{days}\cdot\text{year}^{-1}$). CF is the conversion factor ($1.0 \times 10^{-6} \text{ kg}\cdot\text{mg}^{-1}$). PEF is the particle emission factor ($1.36 \times 10^9 \text{ m}^3\cdot\text{kg}^{-1}$). CSF represents the cancer slope factor. Non-cancer risks of EDCs exposure via soil were determined by the hazard quotient (HQ) and hazard index (HI) using equations (4–5) where RfD is the reference dose value of each EDC ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$), HQ represents the health risks of the individual EDC to human health via different exposure routes, and i represents different exposure routes. The carcinogenic EDC was determined from equation (6). Individuals are exposed to non-cancer risks if the value of HQ is >1 (J. Wang et al., 2015). The estimated carcinogenic risks may be considered very low if the value of risk is less than 1×10^{-6} , low in the range of 1×10^{-6} to 1×10^{-4} , moderate from 1×10^{-4} to 1×10^{-3} , high from 1×10^{-3} to 1×10^{-1} and very high if the value is greater than 1×10^{-1} (Niu, Xu, Xu, Yun, & Liu, 2014).

Statistical analysis

Descriptive statistics were used to analyze soil properties, potential toxic elements and endocrine disrupting chemicals found at the various sites. The data were further analyzed using multivariate statistics (Pearson product

moment correlation, cluster analysis and principal component analysis) in SPSS 20.0 for Windows (IBM SPSS Inc., Chicago, IL). Statistical significance was set to $p < 0.05$.

4.3 Results

Soil properties

Generally soil properties (SP) of the four different sites (dump, Agricultural, industrial and reserved), analyzed based on anthropogenic influence indicated deficiency in some of the essential soil nutrient required for optimum crop growth. The texture of soils from the dump and industrial sites is sandy loam, Agricultural soil is loamy sand and reserved soil is clay loam. The mean values of the soil chemical properties analyzed showed low levels of potassium (K), Phosphorus (P) and sodium (Na) and moderate levels of calcium (Ca), Organic carbon (OC), Magnesium (Mg) and nitrogen (N). Cation exchange capacity (CEC) was moderate while pH was basic as indicated in Table 4.1. Indication of variations in the distribution of the chemical properties between the sites was observed. Measures of central tendency, dispersion and distribution are shown in table 4.1

Table 4.1 General descriptive statistics of soil properties of the sites

	Mean	Std. Deviation	Skewness	Kurtosis	Minimum	Maximum
OC (%)	2.66	1.93	.821	-.602	.48	6.60
N (%)	0.17	0.12	1.078	-.174	.05	.43
Ca (mg kg ⁻¹)	3338.48	2411.66	.354	-1.395	648.56	7710.08
Mg (mg kg ⁻¹)	251.22	212.61	1.116	-.097	53.94	742.40
Na (mg kg ⁻¹)	103.68	96.74	1.927	3.679	14.55	470.57
K (mg kg ⁻¹)	5.47	7.19	2.069	3.722	.24	29.10
CEC (cmol(+)kg ⁻¹)	19.25	13.38	.450	-1.193	3.96	43.64
P (mg kg ⁻¹)	1.46	1.57	.815	-.821	.06	4.65
pH	7.45	1.35	-1.043	-.704	4.95	8.68
EC (μs)	290.88	264.19	1.865	2.684	75.97	1142.00

Potentially toxic elements and endocrine disrupting chemicals

The PTEs and EDC studied showed considerable variations in concentration across sites, indicating that some areas were less influenced while others were heavily influenced with human activity (Table 4. 2). PTEs analyzed were within the EU recommended threshold (MEF, 2007; The Council of the European Communities, 1986) except Arsenic (As) that was above the 5 mg kg^{-1} threshold. Similarly, EDCs investigated revealed that the phthalates were within the New York State Department of Environmental Conservation acceptable threshold (NYSDEC, 2010) for all sites however, BPA concentration at the dump site was above the recommended threshold (Table 4. 3). The dump site had the highest level of arsenic over 160 fold above the threshold while reserved soils had the least arsenic concentration with over 45 fold the recommended threshold (Table 4. 3). Also Arsenic was most varied in concentration with a minimum value of 2.58 and a maximum value of $2455.75 \text{ mg kg}^{-1}$. The dump site was most influenced with PTEs and EDC than all the sites. It had the highest level of Mn, Pb, Ni, Co, Cu, Zn, As, BPA, DEP and DNOP compared to industrial site that had the highest level of Cd, DMP, DBP and DEHP while forest reserve site had the highest level of Fe, DEHA and BBP.

Table 4. 2. Descriptive statistics results of potentially toxic elements and endocrine disrupting chemical of the sites (mg kg⁻¹)

Parameters	Std.		Skewness	Kurtosis	Minimum	Maximum
	Mean	Deviation				
Fe	420.529	183.154	-.455	-1.143	46.376	683.801
Mn	5.409	3.879	1.063	-.396	1.471	14.781
Cd	0.020	0.029	2.424	5.945	.0020	0.124
Pb	1.301	1.068	.631	-.879	.1430	3.724
Ni	0.213	0.109	1.444	1.869	.0780	0.534
Co	0.070	0.028	.308	-1.158	.0280	0.123
Cu	0.999	1.226	1.578	1.635	.0950	4.568
Zn	4.160	3.818	.642	-1.259	.4030	10.695
As	478.451	433.269	2.966	10.026	2.5800	2455.750
BPA	92.519	295.240	3.643	11.984	.0000	1215.466
DMP	.0282	0.0154	-.278	-.038	.0000	0.0559
DEP	.0352	0.0196	.796	1.492	.0025	0.0985
DBP	.0483	0.0222	.007	-.854	.0119	0.0873
BBP	.0061	0.0197	4.602	20.452	.0000	0.0988
DEHA	.0357	0.0300	1.510	1.823	.0022	0.1334
DEHP	.5486	0.3449	.705	-.297	.0910	1.2988
DNOP	.0082	0.0095	2.619	6.980	.0003	0.0410

Source: Researcher, 2022

Table 4. 3 Mean levels of potentially toxic elements (mean \pm and SD) endocrine disrupting chemicals at locations compared with threshold. All values reported in mg kg⁻¹

Parameter	Dump	Agricultural	Industrial	Reserve	(CEC,1986)	Threshold
Fe	361.338 \pm 61.97 11.713 \pm	165.506 \pm 62.01	549.426 \pm 49.31	605.845 \pm 36.12	NA	NA
Mn	1.17	3.373 \pm 1.53	4.049 \pm 0.68	2.501 \pm 0.49	NA	NA
Cd	0.035 \pm 0.01	0.002 \pm 0.00	0.041 \pm 0.05	0.002 \pm 0.00	3.0	1 ^c
Pb	2.693 \pm 0.66	0.309 \pm 0.18	1.766 \pm 0.49	0.436 \pm 0.03	300.0	60 ^c
Ni	0.367 \pm 0.10	0.154 \pm 0.06	0.177 \pm 0.01	0.153 \pm 0.04	75.0	50 ^c
Co	0.093 \pm 0.02	0.066 \pm 0.03	0.076 \pm 0.02	0.044 \pm 0.01	NA	20 ^c
Cu	2.787 \pm 1.23	0.143 \pm 0.02	0.910 \pm 0.30	0.157 \pm 0.03	140.0	100 ^c
Zn	9.939 \pm 0.61	0.652 \pm 0.13	4.806 \pm 1.62	1.244 \pm 0.28	300.0	200 ^c
As	830.175 \pm 441.46	436.804 \pm 93.29	401.948 \pm 61.81	244.878 \pm 88.11	NA	5 ^c
BPA	350.671 \pm 193.35	16.588 \pm 1.95	2.684 \pm 0.96	0.136 \pm 0.03	NA	310 ^b
DMP	0.028 \pm 0.01	0.029 \pm 0.00	0.036 \pm 0.01	0.021 \pm 0.02	NA	27.0 ^a
DEP	0.045 \pm 0.03	0.038 \pm 0.01	0.034 \pm 0.01	0.024 \pm 0.02	NA	7.1 ^a
DBP	0.052 \pm 0.03	0.048 \pm 0.01	0.064 \pm 0.02	0.029 \pm 0.02	NA	NA
BBP	0.002 \pm 0.00	0.001 \pm 0.00	0.004 \pm 0.00	0.017 \pm 0.03	NA	122.0 ^a
DEHA	0.044 \pm 0.04	0.025 \pm 0.01	0.026 \pm 0.02	0.048 \pm 0.03	NA	NA
DEHP	0.708 \pm 0.39	0.477 \pm 0.13	0.741 \pm 0.47	0.269 \pm 0.15	NA	435.0 ^a
DNOP	0.015 \pm 0.02	0.005 \pm 0.00	0.008 \pm 0.00	0.005 \pm 0.00	NA	120.0 ^a

(NYSDEC, 2010)^a (USEPA, 2015)^b (MEF, 2007)^c

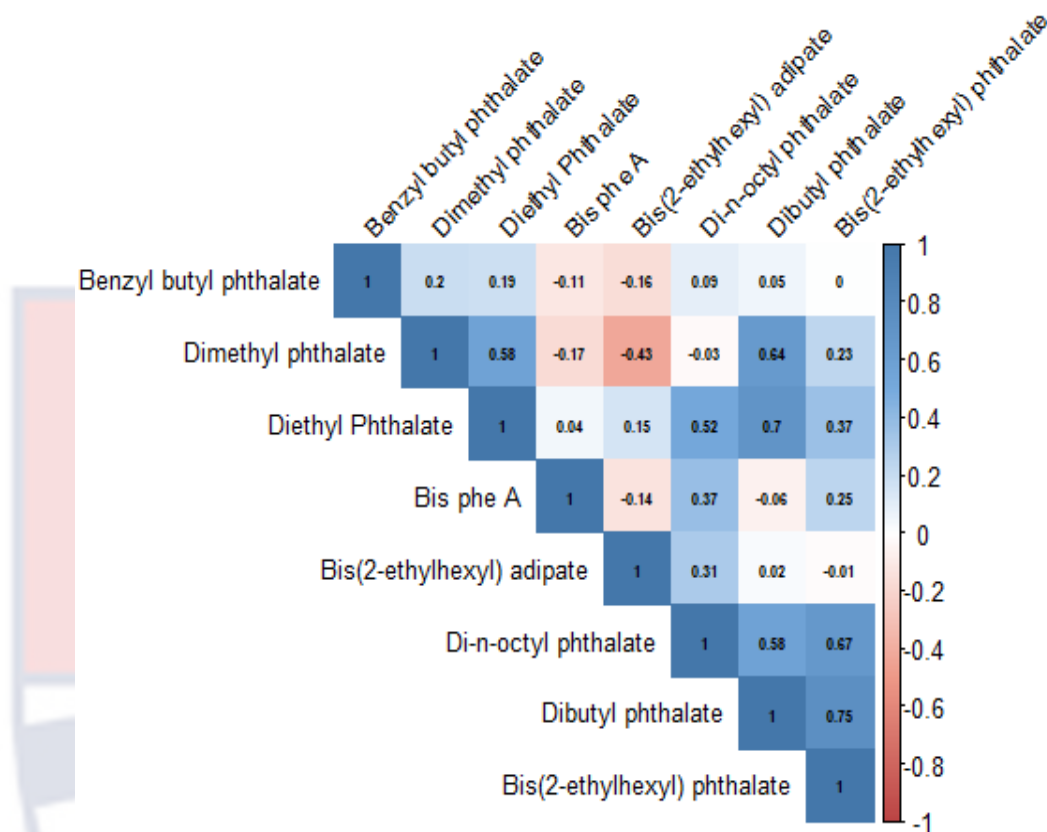


Figure 4.2a. Correlation matrix of endocrine disrupting chemicals

The result (Fig4.2a) showed strong positive correlations among DMP, DEP, DBP, DHEP and DNOP. DEP showed a strong positive correlation coefficient with DMP ($r= 0.58$) and DBP ($r=0.70$). Also DBP showed a strong positive correlation coefficient with DMP ($r=0.64$) and DEHP ($r=0.75$). Similarly DNOP showed a positive correlation with DHEP ($r=0.67$), DBP ($r=0.58$) and DEP ($r=0.52$). However DMP and DEHA showed a strong negative correlation coefficient ($r=-0.43$). Generally, Fig 4.2b showed strong correlation between all parameters except Na, and Fe. However Fe exhibited strong negative correlation with soil Mg and pH. Similarly P showed negative correlation with all parameters except K and Na. There is a strong negative correlation between Ca and P ($r= -0.811$). Conversely, there is a very strong positive correlation between Ca and CEC ($r= 0.99$).

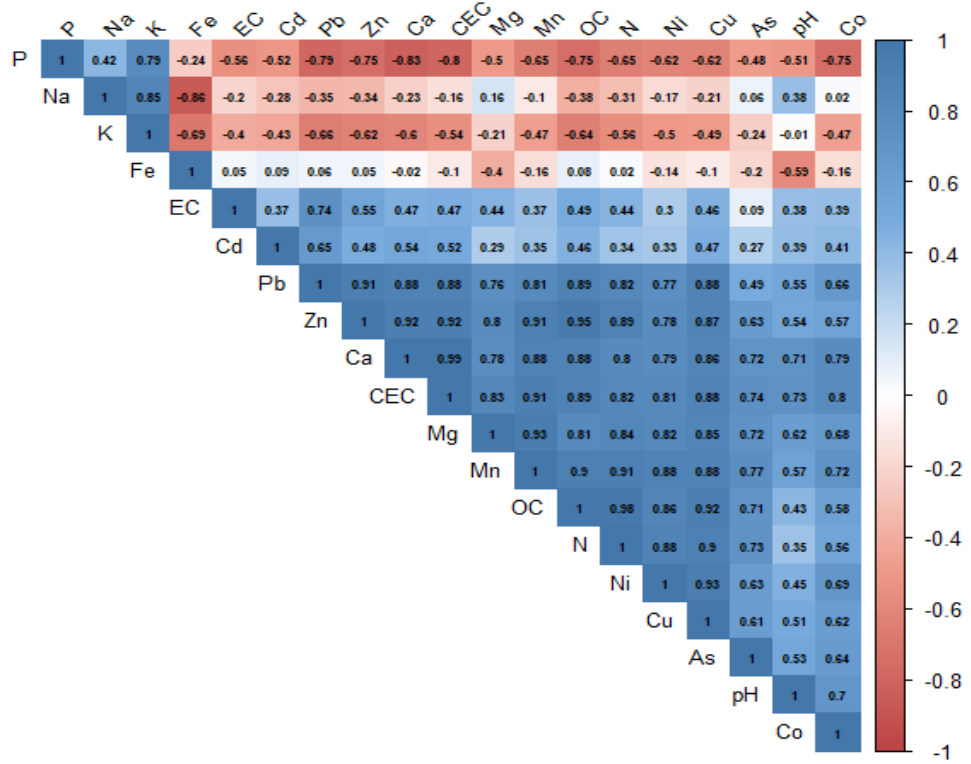


Figure 4.2b. Correlation matrix of soil properties and potential toxic elements

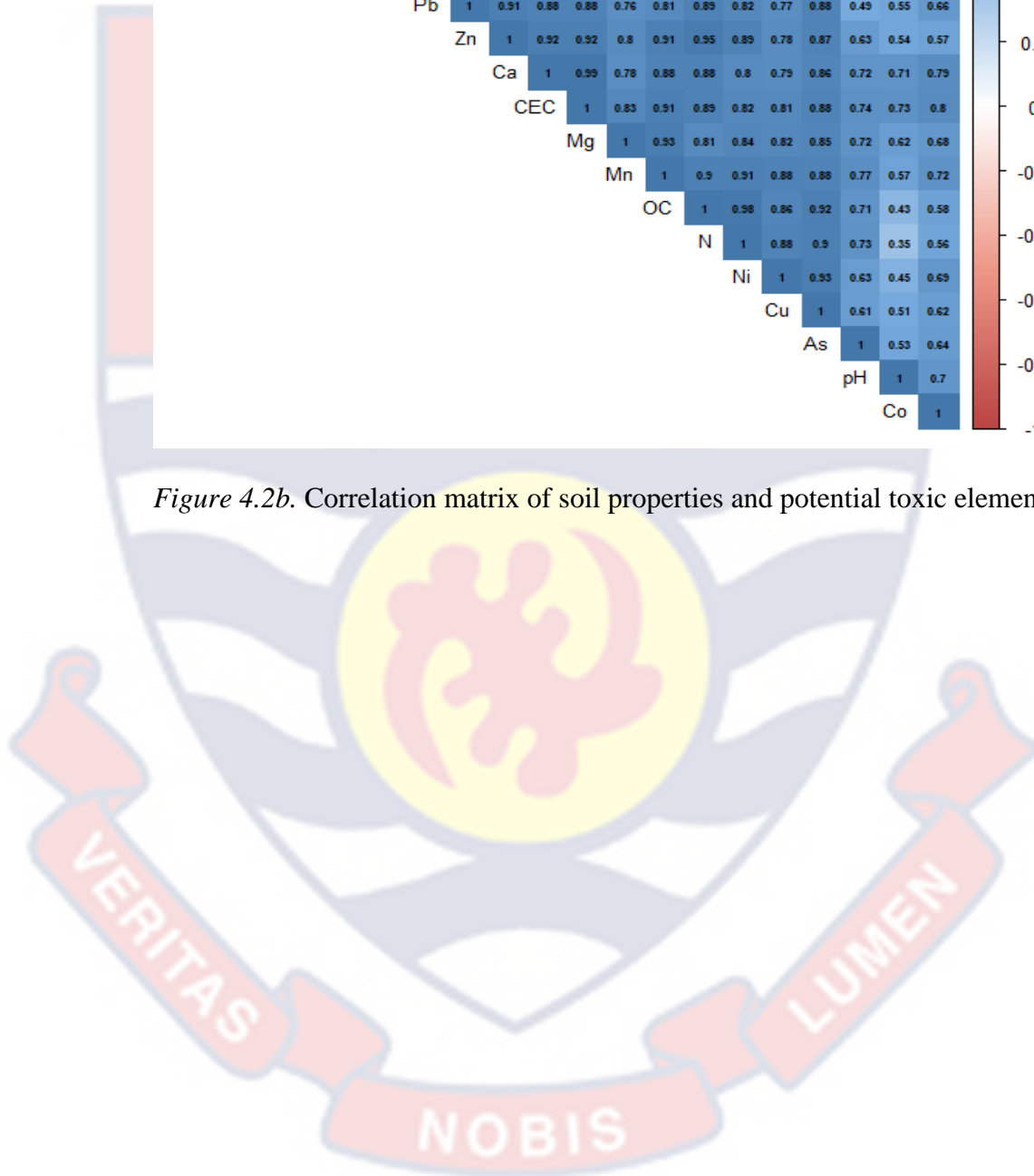


Table 4.4. Rotated component matrix of analyzed parameters among sites

Component						
	1	2	3	4	5	6
OC	0.925	0.166	-0.23	0.044	0.036	-0.071
N	0.931	0.036	-0.149	0.116	-0.042	-0.125
Ca	0.893	0.283	-0.109	-0.125	0.132	0.145
Mg	0.918	-0.036	0.302	-0.032	0.062	-0.152
Na	-0.123	-0.057	0.935	-0.065	0.048	0.021
K	-0.453	-0.079	0.822	0.032	-0.076	-0.091
CEC	0.922	0.249	-0.028	-0.119	0.128	0.111
P	-0.668	-0.284	0.416	0.107	-0.319	-0.223
pH	0.557	0.412	0.446	-0.299	0.31	0.235
EC	0.421	0.102	-0.214	-0.25	0.636	-0.161
Fe	-0.127	-0.116	-0.906	0.045	-0.058	-0.042
Mn	0.964	0.071	0.039	-0.041	-0.025	-0.112
Cd	0.407	0.33	-0.271	-0.368	0.051	0.196
Pb	0.85	0.246	-0.259	-0.187	0.201	-0.076
Ni	0.912	0.083	-0.014	0.116	-0.149	0.012
Co	0.721	-0.083	0.008	-0.246	0.177	0.331
Cu	0.929	0.155	-0.063	-0.026	-0.093	-0.021
Zn	0.884	0.296	-0.194	-0.061	0.129	-0.163
As	0.572	-0.115	0.146	0.037	-0.058	0.446
BPA	0.45	0.063	0.08	0.018	0.099	-0.615
DMP	0.11	0.275	0.024	0.631	0.369	0.490
DEP	0.269	0.558	0.247	0.566	-0.196	0.242
DBP	0.125	0.872	0.029	0.188	0.043	0.313
BBP	-0.147	0.069	-0.19	0.772	0.016	-0.092
DEHA	0.105	0.123	-0.164	-0.176	-0.847	-0.021
DEHP	0.139	0.867	-0.03	-0.039	0.153	-0.177
DNOP	0.154	0.793	-0.043	0.089	-0.284	-0.219

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 12 iterations (Source: Researcher, 2022)

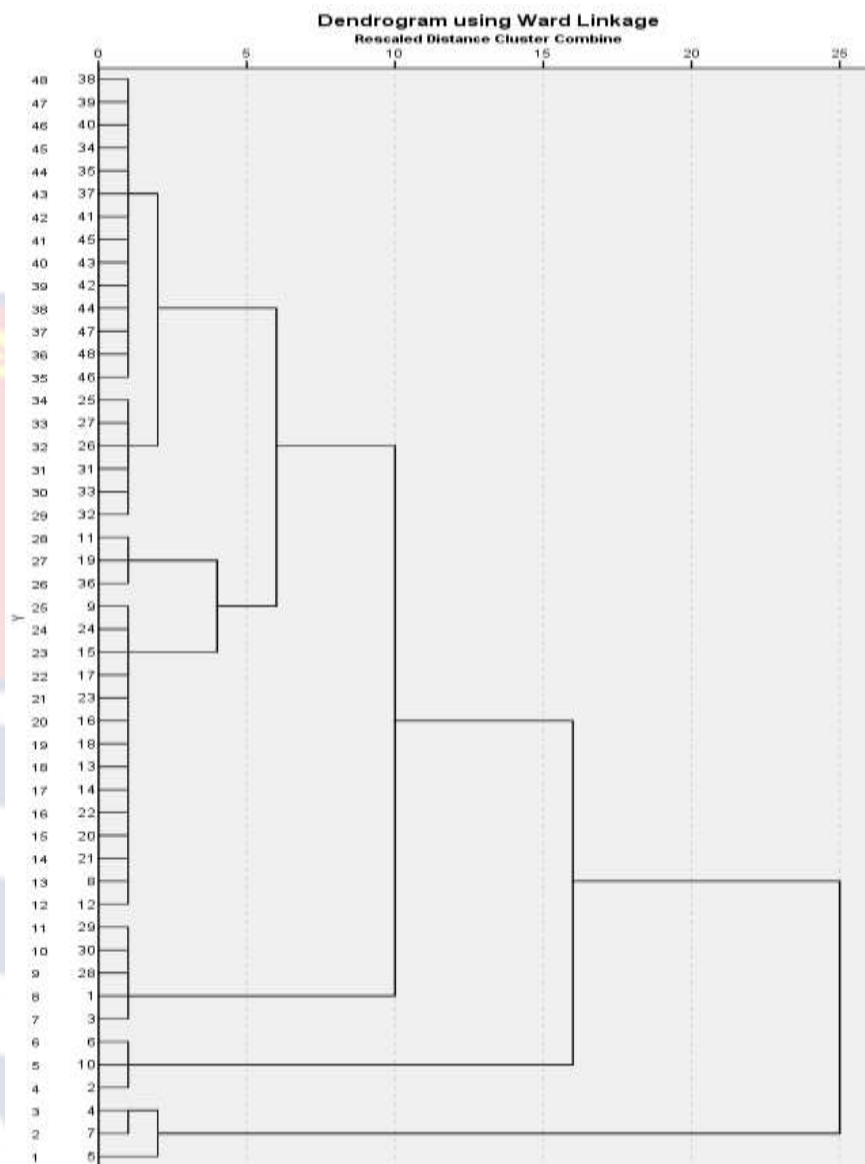


Figure 4. 3. Dendrogram of analyzed parameter relationship among sites

Principal component analysis (PCA) and correlation analysis (CA) were carried out to identify the possible sources of contaminants of the four different monitoring sites. The strong correlation observed was further confirmed by PCA. The components that were extracted cumulatively explained about 83.88% of the total variance. In general, the first principal component (PC1) accounts for about 44 %, the second (PC2) accounts for about 12 % and the third (PC3) for about 11 % of the total variation in the data. The rotated component (Table 4.4) indicated that OC, N, Mg, CEC, Mn,

Ni and Cu had the strongest factor loadings on PC1. DBP, DEHP and DNOP belonged to PC 2 and Na, K belonged to PC3. Figure 4.3 shows the dendrogram using hierarchical cluster analysis (Ward's method) of all the predictors.

Human exposure and health risk assessment

The risks of toxic EDC to individuals via non-dietary routes were estimated based on the concentrations of EDC of the different land use. The results of non-cancer risks via non-dietary routes showed that no single EDC exceeded the recommended allowable level ($HQ < 1$) for DMP, DEP, BPA, BBP, DEHP and DnOP. The carcinogenic exposure risks of BBP and DEHP via non-dietary routes were much lower than 1×10^{-6} . The cancer risk of the PTEs for the various sites indicated a highest risk through ingestion followed by dermal and then inhalation. Again dermal cancer risk of Arsenic of the various sites shows the order: dump soils > cultivated soils > industrial soil > reserved soil. Lead is in the order dump soils > industrial soil > reserved soil > cultivated soil while cadmium is in the order industrial soils > dump soils > reserved and cultivated soil. The PTE that contributed most to carcinogenic and non-carcinogenic risk is arsenic whereas DEHP contributed most to cancer risk and BPA contributed most to non-cancer risk. The results of the risk assessment are summarized in table 4.5. However the ingestion cancer risk (CR) values of Cd, Pb and As exceeded the acceptable threshold value of 1×10^{-4} .

Table 4.5. Human Health risks to cancer and non-cancer from exposure to EDCs

Non cancer risk				Cultivated land				Industrial land				Reserved Land				
Decommissioned Dump				Contribution Per site %	HQing	HQder	HQinh	Contribution Per site %	HQing	HQder	HQinh	Contribution Per site %	HQing	HQder	HQinh	Contribution Per site %
DMP	8.11E-09	1.51E-10	2.62E-08	0.00	8.48E-09	1.57E-10	2.74E-08	0.00	1.05E-08	1.96E-10	3.4E-08	0.00	6.05E-09	1.12E-10	1.95E-08	0.01
DEP	1.65E-07	3.06E-08	5.32E-07	0.00	1.38E-07	2.57E-08	4.46E-07	0.01	1.25E-07	2.33E-08	4.05E-07	0.05	9.04E-08	1.68E-08	2.92E-07	0.19
BBP	3.32E-08	6.16E-10	1.07E-07	0.00	1.48E-08	2.74E-10	4.76E-08	0.00	5.53E-08	1.03E-09	1.78E-07	0.02	2.54E-07	4.72E-09	8.21E-07	0.51
BPA	0.0207	0.000384	0.0668	99.48	0.000979	1.82E-05	0.00316	93.16	0.000158	2.94E-06	0.000511	58.56	8.01E-06	1.49E-07	2.58E-05	16.19
DEHP	0.000104	1.94E-06	0.000337	0.50	7.04E-05	1.31E-06	0.000227	6.69	0.000109	2.03E-06	0.000353	40.44	3.96E-05	7.35E-07	0.000128	80.26
DNOP	4.35E-06	8.07E-08	0.000014	0.02	1.4E-06	2.6E-08	4.52E-06	0.13	2.51E-06	4.65E-08	8.09E-06	0.93	1.4E-06	2.6E-08	4.52E-06	2.83
Cd	1.03E+01	3.30E-03	1.07E-07	0.00	5.90E-01	1.88E-04	6.09E-09	0.00	1.21E+01	3.86E-03	1.25E-07	0.00	1.13E-05	1.88E-04	6.09E-09	12.22
Pb	5.68E+03	1.94E-03	NA	0.69	6.51E+02	2.23E-04	NA	0.15	3.72E+03	1.27E-03	NA	0.38	9.19E+02	3.14E-04	NA	0.36
As	8.16E+05	1.40E+00	4.80E-04	99.31	4.30E+05	7.35E-01	2.53E-04	99.85	3.95E+05	6.76E-01	5.85E+05	99.60	2.21E+05	3.78E-01	1.30E-04	87.41
Cancer risk				Contribution Per site %	CRing	CRder	CRinh	Contribution Per site %	CRing	CRder	CRinh	Contribution Per site %	CRing	CRder	CRinh	Contribution Per site %
BBP	5.26E-12	6.44E-13	2.61E-16	0.04	2.34E-12	2.86E-13	1.16E-16	0.03	8.76E-12	1.07E-12	4.35E-16	0.07	4.03E-11	4.94E-12	2.00E-15	0.09
DEHP	1.22E-08	1.49E-09	6.05E-13	99.96	8.21E-09	1.01E-09	4.07E-13	99.97	1.28E-08	1.56E-09	6.33E-13	99.93	4.62E-09	5.66E-10	2.29E-13	99.1
Cd	2.04E-02	1.63E-07	1.20E-11	0.02	1.16E-03	9.29E-09	6.85E-13	0.00	2.39E-02	1.91E-07	1.40E-11	0.04	1.16E-03	9.29E-09	6.85E-13	0.00
Pb	2.12E-03	7.24E-10	1.24E-12	0.00	2.43E-04	8.30E-11	1.43E-13	0.00	1.39E-03	4.75E-10	8.16E-13	0.00	3.43E-04	1.17E-10	2.02E-13	0.00
As	1.15E+02	1.97E-04	6.77E-08	99.98	6.06E+01	1.04E-04	3.56E-08	100	5.57E+01	9.53E-05	3.28E-08	99.96	3.12E+01	5.33E-05	1.83E-08	100

Source: Researcher, 2022

4.4 Discussion

Soil properties

The variations observed in the soil chemical properties are due to the different soil uses. Soils from the dump have high level of N, Ca and OC as a result of the waste composition and the open burning while the high level of Na of agricultural soils compared to the other sites is due to the indiscriminate and continues use of sodium containing fertilizers (Savci, 2012; Vitosh, 1996). Previous studies indicated that municipal waste generated consist of about 60% organic material out of the total waste generated that are good sources of nitrogen and carbon (Miezah et al., 2015). Generally, all the sites are deficient in some of the chemical properties studied making the soils less fertile for optimum crop growth.

Potentially toxic elements

Generally, potentially toxic elements (PTE) analyzed were all within the EU recommended threshold (MEF, 2007; The Council of the European Communities, 1986) except arsenic. Concentrations of PTE of the Agricultural soils are comparable to similar studies (Khan et al., 2013) however lower than what was reported in other agricultural soils (Jean-Philippe, Labbé, Franklin, & Johnson, 2012). In comparison, the concentration of PTEs in the dump was higher than other study undertaken at Sunyani municipal dump (Agbeshie, Adjei, Anokye, & Banunle, 2020b) due to utilized duration and composition of the disposed waste materials. PTE may persist in the soil for a longer period and bioaccumulation due to the non-degradable nature (Briffa et al., 2020). The levels of PTE of the industrial soils was much lower than a similar work carried out to determine PTE levels within the vicinity of an industrial area

(Cristina, 2014; Krishna & Govil, 2007). The concentrations were comparatively higher presumably due to where the study was carried out within the environs of textiles, petrochemical, refinery, natural gas, cement, steel plant etc. The cluster of different industries may produce more waste to the environment. Also, low levels of PTE was recorded compared to a decade cumulative studies of an industrial soil to evaluate the influence of industrial settlement in an area previously geared to agriculture and livestock (D'Emilio, Caggiano, Macchiato, Ragosta, & Sabia, 2013). The outcome of the work compared with previous study of pristine botanical gardens (Akoto et al., 2017) showed that the levels of PTE in reserved soils were lower except Arsenic which was higher for the reserved soils.

The main factors influencing the relatively high concentration of arsenic and iron in soils of agriculture, dump and industrial sites are anthropogenic sources and precipitation. Human activities may come from industrial waste and agricultural practice with the use of arsenical pesticides (L. Zhang, Yan, Guo, Zhang, & Ruiz-Menjivar, 2018). However, the concentrations of arsenic and iron of the reserved soils are largely due to the parent rock and precipitation (Cullen & Reimer, 1989; Smedley & Kinniburgh, 2002). The underlying rock of the forest reserved are Paleozoic consolidated sedimentary formations (Dapaah-Siakwan & Gyau-Boakye, 2000), which is usually associated with high levels of arsenic. Previous studies have shown that clay minerals may tend to adsorb and trap arsenic more effectively (Perez et al., 2019). In many soils and sediments, the mobility of arsenic (V) is limited by adsorption to clay minerals, organic matter or iron oxides (Inskeep & McDermott, 2021; Perez et al., 2021).

Endocrine disrupting chemicals

Soils remain an important sink for endocrine disrupting chemicals within the environment. The concentration of the EDCs analyzed was below the recommended threshold except BPA which had higher concentration above the threshold. Investigations of the concentrations of phthalate esters in soils sampled from different land-use types in urban, industrialized areas, suburban areas, rural areas and villages in China reported average highest levels of phthalate esters in soils of an electronics manufacturing area, followed by urban soils and then suburban soils (Y. Li et al., 2018c). In comparison the low level of phthalates recorded (Table 3) is due to the climatic conditions of tropical *regions* that *contribute* to increase microbial activity (Zhou et al., 2015) which enhances the breakdown of potential soil pollutants. Conversely, the high concentration of BPA of the dump soil is due to the proliferation of the dump with waste products that contain BPA. It is used in paints, binding materials, and filling materials. It is also an additive for flame-retardants, brake fluids, and thermal papers. BPA produced in industry is used to make plastics, in particular polycarbonate resins (Groshart, Okkerman, & Pijnenburg, 2001; Y. Q. Huang et al., 2012). The production of BPA has constantly grown over the years due to the demand (Flint et al., 2012; Y. Q. Huang et al., 2012).

The level of DEHP and DBP were comparatively higher than the other phthalates. The principal component analysis (PCA) indicated that observed EDCs and PTE are primarily anthropogenic. PC1 are from domestic and industrial waste. Components of PC2 are from plastic waste while component of PC3 are from agricultural sources. Previous studies established that in soil, DBP and DEHP are the most abundant phthalate esters as a result of

atmospheric deposition and amendment (Giuliani, Zuccarini, Cichelli, Khan, & Reale, 2020b). The use of plastics in agricultural production are considered important sources of phthalate esters in soil as generally pristine soils contain lowest phthalate esters (Giuliani et al., 2020b). DEHP is the most widely used phthalate and is used mainly as a plasticizer in polyvinyl chloride (PVC) products (Barakat & Ko, 2018b; Stamatelatou, Pakou, & Lyberatos, 2011). Similarly, DBP is also used as plasticizers in resins and polymers such as polyvinyl chloride. The ubiquity of DBP in consumer products is demonstrated by its wide usage (Saillenfait, Langonné, & Leheup, 2001).

Human exposure and health risk assessment

Continuous human exposure to the possible health threat posed by organic compounds (OCs) that are endocrine disrupting in nature is an important issue that requires frequent monitoring. The risk posed by selected EDCs compared to the reference doses as recommended by the U.S. EPA, shows that the estimated average daily intake doses of BPA, BBP, DEP, DMP, DnOP and DEHP via non-dietary routes were within acceptable levels (HQs < 1). This indicates an absence of non-cancer risks of EDC at all sites and they are relatively safe for human habitation. However, the relatively high level of BPA is a result of proliferation of the dump with waste products that contain BPA particularly plastics coupled with frequent burning. Similarly, the carcinogenic risks posed by DEHP and BBP in soils via the non-dietary routes were all very low than the recommended 1×10^{-6} which is comparable to similar research (Başaran et al., 2020; X. Li et al., 2021; L. Wang et al., 2018; Zhu et al., 2019). The ingestion cancer risk (CR) values of Cd, Pb and As exceeded the acceptable threshold value of 1×10^{-4} which indicates potential

lifetime carcinogenic risk (Jia et al., 2018; US Environmental Protection Agency, 2012; US EPA, 2002).

4.5 Conclusion

Generally, EDCs were below the recommended threshold for all the sites studied. The risk posed by selected EDCs compared to the recommended U.S. EPA reference doses showed that an estimated average daily intake doses of BPA, BBP, DEP, DMP, DnOP and DEHP via non-dietary routes were within acceptable levels. Similarly, the carcinogenic risks posed by DEHP and BBP in soils via the non-dietary routes were within acceptable levels. The level of phthalates recorded could be attributed to the climatic conditions of tropical *regions* that *contribute* to increase microbial activity which enhances the breakdown of potential soil pollutants. However the high concentration of BPA above the threshold of the dump soil is attributed to the proliferation of the dump with waste products that contain BPA. The ingestion cancer risk of Cd, Pb and As exceeded the acceptable threshold which indicates potential lifetime carcinogenic risk and attributable to both anthropogenic and natural sources. Also the observed influence of reserved soil is an indication of the ubiquity of EDCs though it was within the accepted threshold. The outcome of considerable variations in concentration of PTEs and EDCs across sites is an indication that some areas were less influenced while others were heavily influenced. Though BPA and phthalates have rapid half-life in soil they remain an important pollutants due to the continuous release and ubiquity in the environment. The possible health threat posed by substances that are endocrine disrupting in nature is an important issue that cannot be overlooked. There is therefore the need for continuous systematic monitoring of the various sites and a proper effort to forestall further contamination.

CHAPTER FIVE

SOIL QUALITY INDEX OF LAND IMPACTED BY
ANTHROPOGENIC ACTIVITIES IN COASTAL GHANA

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Abstract

The excessive use of weedicide and fertilizer by farmers, indiscriminate waste disposal as well as unregulated and pervasive chemical use for mining and industry has huge impacts on the sustainability of soil resource. However, land use-specific characterization of soil has not been extensively studied. The soil quality of 4 different land use classes—cultivated soils, industry, decommissioned waste dump and forest reserve that depict different anthropogenic effect in urban and rural settings were assessed. Twelve composite samples were taken per site at a depth of 30cm with an auger, air dried and sieved with 2mm mesh and portions used for analysis. Soil mineral parameters analyzed include bulk density, reaction pH, organic carbon, total nitrogen, phosphorus, exchangeable cations: sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and extractable trace elements: manganese (Mn), nickel (Ni), iron (Fe), cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb). The mean %SQIs for soil samples collected from cultivated soils, decommissioned dump, industrial and forest reserved sites are 54.9%, 57.6%, 60.6% and 61.4% respectively. Mean concentrations of Cd, Pb and Ni are 0.020 mg/kg, 1.301 mg/kg and 0.213 mg/kg, respectively. There were significant variations pairwise between cultivated soil and forest reserve soil and then cultivated and industrial soil ($p < 0.05$). Assessing soil quality (SQ) through evaluation of changes in soil properties across different land use classes is an essential tool for proper management to promote sustainable use to sustain life.

Keywords

Soil, Pesticide, Waste, Heavy metal, Ghana, Industry, Agriculture

5.1 Introduction

Flora and fauna derive their very existence from soil hence soil quality is very important for sustainability of the earth. It is apparently clear that proper land use practices have not been adhered to by mankind thereby creating problems for many communities. Upholding soil quality is the most effective means of ensuring food security to support life (de la Guardia & Garrigues, 2012). Man typically satisfies the basic physiological needs of air, water, and food before considering issue of safety (Block, 2011) and other qualities of life, such as the environment in which they live. The increase in anthropogenic influence on the soil resource globally is largely contributed by climate change and the phenomenon of agriculture and industry. The increase in inappropriate land use practices on soil resource has necessitated the need to measure the effects on the soil resource in order to provide solutions to ensure sustainability of the practices (D. P. Oliver, Bramley, Riches, Porter, & Edwards, 2013). Generally soil quality will have to take into account societal goals for a specific ecosystem and land use (Doran & Parkin, 2015). There is also the need for a concerted effort to permanently prevent further environmental degradation of soil resource by applying sound and effective management strategies to soils that are prone to contamination (Sims, Cunningham, & Sumner, 1997).

Varied definitions are given to soil quality and the key phrase that runs through most of the definitions is the concept of specific function of the soil that is critical to meet management goals (Andrews, Karlen, & Cambardella, 2004; Carter, 2002). Similarly, Karlen et al. (1997) proposed that soil quality be defined as “the capacity of a specific kind of soil to function, within natural

or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation.” Soils have various functions that are inextricably linked to its quality. As mankind becomes more aware of the environment, soil quality definitions have expanded from the simple association with production and serving as an environmental buffer to protection of watersheds and ground waters from agricultural chemicals, industrial and municipal wastes and sequestering carbon that would otherwise contribute to global climate change (Reeves, 1997).

Soil is an important source of nutrients in food supply and plant based medicines however poor soil fertility and high levels of potential toxic compounds, heavy metals and antibiotics pose threat to these vital resources. Contributing to these is the excessive use of weedicide by farmers, indiscriminate waste disposal along with unregulated and pervasive chemical use for mining and industry. Soil properties and conditions are critical in the production of sufficient and nutritious crops. Contaminated soils may be toxic and can transfer those substances to humans through crop uptake, leading to contaminated foods that compromise food security (Steffan et al., 2018). In Africa, most people rely on plants as a source of medicine besides food which makes it imperative to maintain proper soil quality to avoid exposure to contaminants through soil.

Till date, there has been no systematic assessment of heterogeneities in soil quality index in Ghana across land use types (cultivated soil, industry, decommissioned waste dump and forest reserve). This is a fundamental motivation for this study. In assessing the quality on the backdrop of the

possible physical and chemical changes in soil properties, Visual soil quality assessment and interpretation is vital, but visual soil assessment alone cannot be used to assess effectively the status of ecosystem services determined by biological and chemical soil processes (Ball et al., 2017). Since visual soil assessment gives different information than laboratory approaches (Emmet-Booth et al., 2016) the combination of both is imperative. Visual soil assessment is important in yield gap analysis and land management programs (McKenzie et al., 2015)

it is expedient to develop soil quality index (SQI) that integrates the specific measured soil properties into a single parameter that could be used as an indicator of soil quality (Amacher, O'Neill, & Perry, 2007). Human practice regarding land use in rural settings may differ from that of the urban in relation to agriculture production, waste disposal and industrial use. However, the soil quality index of agricultural soils could be compared with soils under different land uses. This study is aimed at analyzing the physical and chemical properties of soils with different uses to generate a soil quality index data.

5.2 Materials and Methods

Soil sample locations

Soil sampling was conducted in four sites within Greater Accra and Central Regions of Ghana. Three of the sampling sites are in the Greater Accra and one site in the Central Region. The sampling sites represent four land use classes—cultivated soil, industry, waste dump and forest reserve that depict different anthropogenic effect in urban and rural settings. The sites in Accra are within an urban area and separated about 9km apart and 140km from the

last location in the Central Region. Cultivated soils were sampled from the environs of the Council for Scientific and Industrial Research (CSIR) head office within an urban setting. The area remains a major vegetable growing site all year for over 50 years and the continuous application of pesticides, organic and inorganic fertilizer. Soil from the dump was taken within 200m from the Adenta decommissioned dump that received all manner of solid waste from most part of the capital for many decades. The industrial soils were taken from Accra North industrial area that has most of the companies that make plastic products and samples from the forest reserve were taken from Kakum National Park, in the Central Region. The park is located in the rural coastal environs of the Central Region and covers an area of 375 square kilometres with tropical forest.

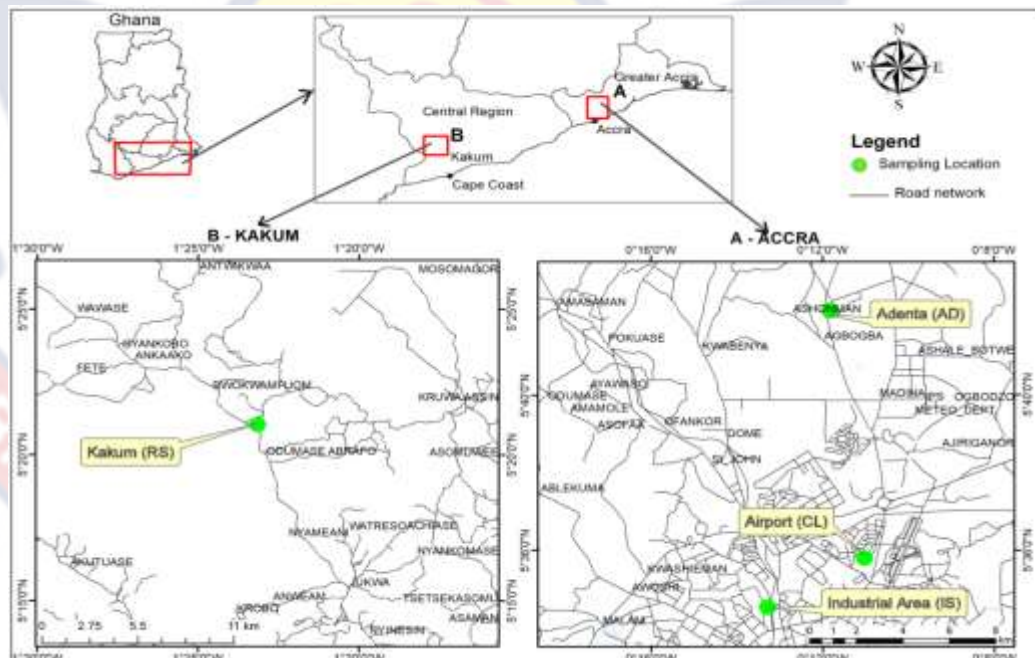


Figure 5.1 Map of geographical location of sampling areas

Soil sample collection

Soils were randomly sampled with auger at a depth of 30 cm from four (4) different locations to represent decommissioned dump, agricultural soils,

industrial and forest reserved soils. Composite soil samples were generated by physically mixing soil samples taken within an area of a location into one homogenous sample. Twelve (12) of such homogeneous samples were made per location, initially stored in aluminum foil and taken through preparatory procedures. The samples were air dried at room temperature, homogenized and sieved (2mm mesh) before use to determine the physicochemical characteristics properties of the soils.

Physicochemical analysis of soil samples

Soil particle size analysis was carried out using the pipette method as described by (Rowell, 1994). Soil reaction pH and electrical conductivity (EC) were measured in 1:2.5 soil: water suspension. Total nitrogen was determined by the Kjeldahl method (Sparks et al., 1996). Available phosphorus contents in soils were extracted by Bray's P1 solution and measured on Genesys 20 spectrophotometer (Bray & Kurtz, 1945). Organic carbon was determined by the wet oxidation method (Nelson & Sommers, 1996). Analyses of the exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ and Na^+) were done by the method described by (Rowell, 1994) and determined with Jenway PFP7 flame photometer. Heavy metals were extracted using aqua regia according to (Verloo and Demeyer 1997) and determined with Atomic adsorption spectrophotometer (AAS), Agilent Technologies 200 series 240FS AA and Graphite Tube Atomizer 240ZAA.

Mineral soil property threshold values shown in table 5. 1 (Amacher et al., 2007) were used as basis for the determination of the SQI. The individual index values for all the mineral soil properties are computed to give a total SQI: The SQI which was originally developed by Amacher et al 2007 was

meant to assess forest soil quality and establish baseline levels for different soil.

Total SQI = \sum individual soil property index values.

The maximum value of the total SQI is 26 if all 19 soil properties are measured however 16 properties were measured with a total SQI value of 22.

The total SQI is then expressed as a percentage of the maximum possible value of the total SQI for the soil properties that are measured:

$$\% \text{ SQI} = (\text{total SQI} / \text{maximum possible total SQI for properties measured}) \times 100$$

Table 5.1 Soil quality index values and associated soil property threshold values (Amacher et al., 2007)

Parameter	Level	Index
Bulk density (g/cm ³)	> 1.5	0
	1.5	1
pH	<3.0	-1
	3.01 to 4.0	0
	4.01 to 5.5	1
	5.51 to 6.8	2
	6.81 to 7.2	2
	7.21 to 7.5	1
	7.51 to 8.5	1
Total organic carbon in mineral soils (percent)	> 8.5	0
	> 5	2
	1 to 5	1
Total nitrogen in mineral soils (percent)	< 1	0
	> 0.5	2
	0.1 to 0.5	1
Exchangeable Na percentage (exchangeable Na/ECEC x 100)	< 0.1	0
	> 15	0
	≤15	1
K (mg/kg)	> 500	2
	100 to 500	1
	< 100	0
Mg (mg/kg)	> 500	2
	50 to 500	1
	< 50	0
Ca (mg/kg)	> 1000	2
	101 to 1000	1
	> 10 to 100	0

	< 10	-1
	> 100	0
Mn (mg/kg)	11 to 100	1
	1 to 10	1
	< 1	0
Fe (mg/kg)	> 10	1
	0.1 to 10	1
	< 0.1	0
Ni (mg/kg)	> 5	0
	0.1 to 5	1
	< 0.1	1
Cu (mg/kg)	> 1	0
	0.1 to 1	1
	< 0.1	0
Zn (mg/kg)	> 10	0
	1 to 10	1
	< 1	0
Cd (mg/kg)	> 0.5	0
	0.1 to 0.5	1
	< 0.1	1
Pb (mg/kg)	> 1	0
	0.1 to 1	1
	< 1 0.	1
0.03 M NF ₄ + 0.025 M HCl (Bray 1) P (mg/kg)	> 30	1
	15 to 30	1
	< 15	0

5.3 Results and Discussion

The results of Table 5.2 show the variations in soil mineral parameters of the study sites, indicating high variation in iron levels. Manganese level of dump soils was about 3 fold that of industry and cultivated soil while zinc level was about 8 fold that of cultivated and reserved soils. The high levels of zinc and manganese in the dump soils originate from combustion and decay of waste products containing these metals. Soil exchangeable cations are important nutrient parameter and they remain fairly distributed across sites.

Table 5.2 Statistical results of mean soil quality parameters and threshold

Parameter	Dump	Agricultural	Industrial	Reserve	Threshold	
					(CEC, 1986)	(MEF, 2007)
Fe (mg/kg)	361.338 ± 61.97	165.506 ± 62.01	549.426 ± 49.31	605.845 ± 36.12	NA	NA
Mn (mg/kg)	11.713 ± 1.17	3.373 ± 1.53	4.049 ± 0.68	2.501 ± 0.49	NA	NA
Cd (mg/kg)	0.035 ± 0.01	0.002 ± 0.00	0.041 ± 0.05	0.002 ± 0.00	3.0	1
Pb (mg/kg)	2.693 ± 0.66	0.309 ± 0.18	1.766 ± 0.49	0.436 ± 0.03	300.0	60
Ni (mg/kg)	0.367 ± 0.10	0.154 ± 0.06	0.177 ± 0.01	0.153 ± 0.04	75.0	50
Cu (mg/kg)	2.787 ± 1.23	0.143 ± 0.02	0.910 ± 0.30	0.157 ± 0.03	140.0	100
Zn (mg/kg)	9.939 ± 0.61	0.652 ± 0.13	4.806 ± 1.62	1.244 ± 0.28	300.0	200
OC (%)	1.272 ± 0.297	1.174 ± 0.432	1.046 ± 0.476	0.913 ± 0.471	NA	NA
N(%)	0.106 ± 0.030	0.098 ± 0.038	0.088 ± 0.041	0.076 ± 0.039	NA	NA
Ca (mg/kg)	3.559 ± 1.227	3.309 ± 1.450	3.032 ± 1.557	2.558 ± 1.399	NA	NA
Mg(mg/kg)	0.534 ± 0.184	0.496 ± 0.218	0.455 ± 0.234	0.384 ± 0.210	NA	NA
Na (mg/kg)	0.177 ± 0.054	0.160 ± 0.066	0.147 ± 0.072	0.124 ± 0.064	NA	NA
K (mg/kg)	0.012 ± 0.003	0.010 ± 0.004	0.009 ± 0.004	0.008 ± 0.004	NA	NA
P (mg/kg)	2.566 ± 0.782	2.187 ± 0.744	1.885 ± 0.780	1.662 ± 0.808	NA	NA
pH	4.668 ± 1.689	4.193 ± 1.897	3.731 ± 1.949	3.196 ± 1.817	NA	NA
BD	1.413 ± 0.039	1.472 ± 0.019	1.466 ± 0.028	1.336 ± 0.023	NA	NA

The SQI is a tool for determining baselines and classifying soil health trends. Soil quality index for the various sites are shown as plotted bars to allow for sites comparisons of the different SQI values (fig 5.2). The mean SQIs for soil samples collected from cultivated soils, decommissioned dump, industrial and forest reserved sites are 12.08, 12.67, 13.33 and 13.5 representing 54.9%, 57.6%, 60.6% and 61.4% quality, respectively. The distribution of SQIs for soil samples collected from the different sites shows that there were variations in individual mineral soil property among sites

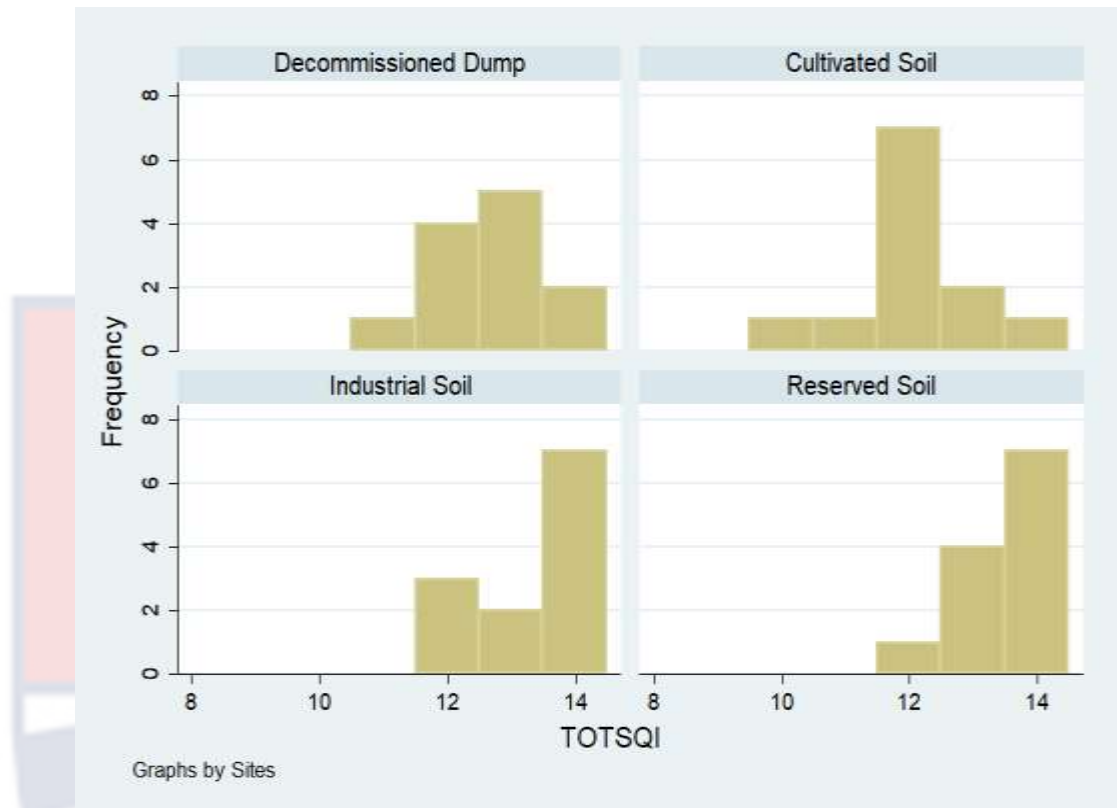


Figure 5.2 Comparison of total soil quality index of twelve samples among locations

The observed percentage SQI values are shown for each site in box plots (fig.5.3). The results in fig. 5.2 and 5.3 indicates that forest reserve soils have the highest quality index (QI) which is due to the less human influence while cultivated soil is least as a result of continuous cultivation and application of pesticides and fertilizers.

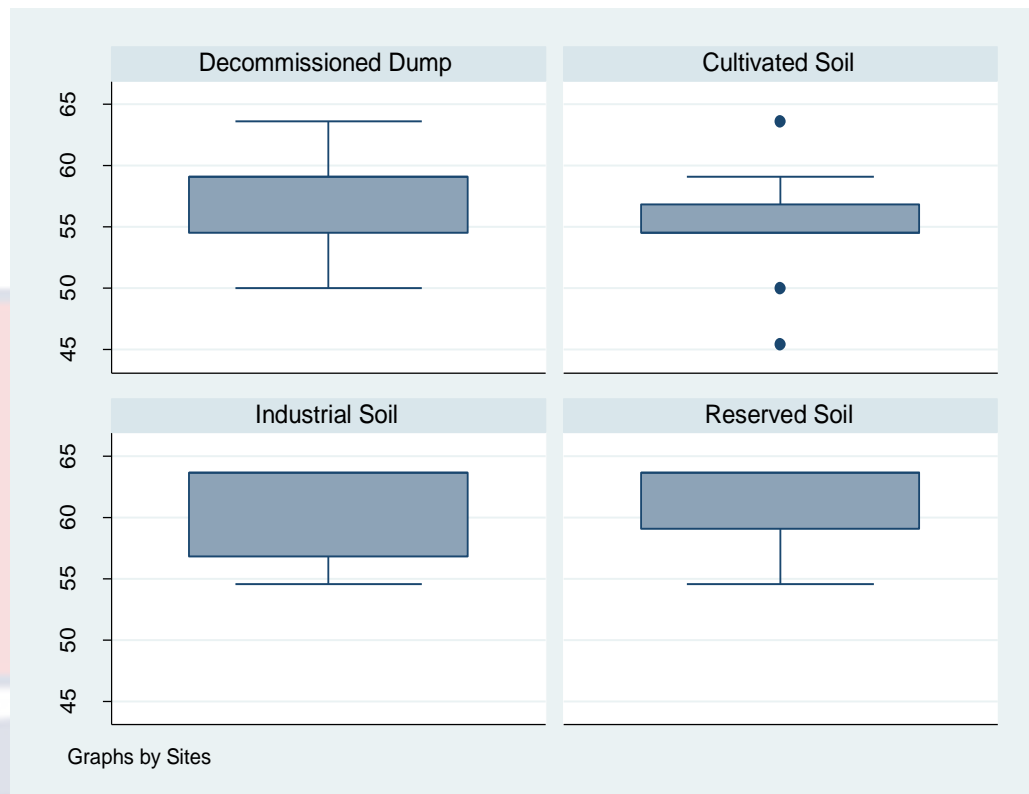


Figure 5.3 Percentage SQI of analyzed parameters among sites

Decommissioned soils also had lower SQI compared to industrial soils due to the substantial anthropogenic influence with regards to waste management. Substantial quantity of waste generated are left unattended to and eventually end up in the environment and this supports the observation by (Abalo et al., 2018). The SQI of decommissioned soils and industrial soils are however below the reserved soils. Table 5.3 shows that there were significant variations pairwise between cultivated soil and reserved soil and then cultivated and industrial soil ($p < 0.05$).

Table 5.3 Multiple Comparisons of analyzed parameters among sites

(I) Sites	(J) Sites	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Decommissioned Dump	Cultivated Soil	.583	.355	.365	-.36	1.53
	Industrial Soil	-.667	.355	.252	-1.61	.28
	Reserved Soil	-.833	.355	.103	-1.78	.11
Cultivated Soil	Decommissioned Dump	-.583	.355	.365	-1.53	.36
	Industrial Soil	-1.250*	.355	.005	-2.20	-.30
	Reserved Soil	-1.417*	.355	.001	-2.36	-.47
Industrial Soil	Decommissioned Dump	.667	.355	.252	-.28	1.61
	Cultivated Soil	1.250*	.355	.005	.30	2.20
	Reserved Soil	-.167	.355	.965	-1.11	.78
Reserved Soil	Decommissioned Dump	.833	.355	.103	-.11	1.78
	Cultivated Soil	1.417*	.355	.001	.47	2.36
	Industrial Soil	.167	.355	.965	-.78	1.11

Dependent Variable: TOTSQI. *.The mean difference is significant at the 0.05

level (Source: Researcher 2022)

Cultivated soil showed more variation with lower SQI compared to the others that have reduced variations with higher SQI values. Soil mineral parameters that significantly predict SQI are manganese, iron and cadmium as indicated in table 5.4. Unit increases in manganese, iron and cadmium affects soil quality index by -0.254, 0.003 and 12.544 respectively indicating that cadmium influences soil quality the most followed by iron then Manganese.

Table 5. 4. Parameter estimates of soil mineral variables and total SQI

Model	Unstandardized Coefficients		Standardized Coefficients		Sig.
	B	Std. Error	Beta	t	
(Constant)	8.510	3.657		2.327	.027
BD	3.657	2.765	.207	1.322	.196
OC	-.447	.415	-.794	-1.076	.290
N	7.118	4.419	.768	1.611	.117
Ca	-.064	.042	-.716	-1.529	.136
Mg	.403	.229	.657	1.764	.088
Na	.566	.934	.219	.606	.549
K	-40.475	23.561	-.687	-1.718	.096
P	-.113	.166	-.163	-.678	.503
pH	-.288	.341	-.358	-.846	.404
Fe	.003	.001	.541	2.209	.035
Mn	-.254	.117	-.905	-2.164	.038
Cd	12.544	4.233	.340	2.963	.006
Pb	-.700	.358	-.688	-1.956	.059
Ni	5.540	2.831	.555	1.957	.059
Cu	.219	.336	.247	.651	.520
Zn	.191	.125	.673	1.526	.137

Dependent Variable: Total SQI (Source: Researcher 2022)

Total organic carbon and nitrogen are highly related and also correlate to exchangeable cations (K, Mg, Ca) except bulk density. Individual indicators of soil health are correlated with a range of soil physical and chemical properties in an effort to identify which property or properties are linked with soil health. Soil physical and chemical properties were measured as part of the soil health indicators to evaluate the position of the developments in soil quality.

5.4 Conclusion

In this study however, 16 measured soil physical and chemical properties were used to assess the SQI of the selected soils. Generally, all the sites were deficient in some of the chemical properties studied making the soils less fertile for optimum crop growth and support essential environmental benefits. The cultivated soil showed more variation with lower SQ compared

to the others that have more points with higher SQI values. Continuous cultivation of land without proper agronomic management has a lot of adverse effect on soil quality. Similarly proper waste management is critical to ensure soil quality. We recommend above 70% SQI for agricultural soils that are not sodic, strongly acidic or strongly alkaline as well as forest soils this is because SQI is highly sensitive to these parameters. Again industrial and decommissioned dump soils must have above 60% SQI when all heavy metals are within recommended acceptable limit. Soils have various functions therefore it is exceedingly important to make conscious effort to protect the soil resource to enhance the protection of watersheds and ground waters from agricultural chemicals, industrial and municipal wastes and sequestering carbon that would otherwise contribute to global climate change to ensure sustainability. Protection of soil resource for optimum function is vital and requires individual conscious effort to achieve it. Proper soil quality indicative tools such as visual soil assessment and laboratory approaches must be used to determine soil quality since many soil properties are related with each other to the extent that using a single dependent variable may not offer a comprehensive assessment of soil health.

CHAPTER SIX
CHARACTERIZATION AND QUANTIFICATION OF ENDOCRINE
DISRUPTORS IN FEMALE BLOOD SAMPLES

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Abstract

Endocrine disrupting chemicals (EDCs) in adult female menstrual blood were determined for the first time in Africa taking into account the importance of non-invasive means of matrices sampling particularly in vulnerable groups, such as pregnant women, the elderly or chronically ill people. The menstrual blood samples of twenty (20) female adults between the ages of 25-45 years were sampled. The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method was applied for the extraction and clean up while GC-MS was used for the analysis to measure EDCs in adult female menstrual blood taking into account the composition of menstrual discharge. Diethyl phthalates (DEP), Dibutyl phthalate (DBP) and Bis (2-ethylhexyl) phthalate (DEHP) were detected in all samples whereas bisphenol A (BPA) was found in thirteen participants. Similarly, Dimethyl phthalate (DMP), was detected in 7 participants, Di-n-octyl phthalate (DNOP) and progesterone were detected in 3 participants, Bis (2-ethylhexyl) adipate (DEHA) and pyrimidine were detected in 2 participants while benzyl butyl phthalate (BBP) was detected in only 1 participant. The maximum concentration of DEP recorded from one of the participant is 1.156 mg l^{-1} and the minimum is 0.439 mg l^{-1} compared with DEHP that was the next most abundant phthalate at a maximum concentration of 0.982 mg l^{-1} and minimum value of 0.095 mg l^{-1} .

The identification of parent phthalates (instead of metabolites) in menstrual blood of all participants studied suggests that bioaccumulation of selected phthalate compounds such as DEHP, DEP and DBP may be occurring

with appreciable human toxicity though the carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} .

Key words

Menstrual, Endocrine disrupting chemical, Blood, Women



6.1 Introduction

Endocrine disrupting chemicals (EDCs) consist of many natural and synthetic organic compounds that are known to interrupt with the normal function of the endocrine system in various ways. This class of chemicals is usually found in plastics products, most household products as well as the environment (Basak et al., 2020; Kumar et al., 2020). Human exposure pathways to EDCs are mainly through the intake of food, water and dust, inhalation of gases and particles and dermal contact (Heshmati, 2020). EDCs have been found in surface waters, sediments, groundwater, and even drinking water in many countries (Brueller et al., 2018; Gonsioroski et al., 2020). They can interfere with the production of hormones needed for the normal functioning of the human body either through over production of hormone, under production or cause a break in the hormone production (Gupta et al., 2010; Kavlock et al., 1997). These hormones are required in small quantities and at specific moments to regulate the body's growth.

EDCs are proven to be connected with changed reproductive function in males and females such as high occurrence of cancers. Their effect on female health can be complicated, impairing reproductive functions across the life cycle and inducing early puberty to increasing rates of miscarriage and infertility (Diamanti-Kandarakis et al., 2009a; Zama & Uzumcu, 2010). It affects reproductive function with increased cases in reproductive cancers especially breast, ovarian, and endometrial cancers as well as neurodevelopmental delays and abnormal growth patterns in children, in addition to changes in immunity (Crain et al., 2008; Gore et al., 2015;. Kumar et al., 2020). The impact of EDCs on female health is critical since these

compounds can stimulate estrogenic responses at very low concentrations that could affect pregnant mothers and their unborn babies (Gore et al., 2014; Tang et al., 2020). The effect can be transferred from the pregnant woman to the growing foetus through the placenta and also to the baby through breast milk.

Adult exposure to EDC may have different consequences from exposure to a developing foetus or infant (Diamanti-Kandarakis et al., 2009). The exposures to EDCs and concomitant health effect may not manifest until later in life (Gore et al., 2015). The exposure of women is heightened with the increased use of personal care products and chemical products that may contain EDCs.

Research on EDCs with regards to human subjects in obtaining information pertaining to exposure effects and diseases is achieved mainly by analyzing compounds in human biological matrices such as blood, urine or breast milk. Similarly, other matrices are also used such as saliva, amniotic fluid, hair; semen and so forth have been used in laboratory diagnosis of diseases affecting women's health. However not much is known about menstrual blood potential in diagnosis of women's health. Careful choice of a particular matrix is important, considering their toxicokinetics, stability, specificity and reliability. Research based on the use of menstrual blood is scarce probably due to the difficulty in obtaining it especially in Africa where a lot of myth is attributed to it. Nonetheless, menstrual blood like other matrix could be used to obtain vital information on exposure and disease.

Humans may come into contact with environmental contaminant through endogenous (through blood) and exogenous (atmospheric deposition) routes (Altshul et al., 2004; Smolders et al., 2009). Monitoring of these contaminants is essential for the determination of its effect on individuals.

Increased patronage and use of plastic products, pesticides, personal care products, pharmaceuticals and industrial chemicals pertains during this era of lifestyle change among Ghanaians. Though the use of pesticides and other chemicals cannot be done away with entirely, it is imperative to ensure that adverse health effects of product that contain are well understood and monitored to curb the upsurge in use. In monitoring there are varied considerations for the selection of a suitable matrix for human biomonitoring of contaminants. Some of which are gender, age, frequency of monitoring and the type of contaminant. Depending on the purpose, invasive or non-invasive method of matrix sampling could be employed. Blood has been used widely for various research and survey mainly due to its interaction with all tissues and organs (Smolders et al., 2009). However, blood sampling is an invasive procedure accompanied with practical constraints, particularly for children or other susceptible populations (Esteban & Castaño, 2009; Stout et al., 2017). In addition, frequent biomonitoring is necessary for the effective evaluation of risk management options and effectiveness of environment and health policies (Smolders et al., 2009). For chemicals with short half-life such as volatile organic compounds or agricultural pesticides, repeated sampling of exposure subjects provides more insight into the true nature of these chemicals and their toxicological consequences. In these wise non-invasive means of matrices collection is preferable particularly in vulnerable groups, such as pregnant women, elderly, or chronically ill people. It is a good alternative to invasive matrices for most contaminants. Since non-invasively collected matrices need less specialized personnel for sampling, costs associated with large sampling designs may be significantly reduced (Smolders et al., 2009).

Considering the advantages, there is a strong case for non -invasive collection of matrices for human biomonitoring as an ethically appropriate, cost-efficient and toxicologically relevant alternative for many of the biomarkers currently determined in invasive matrices. However, the use of menstrual discharge sampled non -invasively as a biomonitoring matrix has been minimal probably due to the myth surrounding it particularly in Africa. In other jurisdictions however, menstrual matrix has been used in few instances for human biomonitoring. Menstrual discharge is composed of three distinct body fluids that consist of blood, vaginal secretions, and the endometrial cells of the uterine wall (Yang et al., 2012). It may therefore be suitable for the monitoring of females within child bearing age and offers an advantage of early detection of contaminants before conception. EDCs are found in many African countries however biomonitoring is scarce and the early detection of harmful impact of environmental contaminants is critical in the protection of neonates. The aim of the study was to measure the content of EDCs in adult female menstrual blood taking into account the composition of menstrual discharge.

6.2 Materials and Methods

Collection and storage of blood samples

Menstrual blood samples for the analysis were collected by the engaged volunteers. It was collected three consecutive days from the second day of flow within the month (cycle). In all twenty (20) females were engaged between the ages of 25- 45. Participants refrained from sex during sample collection. Since there is no standard protocol for the collection of menstrual blood, samples were collected on aluminum foil and transferred into a

vacutainer tube containing anticoagulant. The collected blood samples were stored in sealed sterile containers at $-10\text{ }^{\circ}\text{C}$ ($\pm 2\text{ }^{\circ}\text{C}$) until extraction. All subjects used in the study gave their consent to participate voluntarily in the study and ethical approval was granted by the Ghana Health Service Ethical Review Board.

Extraction and clean up

The method described by (Usui et al., 2012) was used for the extraction and clean up. About 0.5ml of blood serum samples were diluted three fold with distilled water (1.5ml). Samples were placed in 5ml centrifuge tube containing 6g of magnesium sulphate and 1.5g sodium chloride with 1ml of 1% acetic acid in acetonitrile (v/v). The mixture was vigorously vortexed for 30 sec, shaken up and down for 5 min, vortexed again for 30 sec and centrifuged at 4400rpm for 15 min at 4°C . For sample clean-up 600 μl supernatant of each sample was transferred into a 1.5ml tube containing the solid phase extraction sorbent (25mg of primary secondary amine, 25mg of end-capped octadecylsilane (C18) and 150mg of magnesium sulphate), the tube was mixed by hand (up and down) for 10mins vortexed for 30 sec and centrifuged at 4400rpm for 10 min at 4°C . Supernatant were collected and filtered through 0.22PTEF filter into vials. About 1 μl of each sample was injected directly into GC-MS/MS system for analysis.

Analysis of EDCs

The blood samples were analyzed for EDCs with GC-MS QP 2020 Shimadzu equipped with RTS-5MS trace analysis column (30 m \times 0.25 mm \times 0.25 μm). The carrier gas was helium of high purity (99.99 %). Flow rate

was 1 mL min^{-1} at a pressure of 83.1 kPa. Sample volume of $1\ \mu\text{L}$ was injected in pulsed splitless mode with an inlet temperature of 265°C .

To quantify Phthalates, the column temperature was programmed as follows: the initial oven temperature was set at 70°C for 2 min, increased to 200°C at $15^\circ\text{C}/\text{min}$. It was further ramped at $6^\circ\text{C}/\text{min}$ to 310°C and held for 1 minute. The interface and ion source temperatures were set at 265°C and 220°C respectively. Also for bisphenol A, the column temperature program was as follows: 50°C for 1 min. ramped at $15^\circ\text{C}/\text{min}$. to 180°C and further ramped at $8^\circ\text{C}/\text{min}$. to 300°C and held for 1 min. The interface and ion source temperatures were set at 270°C and 220°C respectively. Quantifications were all carried out in the selected ion monitoring mode (SIM) selecting two characteristic fragments ions for each.

Quality control

All glassware used were thoroughly washed with hexane and acetonitrile, and then heated at 140°C for 1 h to ensure that contamination of the glassware is reduced. The EDC extraction solvent and matrix adsorbent were studied using blank samples spiked with standards. The blank values of the analytical procedure were determined by extracting the spiked sample by the same method as the real blood sample with recovery of spiked sample in the range of 86%–116%. The estimation of the limit of detection (LOD) for the EDCs in the blood samples was conducted based on U.S. EPA guidelines (USEPA, 1995) with a confidence level of 95%. An LOD of $3\times$ (detection peak/blank peak + standard deviation) was observed. Instrumental detection limits were calculated by a signal-to-noise ratio of 3 times the sample concentration and ranged from 0.10 to $0.31\ \text{mg L}^{-1}$. Method detection limits of

the EDCs were 0.005, 0.007, 0.01, 0.005, 0.015, 0.01, 0.007 and 0.4 mg L⁻¹ for DMP, DEP, BBP, DEHP, DBP, DnOP, DEHA and BPA, respectively. Surrogate standards and internal standards concentration of 20µl of 5ppm and 50µl of 20ppm in 1ml respectively were added to all the samples to monitor the matrix effects, calibration and quantification. A calibration curve was made by serial dilutions of calibration standards with at least five concentrations for each EDC compound monitored. Linear regression with coefficient of (R²) > 0.99 was accepted.

Human exposure and health risk assessment

The cancer risks of the endocrine disrupting chemicals in the menstrual blood samples were estimated according to the US EPA recommendation. The formulas with modification from the US EPA, (U.S. EPA, 2015) which have been widely employed in previous studies (Başaran et al., 2020; X. Li et al., 2021; L. Wang et al., 2018; Zhu et al., 2019) were used to assess the average daily dosage (ADD, mg·kg⁻¹·d⁻¹) of EDCs via different exposure pathways, namely ingestion (ADD_{ing}), dermal absorption (ADD_{der}) and inhalation (ADD_{inh}) as Equations. (1–6).

$$ADD_{ing} = \frac{C_S \times I_S \times EF \times ED}{BW \times AT} \times CF \quad (1)$$

$$ADD_{der} = \frac{C_S \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (2)$$

$$ADD_{inh} = \frac{C_S \times I_i \times EF \times ED}{PEF \times AT \times BW} \quad (3)$$

$$HQ_i = \left(\frac{ADD_i}{RfD} \right) \quad (4)$$

$$HI = \sum HQ_i \quad (5)$$

$$CR = \sum (ADD_j \times CFS) \quad (6)$$

Where C_b is the individual concentration of EDCs measured in blood ($\text{mg}\cdot\text{L}^{-1}$). I is the daily intake rate; (I_g) is the ingestion rate ($\text{mg}\cdot\text{d}^{-1}$). (I_h) is the inhalation rate ($\text{m}^3 \cdot \text{d}^{-1}$). SA is the dermal exposure area (cm^2). ABS is the dermal adsorption fraction. AF is the dermal adherence factor ($\text{mg}\cdot\text{cm}^{-2} \cdot \text{d}^{-1}$). BW is the body weight (kg). AT is the averaging time (Days): for non-cancer risks, $AT = ED \times 365$; for carcinogens risks, $AT = \text{average lifetime} \times 365$. ED is the exposure duration. EF is the exposure frequency ($\text{days}\cdot\text{year}^{-1}$). CF is the conversion factor ($1.0 \times 10^{-6} \text{ kg}\cdot\text{mg}^{-1}$). PEF is the particle emission factor ($1.36 \times 10^9 \text{ m}^3 \cdot \text{kg}^{-1}$). CSF represents the cancer slope factor. Non-cancer risks of EDCs exposure is determined by the hazard quotient (HQ) and hazard index (HI) where RfD is the reference dose value of each EDC ($\text{mg}\cdot\text{kg}^{-1} \cdot \text{d}^{-1}$), HQ represents the health risks of the individual EDC to human health via different exposure routes, and i represents different exposure routes. The carcinogenic EDC was determined from equation (6). Individuals are exposed to non-cancer risks if the value of HQ is >1 (J. Wang et al., 2015). The estimated carcinogenic risks may be considered very low if the value of risk is less than 1×10^{-6} , low in the range of 1×10^{-6} to 1×10^{-4} , moderate from 1×10^{-4} to 1×10^{-3} , high from 1×10^{-3} to 1×10^{-1} and very high if the value is greater than 1×10^{-1} (Niu et al., 2014).

Table 6.1. Parameters for human health risk assessment

Parameters	Reference Value	Reference
I _g	100 (adults), 200	(Kamunda et al., 2016; Li et al., 2018)
I _h	(children) 20 (adults), 10 (children)	(Kamunda et al., 2016; Li et al., 2018)
EF	350	(Kamunda et al., 2016; Li et al., 2018)
ED	30	(Kamunda et al., 2016)
BW	70 (adults), 15 (children)	(Kamunda et al., 2016; Li et al., 2018)
AT	70 _ 365 (carcinogenic), ED X 365 (non - carcinogenic)	(Kamunda et al., 2016; Li et al., 2018) (Kamunda et al., 2016; Li et al., 2018)
CF	1 X 10 ⁻⁶	(Kamunda et al., 2016; Li et al., 2018)
AF	0.07 (adults),	(Kamunda et al., 2016; Li et al., 2018)
SA	5700 (adults),	(Y. Li et al., 2018b)
ABS	0.1	(Kamunda et al., 2016; Li et al., 2018)
PEF	1.36X10 ⁹	(Kamunda et al., 2016; Li et al., 2018)
RfDo (BBP)	0.02	(Y. Li et al., 2018b)
RfDo (DEHP)	0.002	(Y. Li et al., 2018b)
CSFo (BBP)	0.00019	(Y. Li et al., 2018b)
CSFo (DEHP)	0.014	(Y. Li et al., 2018b)

6.3 Results

Assessment of organic contaminants in the menstrual blood samples of twenty (20) female adults between the ages of 25- 45 indicated the presence of phthalates and bisphenol A however phthalates were more abundant. Table 6.2 indicates that only one participant had detectable levels of benzyl butyl phthalate, two participants had bis (2- ethyl hexyl) adipate and pyrimidine detected while three participants had di-n- octyl phthalate and progesterone identified. Three contaminants, diethyl phthalate, dibutyl phthalate, bis (2- ethyl hexyl) phthalate were detected in samples of all participants. BPA was positive in blood samples of thirteen participants while DMP was detected in 7 participants.

Table 6.2. Percentage of individuals with detection of contaminants in menstrual blood sample

Contaminant	Percentage (n= 20)
Bisphenol A	65
Dimethyl phthalate	35
Diethyl phthalate	100
Dibutyl Phthalate	100
Benzyl Butyl Phthalate	5
Bis (2- ethyl hexyl) adipate	10
Bis (2- ethyl hexyl) phthalate	100
Di-n- octyl Phthalate	15
Progesterone	15
Pyrimidine	10

Source: Researcher, 2022

Again three participants had six of the various contaminants, one of the participants had three, six participants had five and ten participants four of the contaminants as shown in fig 6.1

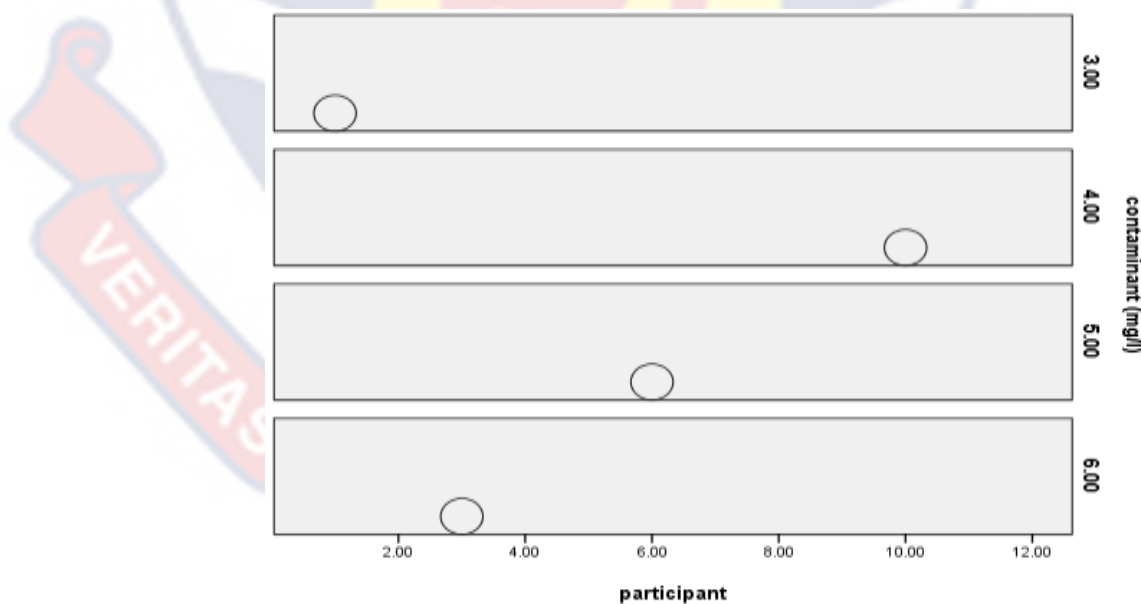


Figure 6.1 Participant with number of contaminants in menstrual blood sample

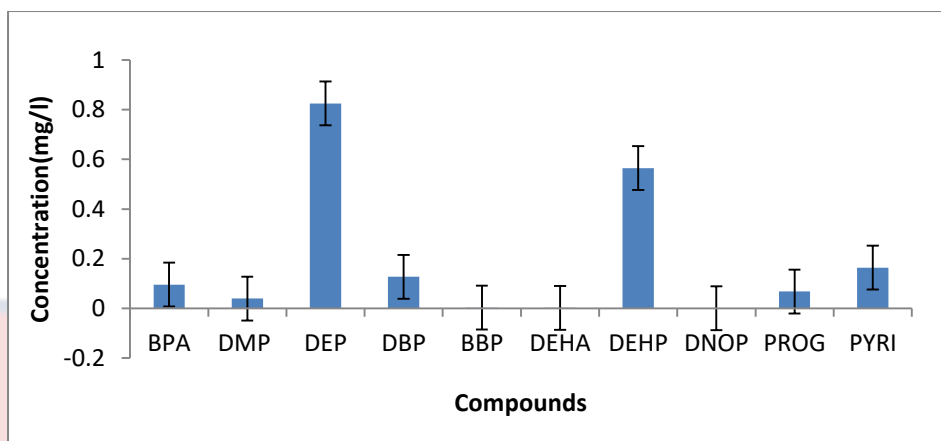


Figure 6.2 Mean level of EDCs in menstrual blood sample of participants

The contaminants that showed appreciable levels were DMP, DEP, DEHP, DBP and BPA compared with BBP, DEHA, and DNOP that had negligible concentrations as indicated in fig 6.2. Considering the phthalates, DEP had the highest concentration followed by DEHP, DBP and then DMP which were all higher than BPA except DMP.

Table 6.3. Descriptive statistics of contaminants in menstrual blood sample of Participants

Contaminant (mg.L ⁻¹)	Minimum	Maximum	Mean	Std. Deviation	Skewness	Kurtosis
BPA	.000	.208	.096	.074	-.509	-1.558
DMP	.000	.187	.040	.067	1.457	.569
DEP	.439	1.156	.825	.173	-.219	-.072
DBP	.081	.244	.127	.035	2.131	6.433
BBP	.000	.06	.003	.013	4.472	20.000
DEHA	.000	.047	.004	.010	4.443	19.809
DEHP	.095	.982	.565	.288	-.376	-1.122
DNOP	.000	.007	.001	.002	2.977	8.161
PROG	.000	.555	.068	.170	2.291	3.935
PIRI	.000	2.149	.164	.532	3.369	11.308

Source: Researcher, 2022

Considering table 6.3 it is observed that pyrimidine and DEHP showed much variability with a standard deviation of 0.5317 and 0.288 respectively. DEP and progesterone showed similar deviation from the mean whilst the others had less than 0.1 deviations. DEP had the highest mean concentration of 0.8248mgL⁻¹ whereas DNOP recorded the least concentration of 0.00065mgL⁻¹

¹. The maximum concentration of DEP recorded from one of the subjects is 1.156 mg⁻¹ and the minimum is 0.439 mg⁻¹ compared with DEHP that was the next most abundant phthalate at a maximum concentration of 0.982 mg⁻¹ and minimum value of 0.095 mgL⁻¹.

Human exposure and health risk assessment

This study only evaluated the CR of DEHP using cancer slope factor of 0.014. The risks of toxic EDC to individuals via ingestion, inhalation and dermal contact were estimated based on the concentrations of EDC of the individual menstrual blood sample. Reference was made to the acceptable risk level recommended by the USEPA (1×10^{-6}) when estimating the lifetime excess CR of phthalate esters. The assessment of cancer risks via all the routes showed that none of the routes exceeded the recommended allowable level. The carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} . The results of the risk assessment are summarized in table 6.4

Table 6. 4 Health risk assessment of participants

Sample ID	DEHP			Total
	INGESTION	DERMAL	INHALATION	
1	2.532E-09	1.010E-10	3.723E-13	2.633E-09
2	5.786E-09	2.309E-10	8.509E-13	6.018E-09
3	1.159E-09	4.624E-11	1.704E-13	1.205E-09
4	8.005E-09	3.194E-10	1.177E-12	8.326E-09
5	3.929E-09	1.568E-10	5.778E-13	4.086E-09
6	1.093E-09	4.362E-11	1.608E-13	1.137E-09
7	6.542E-09	2.610E-10	9.621E-13	6.804E-09
8	1.068E-09	4.263E-11	1.571E-13	1.111E-09
9	3.616E-09	1.443E-10	5.318E-13	3.761E-09
10	6.649E-09	2.653E-10	9.778E-13	6.916E-09
11	5.959E-09	2.378E-10	8.763E-13	6.198E-09
12	3.460E-09	1.381E-10	5.089E-13	3.599E-09
13	6.625E-09	2.643E-10	9.742E-13	6.890E-09
14	3.616E-09	1.443E-10	5.318E-13	3.761E-09
15	5.926E-09	2.364E-10	8.715E-13	6.163E-09
16	5.326E-09	2.125E-10	7.832E-13	5.539E-09
17	7.808E-10	3.115E-11	1.148E-13	8.121E-10
18	6.625E-09	2.643E-10	9.742E-13	6.890E-09
19	8.071E-09	3.220E-10	1.187E-12	8.394E-09
20	6.049E-09	2.414E-10	8.896E-13	6.292E-09

Source: Researcher, 2022

6.4 Discussion

Human exposure pathways to EDCs varies and obtaining information pertaining to exposure effects and diseases is mainly by analyzing compounds in human biological matrices. In all ten different compounds were detected in the menstrual blood samples. Studies conducted on BPA in human biological matrix so far in Africa were mostly on urinary BPA (Rotimi et al., 2021) The maximum concentration found in menstrual blood of the participants were similar to the maximum concentrations found in urine samples reported by Abo et al., 2018. However (Gounden et al., 2019) conducted a study on maternal and cord blood with concentrations lower than 0.208ng/mL detected. In neonates and infants however, exposure to EDCs may come through the placenta or breast-feeding and the associated effect (Martino & Prescott, 2011). Again lower blood BPA levels were found in children and pregnant women in China (Zhang et al., 2013). The identified concentrations could be attributed to the cumulative effect of three distinct body fluids that consist of blood, vaginal secretions and the endometrial cells of the uterine wall. The main sources of BPA found in the blood is attributed to dietary sources which include food and drinks packaged in cans and polycarbonate bottles as well as paper and plastic films as reported by Corrales et al., 2015.

The phthalate esters of diethyl phthalate (DEP), dibutyl- (DBP) and bis (2 ethylhexyl phthalate) DEHP identified remains the most abundant compounds measured. Study carried out by Wang et al., 2019 reported the corresponding metabolites in urine samples. Biomarkers of human exposure to phthalates is based mainly on the measurement of urinary monoester metabolites, although several secondary and oxidative metabolites have been reported to occur in human specimens (Silva et al., 2003) The identification of phthalate esters

(instead of metabolites) in menstrual blood of all participants studied suggests that bioaccumulation of selected phthalate compounds such as DEHP, DEP and DBP may be occurring with appreciable human toxicity. Similar observation was made in a clinical study of phthalate elimination in blood, urine and sweat (Genuis et al., 2012). The carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} suggesting that there is insignificant cancer risk for DEHP, which is comparable to similar research.

6.5 Conclusion

Menstrual blood is an easily obtainable body fluid and collected through noninvasive means. Continuous human exposure to possible health threat posed by organic compounds that are endocrine disrupting in nature is an important issue that requires frequent monitoring. Hence the use of menstrual discharge sampled non-invasively as a biomonitoring matrix provides an alternative debarring any myth surrounding it particularly in Africa and critical to the protection of vulnerable groups, such as pregnant women, the elderly or chronically ill people. The data obtained demonstrate that many proposed markers of women's health are present in the menstrual blood which could subsequently, be used for diagnostic purposes. Menstrual discharge is composed of three distinct body fluids that consist of blood, vaginal secretions, and the endometrial cells of the uterine wall. Also early detection of harmful impact of environmental contaminants is critical to human protection especially neonates. The identification of phthalates (instead of metabolites) and the levels detected in the menstrual blood of all participants studied suggests the bioaccumulation of phthalate may be occurring with appreciable human toxicity though the carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} .

CHAPTER SEVEN

SUMMARY, CONCLUSIONS, RECOMMENDATION AND SUGGESTION FOR FURTHER STUDIES

7.1 Overview

This chapter summarizes the study that was undertaken and draws conclusions with regards to the outcome of the study. It also makes general recommendations for behavioural change as well as specific policy change needs. It further suggests some future research areas with respect to environmental pollutants especially endocrine disrupting chemicals.

7.2 Summary

The gathering of data on endocrine disrupting chemicals and potentially toxic elements within the environment was attained through mainly quantitative methods to assess public understanding of pesticide use and health effects of endocrine disrupting chemicals, determine the soil quality of the different land use classes, characterize and quantify endocrine disruptive chemicals (EDCs) in contaminated agricultural soils and characterize and quantify EDCs in female menstrual blood samples.

Lifestyles have had considerable influence on the use of pesticides and products that contain EDCs. In particular, population growth and urbanisation have influenced the increase in the use of these chemicals in agriculture in order to increase yields as well as households. The quantitative survey indicated that there is low level of knowledge of the health effects of endocrine disrupting chemicals among the three communities, especially amongst those in rural areas where pesticides are widely used by them. Indeed, it showed that some individuals are dismissive of any possible adverse health effects of pesticide use.

Generally, EDCs were below the recommended threshold for all the sites based on the analytical results. The risk posed by selected EDCs compared to the recommended U.S. EPA reference doses showed that an estimated average daily intake doses of BPA, BBP, DEP, DMP, DnOP and DEHP via non-dietary routes were within acceptable levels. Similarly, the carcinogenic risks posed by DEHP and BBP in soils via the non-dietary routes were within acceptable levels. The studies also showed that all the sites were deficient in some of the chemical properties studied making the soils less fertile for optimum crop growth and support essential environmental benefits. Continuous cultivation of land without proper agronomic management has a lot of adverse effect on soil quality. Similarly proper waste management is critical to ensure soil quality. Soils have various functions therefore it is exceedingly important to make conscious effort to protect the soil resource to enhance the protection of watersheds and ground waters from agricultural chemicals ultimately to protect life. Proper disposal of industrial and municipal wastes contribute to carbon sequestration that would otherwise contribute to global climate change to ensure sustainability. Protection of soil resource for optimum function is vital and requires individual conscious effort to achieve it

Analyzing menstrual discharge as non-invasive biomonitoring matrix provides an alternative debarring any myth surrounding it particularly in Africa and critical to the protection of vulnerable groups, the elderly or chronically ill people. The data obtained demonstrate that many proposed markers of women's health are present in the menstrual blood which could subsequently, be used for diagnostic purposes The identification of phthalates

(instead of metabolites) and the levels detected in the menstrual blood of all participants studied suggests the bioaccumulation of phthalate may be occurring with appreciable human toxicity though the carcinogenic exposure risks of DEHP via various routes were much lower than 1×10^{-6} .

7.3 Conclusion

The use of pesticides, personal care products and other chemicals that are endocrine disrupting in nature cannot be done away with entirely, however, due to illiteracy or apathy of individuals about the health risks and environmental implications had resulted in greater reliance on these chemicals. Studies have shown that EDCs have such subtle effects that they may be extremely difficult to detect instantly and yet have significant impacts on human health over an extended time period. The essence of the study was therefore to determine knowledge of the health effect of endocrine disrupting chemicals and the extent to which soil and female menstrual blood are contaminated. This was achieved through the four specific objectives that guided this study.

Three key factors—biosocial, sociocultural, and contextual factors—were conceptualized as constituting pesticide usage and awareness of the health impacts of EDCs on people and the environment. Despite the reported adverse health effects of EDCs on humans, the study has shown that public awareness is low in Ghana. It has also brought to the fore that all the sites studied indicated an ingestion cancer risk of Cd, Pb and As that exceeded the acceptable threshold hence indicates potential lifetime risks. Generally, all the sites were deficient in some of the chemical properties studied making the soils less fertile for optimum crop growth and support essential environmental

benefits. The observation of Phthalate esters (instead of metabolites) in the menstrual blood of all participants studied suggests bioaccumulation of selected phthalate compounds such as DEHP, DEP and DBP may be occurring with appreciable human toxicity.

7.4 Recommendation

Practical and effective measures are needed to reverse this disturbing trend among populace. A coordinated plan is required to evaluate and disseminate information on health and the environmental effects of chemicals that are endocrine disrupting in nature. The Ghanaian government's Health and Pollution Action Plan (HPAP) seeks to regulate EDCs and other types of pollutant that affect human health, however there is also the need for an integrated and coordinated effort to define the role of pesticides and other EDCs in human health. Health institutions should be encouraged to scale up the education on the adverse health effects of pesticides and other endocrine disrupting chemicals that has become part of everyday life. Again it is recommended that above 70% soil quality index (SQI) for agricultural soils that are not sodic, strongly acidic or strongly alkaline as well as forest soils, this is because SQI is highly sensitive to these parameters. Again, industrial and decommissioned dump soils should have above 60% SQI when all heavy metals are within recommended acceptable limit.

Policy implications

The study outcome has some policy implications that are worth considering. First, institutions that are mandated to ensure that the environment is safe from contamination must work in tandem and complement each other to provide adequate protection of the environment. Again, the rapid

change in lifestyle and its associated health risk requires inter-disciplinary approach that involves academia, industry, government, and professionals to provide more accurate data required to manage the situation as at now and the future.

Furthermore, education on health effects of EDCs and PTEs must be made part of healthcare provision for all especially women to enhance the knowledge of the populace.

7.5 Future work

Future work may include but not limit to the following:

1. Future work to determine the impact of different soil types (e.g. soil physicochemical properties) on degradation to reduce uncertainties in soil function.
2. The mono derivative of phthalates could be considered in menstrual blood considering the half- life of the contaminants
3. Educational attainment as a demographic parameter could be considered in future survey work to elucidate the correlation between knowledge of health effects.

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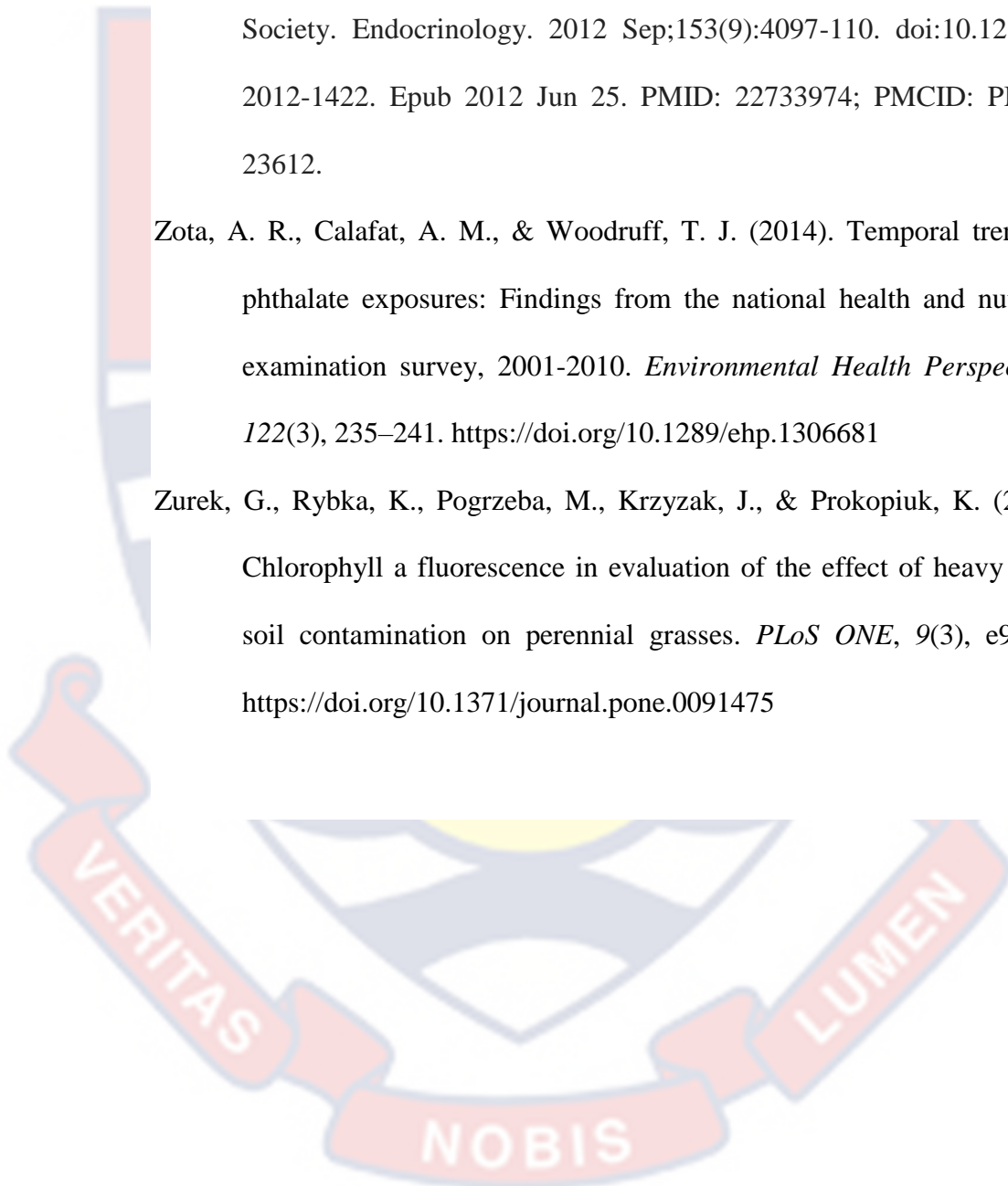
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APPENDICES

APPENDIX A

QUESTIONNAIRE ON KNOWLEDGE OF HEALTH EFFECT OF
EDCS

Personal Data			
1	Age	15-25	1
		25-35	2
		35-45	3
		Above 45	4
2	Gender	Male	1
		Female	2
3	Marital status	not married	1
		married	2
		Divorced	3
4	No of children	No child	0
		1-3	1
		4-5	2
		Above	3
Lifestyle change			
5	use make ups (Type)	Yes	1
		No	0
5b	Do you bleach/ ever bleached	Yes	1
		No	0
6	keeping food in plastics (polythene materials)	Yes	1
		No	0
7	Major food intake (specify)	daily	1
		5 times weekly	2
8	Main source Protein	Meat	1
		Fish	2
9	Source of Drinking water	Tap water	1
		Bottled , sachet	2
		Stream, borehole	3
10	Current Occupation (Duration)	unemployed	0
		self –employed	1
		Formal	2
		employment	
11	Previous Employment (Duration)	Yes	1
		No	0
12	If self –employed ,Type of vocation	High exposure	1
		Low exposure	2
13	Source of vegetable	Self-cultivated	1
		Bought	2
14	Frequency of vegetable intake	Seldom	1
		daily	2
		Every other day	3

15	Type of vegetable	Leafy	1			
		Root	2			
		Bulb	3			
		fruit	4			
		flower	5			
16	Place of residence (Duration)	Rural	1			
		Urban	2			
17	Previous place of residence (Duration)	Rural	1			
		Urban	2			
18	Intake of canned foods	Yes	1			
		No	0			
19	Use of insecticides at home	Yes	1			
		No	0			
Possible reproductive irregularity						
20	Age at first mensuration	Earlier than expected	1			
		within expected	2			
		Delayed	3			
21	No of days flow	<3days	1			
		4-5days	2			
		>5days	3			
22	Frequency of flow	Monthly	1			
		Intermittent	2			
23	pain during flow	no pain	0			
		Slight pain	1			
		Severe pain	2			
Any knowledge of health risk of EDCs						
24	Any knowledge of health risk of EDCs	Yes	1			
		No	0			
25		Strongly disagree	Disagree	Undecided	Agree	Strongly agree
		1	2	3	4	5
a	Obesity					
b	Diabetes					
c	Cancers Breast & testis					
d	miscarriage					
e	Prostate cancer					
f	Decrease in fertility					
g	Behaviour disorders					
h	Cardiovascular disease					
i	Genital problems (undeveloped)					
j	Frequent urination					
k	Erectile dysfunction					

APPENDIX B

**KNOWLEDGE OF BEHAVIOUR DISORDERS DUE TO PESTICIDE
USE AND EDC (n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						Pearson chi2(12) = 22.1551 Pr = 0.036 Cramér's V = 0.1569
15-25yrs	5.81	8.14	84.88	0	1.16	
26-35yrs	13.58	16.05	69.14	0	1.23	
36-45yrs	7.59	6.33	81.01	3.8	1.27	
Above 45 yrs	11.11	20.37	62.96	5.56	0	
Gender						Pearson chi2(4) = 10.2952 Pr = 0.036 Cramér's V = 0.1852
Male	3.37	8.99	86.52	0	1.12	
Female	11.85	13.27	71.09	2.84	0.95	
Marital Status						Pearson chi2(4) = 3.7965 Pr = 0.434 Cramér's V = 0.1125
Not married/divorced	8.78	12.16	75.68	1.35	2.03	
Married	9.87	11.84	75.66	2.63	0	
Parity						Pearson chi2(12) = 19.8910 Pr = 0.069 Cramér's V = 0.1487
No child	4.42	9.73	84.96	0	0.88	
1-3 children	14.05	13.22	69.42	1.65	1.65	
4-5 children	6.67	11.11	75.56	6.67	0	
Above 5 children	14.29	19.05	61.9	4.76	0	
Occupation						Pearson chi2(8) = 10.8447 Pr = 0.211 Cramér's V = 0.1344
Unemployed	8.33	10.71	80.95	0	0	
Self employed	11.43	13.14	70.86	3.43	1.14	
Formal employment	2.44	9.76	85.37	0	2.44	
Vocation						Pearson chi2(20) = 40.1141 Pr = 0.005 Cramér's V = 0.1828
Unskilled labour	20.83	20.83	50	0	8.33	
Farmer	5.66	15.09	79.25	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	18.75	3.13	75	3.13	0	
Student	6.25	7.81	85.94	0	0	
Others	8.47	14.41	72.03	4.24	0.85	

APPENDIX C

**KNOWLEDGE OF CANCER DUE TO PESTICIDE USE AND EDC
(n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						Pearson chi2(12) = 41.0911 Pr = 0.001 Cramér's V = 0.2137
15-25yrs	0	2.33	69.77	25.58	2.33	
26-35yrs	6.17	2.47	44.44	44.44	2.47	
36-45yrs	3.8	3.8	39.24	40.51	12.66	
Above 45 yrs	7.41	5.56	25.93	55.56	5.56	
Gender						Pearson chi2(4) = 7.7957 Pr = 0.099 Cramér's V = 0.1612
Male	4.49	2.25	38.2	44.94	10.11	
Female	3.79	3.79	50.71	37.91	3.79	
Marital status						Pearson chi2(4) = 13.0682 Pr = 0.011 Cramér's V = 0.2087
Not married/divorced	2.7	2.03	56.76	35.14	3.38	
Married	5.26	4.61	37.5	44.74	7.89	
Parity						Pearson chi2(12) = 49.3734 Pr = 0.001 Cramér's V = 0.2342
No child	2.65	2.65	61.06	30.97	2.65	
1-3 children	4.13	0.83	38.02	49.59	7.44	
4-5 children	8.89	2.22	42.22	40	6.67	
Above 5 children	0	23.81	33.33	33.33	9.52	
Occupation						Pearson chi2(8) = 44.3064 Pr = 0.001 Cramér's V = 0.2717
Unemployed	0	2.38	69.05	26.19	2.38	
Self employed	2.86	4.57	39.43	45.71	7.43	
Formal employment	17.07	0	34.15	43.9	4.88	
Vocation						Pearson chi2(20) = 67.0732 Pr = 0.001 Cramér's V = 0.2364
Unskilled labour	0	12.5	41.67	45.83	0	
Farmer	0	3.77	28.3	54.72	13.21	
Sanitary worker	22.22	0	55.56	22.22	0	
Beautician	9.38	3.13	53.13	28.13	6.25	
Student	0	1.56	78.13	18.75	1.56	
Others	5.93	2.54	37.29	48.31	5.93	

APPENDIX D

KNOWLEDGE OF CARDIOVASCULAR DISEASE DUE TO PESTICIDE USE AND EDC (n=300)

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
						Pearson chi2(12) = 28.3227 Pr = 0.005 Cramér's V = 0.1774
Age						
15-25yrs	1.16	2.33	81.4	13.95	1.16	
26-35yrs	6.17	2.47	75.31	16.05	0	
36-45yrs	0	8.86	72.15	18.99	0	
Above 45 yrs	5.56	18.52	61.11	12.96	1.85	
						Pearson chi2(4) = 19.7412 Pr = 0.001 Cramér's V = 0.2565
Gender						
Male	2.25	10.11	85.39	2.25	0	
Female	3.32	5.69	68.72	21.33	0.95	
						Pearson chi2(4) = 10.9754 Pr = 0.027
Marital status						
Not married/divorced	3.38	3.38	71.62	20.95	0.68	Cramér's V = 0.1913
Married	2.63	10.53	75.66	10.53	0.66	
						Pearson chi2(12) = 17.0215 Pr = 0.149 Cramér's V = 0.1375
Parity						
No child	1.77	3.54	81.42	12.39	0.88	
1-3 children	4.96	7.44	69.42	18.18	0	
4-5 children	2.22	11.11	71.11	15.56	0	
Above 5 children	0	14.29	61.9	19.05	4.76	
						Pearson chi2(8) = 6.9335 Pr = 0.544 Cramér's V = 0.1075
Occupation						
Unemployed	1.19	2.38	79.76	15.48	1.19	
Self employed	4	8.57	70.29	16.57	0.57	
Formal employment	2.44	9.76	75.61	12.2	0	
						Pearson chi2(20) = 44.7750 Pr = 0.001 Cramér's V = 0.1932
Vocation						
Unskilled labour	4.17	20.83	54.17	20.83	0	
Farmer	3.77	15.09	81.13	0	0	
Sanitary worker	0	11.11	88.89	0	0	
Beautician	0	0	71.88	25	3.13	
Student	0	1.56	82.81	14.06	1.56	
Others	5.08	5.08	68.64	21.19	0	

APPENDIX E

**KNOWLEDGE OF DIABETES DUE TO PESTICIDE USE AND EDC
(n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
						Pearson chi2(12) = 10.2956 Pr = 0.590 Cramér's V = 0.1070
Age						
15-25yrs	0	4.65	79.07	16.28	0	
26-35yrs	1.23	4.94	66.67	25.93	1.23	
36-45yrs	1.27	5.06	72.15	21.52	0	
Above 45 yrs	0	11.11	70.37	18.52	0	
						Pearson chi2(4) = 29.7047 Pr = 0.001 Cramér's V = 0.3147
Gender						
Male	0	10.11	87.64	2.25	0	
Female	0.95	4.27	65.88	28.44	0.47	
						Pearson chi2(4) = 9.4117 Pr = 0.052 Cramér's V = 0.1771
Marital status						
Not married/divorced	0.68	3.38	68.92	26.35	0.68	
Married	0.66	8.55	75.66	15.13	0	
						Pearson chi2(12) = 20.6875 Pr = 0.055 Cramér's V = 0.1516
Parity						
No child	0	4.42	78.76	15.93	0.88	
1-3 children	0.83	4.13	69.42	25.62	0	
4-5 children	0	8.89	73.33	17.78	0	
Above 5 children	4.76	19.05	52.38	23.81	0	
						Pearson chi2(8) = 10.9077 Pr = 0.207 Cramér's V = 0.1348
Occupation						
Unemployed	0	4.76	77.38	16.67	1.19	
Self employed	1.14	8	67.43	23.43	0	
Formal employment	0	0	82.93	17.07	0	
						Pearson chi2(20) = 59.2815 Pr = 0.001 Cramér's V = 0.2223
Vocation						
Unskilled	0	16.67	41.67	41.67	0	
Farmer	0	16.98	83.02	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	3.13	3.13	71.88	21.88	0	
Student	0	3.13	81.25	14.06	1.56	
Others	0.85	1.69	66.95	30.51	0	

APPENDIX F

KNOWLEDGE OF ERECTILE DYSFUNCTION DUE TO PESTICIDE
USE AND EDC (n=300)

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						
						Pearson chi2(12) = 25.0491 Pr = 0.015 Cramér's V = 0.1668
15-25yrs	1.16	4.65	81.4	12.79	0	
26-35yrs	6.17	6.17	61.73	24.69	1.23	
36-45yrs	0	11.39	18.99	1.27	0	
Above 45 yrs	9.26	14.81	53.7	22.22	0	
Gender						
						Pearson chi2(4) = 68.5636 Pr = 0.001 Cramér's V = 0.4781
Male	11.24	21.35	67.42	0	0	
Female	0.47	3.32	67.77	27.49	0.95	
Marital status						
						Pearson chi2(4) = 22.9389 Pr = 0.001 Cramér's V = 0.2765
Not married/divorced	0.68	3.38	71.62	24.32	0	
Married	6.58	13.82	63.82	14.47	1.32	
Parity						
						Pearson chi2(12) = 18.6961 Pr = 0.096 Cramér's V = 0.1441
No child	1.77	9.73	76.11	12.39	0	
1-3 children	5.79	4.96	63.64	23.97	1.65	
4-5 children	2.22	11.11	66.67	20	0	
above 5 children	4.76	19.05	47.62	28.57	0	
Occupation						
						Pearson chi2(8) = 24.3362 Pr = 0.002 Cramér's V = 0.2014
Unemployed	0	4.76	78.57	16.67	0	
Self employed	6.29	12.57	58.29	21.71	1.14	
Formal employment	0	0	85.37	14.63	0	
Vocation						
						Pearson chi2(20) = 135.4692 Pr = 0.000 Cramér's V = 0.3360
Unskilled	0	12.5	45.83	41.67	0	
Farmer	18.87	35.85	45.28	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	3.13	0	65.63	28.13	3.13	
Student	0	3.13	82.81	14.06	0	
Others	0	1.69	72.03	25.42	0.85	

APPENDIX G

**KNOWLEDGE OF DECREASE FERTILITY DUE TO PESTICIDE
USE AND EDC (n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						Pearson chi2(12) = 33.0513 Pr = 0.001 Cramér's V = 0.1916
15-25yrs	1.16	4.65	84.88	9.3	0	
26-35yrs	3.7	9.88	69.14	13.58	3.7	
36-45yrs	0	6.33	77.22	15.19	1.27	
Above 45 yrs	9.26	22.22	61.11	7.41	0	
Gender						Pearson chi2(4) = 19.7209 Pr = 0.001 Cramér's V = 0.2564
Male	2.25	12.36	85.39	0	0	
Female	3.32	8.53	69.67	16.59	1.9	
Marital status						Pearson chi2(4) = 9.1725 Pr = 0.057 Cramér's V = 0.1749
Not married/divorced	2.7	6.08	73.65	16.22	1.35	
Married	3.29	13.16	75	7.24	1.32	
Parity						Pearson chi2(12) = 19.2801 Pr = 0.082 Cramér's V = 0.1464
No child	1.77	3.54	84.96	8.85	0.88	
1-3 children	3.31	10.74	68.6	14.88	2.48	
4-5 children	4.44	15.56	71.11	8.89	0	
Above 5 children	4.76	23.81	57.14	14.29	0	
Occupation						Pearson chi2(8) = 12.6806 Pr = 0.123 Cramér's V = 0.1454
Unemployed	2.38	3.57	83.33	8.33	2.38	
Self employed	4	13.14	68	13.71	1.14	
Formal employment	0	7.32	82.93	9.76	0	
Vocation						Pearson chi2(20) = 42.1876 Pr = 0.003 Cramér's V = 0.1875
Unskilled	0	29.17	50	20.83	0	
Farmer	3.77	20.75	75.47	0	0	
Sanitary worker	0	0	88.89	11.11	0	
Beautician	3.13	3.13	75	15.63	3.13	
Student	3.13	3.13	85.94	7.81	0	
Others	3.39	6.78	71.19	16.1	2.54	

APPENDIX H

KNOWLEDGE OF GENITAL PROBLEMS DUE TO PESTICIDE USE
AND EDC (n=300)

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						Pearson chi2(12) = 18.2670 Pr = 0.108 Cramér's V = 0.1425
15-25yrs	1.16	8.14	83.72	6.98	0	
26-35yrs	4.94	9.88	76.54	8.64	0	
36-45yrs	2.53	11.39	78.48	6.33	1.27	
Above 45 yrs	11.11	20.37	62.96	5.56	0	
Gender						Pearson chi2(4) = 8.9413 Pr = 0.063 Cramér's V = 0.1726
Male	2.25	12.36	84.27	1.12	0	
Female	5.21	11.37	73.46	9.48	0.47	
Marital status						Pearson chi2(4) = 11.2451 Pr = 0.024 Cramér's V = 0.1936
Not married/divorced	3.38	9.46	75.68	11.49	0	
Married	5.26	13.82	77.63	2.63	0.66	
Parity						Pearson chi2(12) = 20.2669 Pr = 0.062 Cramér's V = 0.1501
No child	1.77	7.08	85.84	5.31	0	
1-3 children	6.61	10.74	71.9	9.92	0.83	
4-5 children	6.67	17.78	68.89	6.67	0	
Above 5 children	0	28.57	71.43	0	0	
Occupation						Pearson chi2(8) = 10.2229 Pr = 0.250 Cramér's V = 0.1305
Unemployed	1.19	8.33	83.33	7.14	0	
Self employed	6.29	14.86	72	6.29	0.57	
Formal employment	2.44	4.88	82.93	9.76	0	
Vocation						Pearson chi2(20) = 37.8179 Pr = 0.009 Cramér's V = 0.1775
Unskilled	4.17	25	58.33	12.5	0	
Farmer	3.77	20.75	75.47	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	6.25	3.13	84.38	3.13	3.13	
Student	0	6.25	87.5	6.25	0	
Others	6.78	11.02	71.19	11.02	0	

APPENDIX I

KNOWLEDGE OF MISCARRIAGE DUE TO PESTICIDE USE AND
EDC (n=300)

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
						Pearson chi2(12) = 8.8357 Pr = 0.717
Age						Cramér's V = 0.0991
15-25yrs	2.33	5.81	80.23	10.47	1.16	
26-35yrs	2.47	13.58	74.07	7.41	2.47	
36-45yrs	1.27	12.66	74.68	11.39	0	
Above 45 yrs	0	11.11	75.93	12.96	0	
						Pearson chi2(4) = 11.9498 Pr = 0.018
Gender						Cramér's V = 0.1996
Male	1.12	8.99	87.64	2.25	0	
Female	1.9	11.37	71.56	13.74	1.42	
						Pearson chi2(4) = 11.4383 Pr = 0.022
Marital status						Cramér's V = 0.1953
Not married/divorced	0.68	9.46	72.97	14.86	2.03	
Married	2.63	11.84	79.61	5.92	0	
						Pearson chi2(12) = 23.3773 Pr = 0.025
Parity						Cramér's V = 0.1612
No child	0.88	4.42	83.19	11.5	0	
1-3 children	2.48	13.22	72.73	9.09	2.48	
4-5 children	0	11.11	73.33	15.56	0	
Above 5 children	4.76	28.57	66.67	0	0	
						Pearson chi2(8) = 9.1385 Pr = 0.331
Occupation						Cramér's V = 0.1234
Unemployed	1.19	7.14	83.33	7.14	1.19	
Self employed	1.71	14.29	72	10.86	1.14	
Formal employment	2.44	2.44	80.49	14.63	0	
						Pearson chi2(20) = 38.4742 Pr = 0.008
Vocation						Cramér's V = 0.1791
Unskilled	0	29.17	41.67	25	4.17	
Farmer	1.89	15.09	83.02	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	3.13	12.5	78.13	6.25	0	
Student	1.56	3.13	85.94	9.38	0	
Others	1.69	9.32	72.88	14.41	1.69	

APPENDIX J

**KNOWLEDGE OF OBESITY DUE TO PESTICIDE USE AND EDC
(n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						Pearson chi2(12) = 17.1549 Pr = 0.144 Cramér's V = 0.1381
15-25yrs	1.16	2.33	74.42	22.09	0	
26-35yrs	1.23	8.64	67.9	17.28	4.94	
36-45yrs	2.53	6.33	72.15	18.99	0	
Above 45 yrs	3.7	9.26	72.22	14.81	0	
Gender						Pearson chi2(4) = 21.9488 Pr = 0.001 Cramér's V = 0.2705
Male	2.25	7.87	86.52	3.37	0	
Female	1.9	5.69	65.4	25.12	1.9	
Marital status						Pearson chi2(4) = 13.8302 Pr = 0.008 Cramér's V = 0.2147
Not married/divorced	2.03	3.38	67.57	24.32	2.7	
Married	1.97	9.21	75.66	13.16	0	
Parity						Pearson chi2(12) = 30.0123 Pr = 0.003 Cramér's V = 0.1826
No child	0.88	5.31	75.22	18.58	0	
1-3 children	3.31	3.31	69.42	20.66	3.31	
4-5 children	0	6.67	77.78	15.56	0	
Above 5 children	4.76	28.57	52.38	14.29	0	
Occupation						Pearson chi2(8) = 9.0683 Pr = 0.337 Cramér's V = 0.1229
Unemployed	0	7.14	75	16.67	1.19	
Self employed	3.43	7.43	68.57	18.86	1.71	
Formal employment	0	0	78.05	21.95	0	
Vocation						Pearson chi2(20) = 71.8725 Pr = 0.001 Cramér's V = 0.2447
Unskilled	0	25	37.5	25	12.5	
Farmer	3.77	13.21	83.02	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	0	3.13	75	21.88	0	
Student	1.56	1.56	78.13	18.75	0	
Others	2.54	3.39	66.95	26.27	0.85	

APPENDIX K

KNOWLEDGE OF PROSTATE CANCER DUE TO PESTICIDE USE AND EDC (n=300)

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						
15-25yrs	1.16	3.49	82.56	10.47	2.33	Pearson chi2(12) = 27.4987 Pr = 0.007 Cramér's V = 0.1748
26-35yrs	3.7	6.17	59.26	25.93	4.94	
36-45yrs	1.27	2.53	63.29	27.85	5.06	
Above 45 yrs	1.85	3.7	44.44	40.74	9.26	
Gender						
Male	1.12	1.12	49.44	40.45	7.87	Pearson chi2(4) = 22.3236 Pr = 0.001 Cramér's V = 0.2728
Female	2.37	5.21	70.62	18.01	3.79	
Marital status						
Not married/divorced	2.03	4.05	70.27	18.92	4.73	Pearson chi2(4) = 5.5585 Pr = 0.235 Cramér's V = 0.1361
Married	1.97	3.95	58.55	30.26	5.26	
Parity						
No child	1.77	4.42	76.11	14.16	3.54	Pearson chi2(12) = 28.0811 Pr = 0.005 Cramér's V = 0.1766
1-3 children	2.48	2.48	56.2	33.06	5.79	
4-5 children	2.22	4.44	66.67	26.67	0	
Above 5 children	0	9.52	42.86	28.57	19.05	
Occupation						
Unemployed	2.38	3.57	79.76	8.33	5.95	Pearson chi2(8) = 26.8001 Pr = 0.001 Cramér's V = 0.2113
Self employed	1.71	4.57	53.71	34.86	5.14	
Formal employment	2.44	2.44	78.05	14.63	2.44	
Vocation						
Unskilled	0	12.5	45.83	29.17	12.5	Pearson chi2(20) = 92.0091 Pr = 0.001 Cramér's V = 0.2769
Farmer	0	1.89	22.64	64.15	11.32	
Sanitary worker	11.11	0	88.89	0	0	
Beautician	0	6.25	75	12.5	6.25	
Student	3.13	3.13	84.38	6.25	3.13	
Others	2.54	3.39	71.19	21.19	1.69	

APPENDIX L

**KNOWLEDGE OF FREQUENT URINATION DUE TO PESTICIDE
USE AND EDC (n=300)**

Variables	Strongly disagree (%)	Disagree (%)	Unaware (%)	Agree (%)	strongly agree (%)	Measure of association
Age						
15-25yrs	2.33	5.81	81.4	9.3	1.16	Pearson chi2(12) = 12.4863 Pr = 0.407 Cramér's V = 0.1178
26-35yrs	2.47	12.35	69.14	16.05	0	
36-45yrs	0	8.86	81.01	8.86	1.27	
Above 45 yrs	3.7	16.67	66.67	12.96	0	
Gender						
Male	0	13.48	86.52	0	0	Pearson chi2(4) = 21.4533 Pr = 0.001 Cramér's V = 0.2674
Female	2.84	9	70.62	16.59	0.95	
Marital status						
Not married/divorced	2.7	7.43	72.97	16.22	0.68	Pearson chi2(4) = 8.4988 Pr = 0.075 Cramér's V = 0.1683
Married	1.32	13.16	77.63	7.24	0.66	
Parity						
No child	2.65	6.19	81.42	9.73	0	Pearson chi2(12) = 16.3333 Pr = 0.176 Cramér's V = 0.1347
1-3 children	0.83	13.22	70.25	14.05	1.65	
4-5 children	0	11.11	77.78	11.11	0	
Above 5 children	9.52	14.29	66.67	9.52	0	
Occupation						
Unemployed	1.19	5.95	78.57	14.29	0	Pearson chi2(8) = 14.8234 Pr = 0.063 Cramér's V = 0.1572
Self employed	2.86	14.86	71.43	9.71	1.14	
Formal employment	0	0	85.37	14.63	0	
Vocation						
Unskilled	0	16.67	50	29.17	4.17	Pearson chi2(20) = 44.9259 Pr = 0.001 Cramér's V = 0.1935
Farmer	0	22.64	77.36	0	0	
Sanitary worker	0	0	100	0	0	
Beautician	0	12.5	75	9.38	3.13	
Student	3.13	6.25	81.25	9.38	0	
Others	3.39	5.93	74.58	16.1	0	

APPENDIX M

ETHICAL CLEARANCE

GHANA HEALTH SERVICE ETHICS REVIEW COMMITTEE

*In case of reply the
number and date of this
Letter should be quoted.*



My Ref. GHS/RDD/ERC/Admin/App 19/6/19
Your Ref. No.

Research & Development Division
Ghana Health Service
P. O. Box MB 190
Accra
GPS Address: GA-050-3303
Tel: +233-302-681109
Mob: 0503539896
Email: ethics.research@ghsmai.org
11th November, 2019

Benjamin Ason
School of Physical Science
University of Cape Coast
Cape Coast

The Ghana Health Service Ethics Review Committee has reviewed and given approval for the implementation of your Study Protocol.

GHS-ERC Number	GIIS-ERC004/09/19
Project Title	Contaminant Fate and Human Exposure to Endocrine Disrupting Chemicals in Contaminated Agricultural Soils in Ghana
Approval Date	11 th November, 2019
Expiry Date	10 th November, 2020
GIIS-ERC Decision	Approved

This approval requires the following from the Principal Investigator

- Submission of yearly progress report of the study to the Ethics Review Committee (ERC)
- Renewal of ethical approval if the study lasts for more than 12 months.
- Reporting of all serious adverse events related to this study to the ERC within three days verbally and seven days in writing.
- Submission of a final report **after completion** of the study
- Informing ERC if study cannot be implemented or is discontinued and reasons why
- Informing the ERC and your sponsor (where applicable) before any publication of the research findings.

Please note that any modification of the study without ERC approval of the amendment is invalid.

The ERC may observe or cause to be observed procedures and records of the study during and after implementation.

Kindly quote the protocol identification number in all future correspondence in relation to this approved protocol

SIGNED.....

Dr. Cynthia Bannerman
(GHS-ERC Chairperson)

Cc: The Director, Research & Development Division, Ghana Health Service, Accra