UNIVERSITY OF CAPE COAST

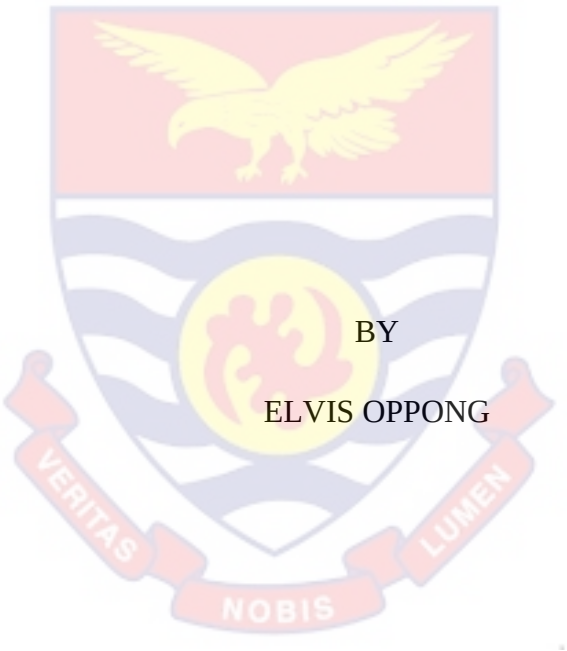
HEALTH RISK ASSESSMENT OF URINARY-PAHs AND THEIR METABOLITES AMONG ARTISANAL AUTO-MECHANICAL WORKERS FROM SELECTED WORKSHOPS IN SIWDU, CAPE COAST.

ELVIS OPPONG

2024

UNIVERSITY OF CAPE COAST

HEALTH RISK ASSESSMENT OF URINARY-PAHs AND THEIR METABOLITES AMONG ARTISANAL AUTO-MECHANICAL WORKERS FROM SELECTED WORKSHOPS IN SIWDU, CAPE COAST.



BY

ELVIS OPPONG

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

May 2024

DECLARATION

Candidate's Declaration

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

Candidate's Signature …… Date……

Name: Elvis Oppong

Supervisors' Declaration

We hereby declare that the preparations and presentation of the thesis were supervised in accordance with the guidelines on supervision of the thesis laid down by the University of Cape Coast.

Principal Supervisor's Signature…… Date ……

Name: Dr. Joseph K. Adjei

Co – Supervisor's Signature…… Date ……

Name: Dr. Albert Ofori

ABSTRACT

Occupational exposure to polycyclic aromatic hydrocarbons (PAHs) and their metabolites have been linked to increased risk for a suite of negative health outcomes such as lung, skin, bladder, kidney, and liver cancers and other diseases. This study sought to conduct a health risk assessment of urinary-PAHs and their metabolites among artisanal auto-mechanical workers from the Siwdu auto-mechanical workshops in Cape Coast Metropolis, Ghana. A total of 59 urine samples from three different artisanal groups namely: auto-mechanics, auto-sprayers, and plastic welders, were extracted in replicates (n = 3) for PAHs and its metabolites using solid phase extraction (SPE) protocol followed by HPLC-UV/RF instrumental analysis. The mean total metabolites and parent PAHs ranged between 490759.50 - 1869.00 ng/L, 129819.00 - 1752.00 ng/L, and 45613.50 - 2020.00 ng/L and 71916.36 -1382.73 ng/L, 12268.80 - 1703.04 ng/L, and 62936.82 -3862.41 ng/L for AM, AS and PW artisans respectively. About 80% of the samples had elevated levels of mean total PAHs (> 200.00 ng/L) set by NIOSH. Statistically, there were significant difference among the artisan group samples analysed with respect to analyte levels ($p < 0.05$). The cumulative non-cancer risk and cancer risk upon exposure ranged between 4.0×10^{-6} - 6.0×10^{-4} and 4.0×10^{-7} - 1.0×10^{-4} for PAH metabolites and 2.0×10^{-6} - 2.0×10^{-5} and 1.0×10^{-6} - 2.0×10^{-5} for parent PAHs for AM, AS and PW artisans respectively. About 70% of the samples had both elevated non-cancer and cancer risk (> 10^{-6}). The study showed that the artisanal auto-mechanical workers were exposed to elevated levels of PAHs due to poor safety culture, which may pose health risks to them.

KEY WORDS

Artisanal Auto-mechanical Workers

Cancer Risk

Health Risk Assessment

Mutagenic Risk

Occupational Health and Safety

Polycyclic Aromatic Hydrocarbons (PAHs)

ACKNOWLEDGEMENTS

I would like to extend my heartfelt appreciation to my supervisors, Dr. Joseph Adjei and Dr. Albert Ofori, both at the Department of Chemistry, for their invaluable support and guidance, which have been instrumental in completing this work. I am really very grateful.

I am also grateful to Samuel and Emelia Brew-Butler-SGS/GRASAG, UCC for their generous research grant contribution to make this work better.

I want to convey my deep gratitude to Mrs. Evelyn Adjei, Mr. Jonathan Ntow, Mr. Emmanuel Birikorang, and Mad. Egoh Yayra Benedicta, Mr. Alex Asante, Mr. Justice Hayfron, and Mr. Denis Otoo for their invaluable assistance and unwavering support. I am again grateful to Mad. Sandra Agyeiwaa for her generous contribution in cash to support my research work. Finally, I wish to thank my family and friends for their moral and financial support, especially my lovely parents (Mr. Kwaku Gyamfi and Mad. Adwoa Gyamfuaa) and my sisters, Erica Frema and Edna Amponsah.

DEDICATION

To my Parent: Mr. Kwaku Gyamfi, and Mad. Adwoa Gyamfuaa as well as my wife: Mad. Sandra Agyeiwaa.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PAHs	Polycyclic Aromatic Hydrocarbons
AM	Auto-mechanic
AS	Auto-sprayer
PW	Plastic welder
PPE	Personal protective equipment
SPE	Solid phase extraction
EPA	Environmental Protection Agency
TEF	Toxicity equivalent factor
MEF	Mutagenicity equivalent factor
WHO	World Health Organization
ILO	International Labour Organization
Ace	Acenaphthene
Acy	Acenaphthylene
Ant	Anthracene
BaP	Benzo(a) pyrene
B(a)A	Benzo(a) anthracene
BbFlt	Benzo(b) fluoranthene
BghiPer	Benzo(g,h,i) perylene
Phe	Phenanthrene
BkFlt	Benzo(k) fluoranthene
Chr	Chrysene
BahA	Dibenzo(a,h) anthracene

I[1,2,3-cd] Pyr	Indeno(1,2,3-c,d) pyrene
Pyr	Pyrene
FlT	Fluoranthene
Flu	Fluorene
1-OHP	1-hydroxypyrene
Nap	Naphthalene
1-MN	1-Methylnaphthalene
2-MN	2-Methylnaphthalene
NIOSH	National Institute for Occupational Safety and Health
ACGIH	American Conference of Governmental Industrial Hygienists
IARC	International Agency for Research on Cancer
HPLC-UV/RF	High-Performance Liquid Chromatography-Ultraviolet Visible / Fluorescence Detectors
OSH	Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
RF%RSD	Response Factors (RF) Percent Relative Standard Deviations
RT	Retention Time
DL	Detection Limit
QL	Quantitation Limit
LOQ	Limit of Quantitation
OHP	Metabolites of Polycyclic Aromatic Hydrocarbons

CHAPTER ONE

Introduction

Chapter one provided background to the study; "Health Risk Assessment of Urinary PAHs and Its Metabolites among Artisanal Auto-mechanical Workers from Siwdu Auto Mechanical Workshops in Cape Coast." It also highlights the problem statement, overall objective, specific objectives, significance of the study, the limitations and delimitations as well as the entire organisation of the study.

Background to the study

Panel-beaters, auto-sprayers, plastic welders, auto-electricians and auto-mechanics all fall under the category of artisanal auto-mechanical workers. Like many other occupational groups, they are exposed to a variety of risks associated with their jobs. An estimated 2 million women and men worldwide lose their lives to work-related illnesses and accidents each year, out of the 2.8 billion people who labour (ILO, 2022). Each year, there are 160 million occupational illnesses and 270 million occupational accidents worldwide. According to estimates by the International Labour Organization, diseases and accidents connected to the workplace cost the global economy 4% of its GDP (ILO, 2022).

Numerous artisanal auto-mechanical workers engage in a number of other dangerous behaviours as part of their work, including applying diesel to injured body parts, suction of gasoline, gasoline-based hand and car part washing , working, eating, and sleeping under cars in unhygienic settings, and not wearing

personal protective equipment (PPE) like overcoats, gloves, and safety boots (Johnson & Bassey, 2016). In Ghana, a sizable portion of people who practice vocational trades are employed in the artisanal auto-mechanical repair sector (Johnson & Bassey, 2016). The majority of artisanal auto-mechanical workers undergo some training or an apprenticeship before they start working in their field (Johnson & Bassey, 2016). However, others leave their apprenticeships early to begin working. As a result, many of them frequently fail to draw a connection between their workplace exposure and the health problems they encounter (Afolabi et al., 2021). Due to the risky habits indicated above, these employees are subject to several occupational risks, including PAHs and their metabolites. PAHs and their metabolites are environmental pollutants that have numerous health risks for humans upon exposure (Teixeira et al., 2017). The direct exposure of artisanal auto-mechanical workers to polycyclic aromatic hydrocarbons and their metabolites may cause toxicity and increase their chances of developing skin, lung, urinary tract, and other cancers (Teixeira et al., 2017).

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants made up of two or more fused benzene rings (León-martínez et al., 2021). Although they may occur naturally (forest fires and volcanic eruptions, for example), the main anthropogenic activities that produce these chemicals include industrial processes, the burning of fossil fuels, biomass cooking and vehicle emissions (León-martínez et al., 2021). The two primary anthropogenic sources of emissions are incomplete combustion of organic material and agricultural waste. Human exposure to PAHs may occur by inhalation, cutaneous exposure, or eating

tainted food (León-martínez et al., 2021). Exposure to PAHs has been associated with a number of health hazards, including growth retardation, low birth weight, teratogenicity, low IQ, skin allergies, and endocrine disruption effects that affect both male and female reproduction system or capability (Abdel-Shafy & Mansour, 2016). The US Agency for Toxic Substances and Disease Registry (ATSDR) states that not all PAHs have the same negative effects on health. The following 16 PAHs are considered EPA-prioritized carcinogenic compounds: dibenzo(a,h) anthracene, fluorine, indeno(1,2,3-c,d) pyrene, phenanthrene, and pyrene acenaphthene, acenaphthylene, anthracene, benzo(a) anthracene, benzo(a) pyrene, benzo(e) pyrene, benzo(b) fluoranthene, benzo(g,h, i) perylene, benzo(j) fluoranthene, benzo(k) fluoranthene, chrysene (León-martínez et al., 2021).

Benzo[a]pyrene has been identified by the International Agency for Research on Cancer (IARC) as a distinct carcinogen (category 1) (IARC, 2016). Lung cancer (2.21million cases) was mentioned as the second most frequently diagnosed disease and recorded the highest frequent death issues among cancers (1.80 million deaths) globally in a recent WHO report on an increase in cancer incidences (IARC, 2020) (Figure 1).

Despite the numerous health risks and dangers that PAHs and their metabolites pose to artisanal workers, in relation to this work, there is no known study that has been conducted in Sub-Saharan Africa to determine how they affect artisanal auto-mechanical workers. Therefore, the need to conduct a study to determine the health risks associated with urinary PAHs and its metabolites upon

exposure to PAHs among artisanal auto-mechanical workers from their major mechanical workshops in Cape Coast, Ghana.

Statement of the Problem

Artisanal auto-mechanical workers are exposed to several risks at their workshops (e.g., PAHs), unfortunately they seem to have been neglected by the public and stakeholders, as far as their health is concerned. The artisanal auto-mechanical workers exhibit poor health and safety culture in their work. Cancer cases are on the rise, aside from other associated diseases, and these PAHs and their metabolites are known to be carcinogenic and mutagenic to humans, thus to artisanal auto-mechanical workers (Fadel et al., 2022). Globally, cancer is the main cause of death; the 2022 GLOBOCAN report on cancer morbidity and mortality estimates that 19.3 million people have cancer worldwide, accounting for approximately 10 million deaths (Chhikara et al., 2023; Tuck et al., 2023).

IARC (2022) classified PAHs and their metabolites as carcinogenic, mutagenic, endocrine disruptors, and teratogenic to humans upon their exposure. Also, prolonged exposure to PAH mixes has been linked to an increased risk of bladder, gastrointestinal, lung, and skin malignancies. (Ravanbakhsh et al., 2023). The direct exposure to these hazardous chemicals by the working class or labour force in Ghana may also be a factor in the country's rising cancer and non-cancer-related incidences, and these ailments may also have a socio-economic impact on Ghana’s economy. As far as this work is concerned and to the best of our knowledge, no known research has been reported in literature for Sub-Saharan

Africa to determine the effects of PAH exposure on artisanal auto-mechanical workers despite all the health risks and dangers they pose to humans. Thus, research has to be done to evaluate the health hazards that come with exposure to PAHs among Ghana's artisanal auto-mechanical workers.

Purpose of the Study

The purpose of this research is to conduct a health risk assessment of urinary-PAHs and their metabolites among artisanal auto-mechanical workers from the Siwdu auto-mechanical workshop in Cape Coast Metropolis, Ghana.

Specific Objectives for the Study

The specific objectives are to:

1. determine the level of perception of artisanal auto-mechanical workers towards health and safety at work.
2. determine the presence and amount of PAHs and their metabolites in the urine samples of artisanal auto-mechanical workers.
3. conduct a health risk assessment using the levels of PAHs and their metabolites.

Research Questions

1. Are the artisanal auto-mechanical workers really exposed to PAHs?

2. What are the levels of perception of health and safety among these artisans?
3. Do the artisanal auto-mechanical workers have any health risks from exposure to parent PAH levels?

Hypothesis

H_1: The concentrations of PAHs and their metabolites in urine samples of artisanal auto-mechanical workers from the Siwdu auto-mechanical workshops in Cape Coast Metropolis, Ghana, may be high compared to the standard acceptable limits of the NIOSH and PHG.

Significance of the Study

The research will be the first of its kind in Ghana and will create awareness of the occupational health risks associated with auto-mechanical works. This may urge artisanal auto-mechanical workers to take their health and safety at the workplace seriously. Again, the study may cause other stakeholders, like the Occupational Health and Safety Board, to come to the aid of the artisanal auto-mechanical workers to safe-guard their health by formulating health and safety protocols and policies for them and also ensure regular surveillance.

Delimitation

The study focused on the samples from artisanal auto-mechanical workers from the Siwdu auto-mechanical workshops in Cape Coast Metropolis, Ghana.

Limitation

Due to the unwillingness of some of the study participants, some sample sizes were not large enough for the analysis to represent the entire population.

Organisation of the Study

There are five chapters in this thesis. The study's background is covered in Chapter 1, along with an explanation of the health risks related to the exposure of artisanal auto-mechanical workers to PAHs and their metabolites in their workshops. The real issue with this research is stated in the problem statement found in Chapter 1: the health risks on artisanal auto- mechanical workers in Cape Coast Metropolis, Ghana, upon their exposure to PAHs and its metabolites at their workshops through inhalation, ingestion, and dermal contacts. Chapter 1 also covers other topics, including the study's importance, particular goals, and overall goal.

The literature review is covered in Chapter 2. In Chapter 2, several concepts such as: sources, pathways of exposure, and health hazards associated with PAHs and their metabolites in humans were covered. Both the HPLC-UV/RF equipment and the SPE methodology, which is the extraction analysis method, were evaluated.

This study's third chapter, looked at the research techniques used in this study. A sampling technique such as purposive sampling was used for artisanal auto-mechanical workers from major, selected workshops in Cape Coast. The

study population, areas, sampling procedure, data collection, data processing, and analysis were discussed.

The study's fourth chapter summarizes the findings and discusses the amounts of urinary PAHs and their metabolites in urine samples from artisanal auto-mechanical workers from the Siwdu workshop in the Cape Coast Metropolis. There was also discussion of the findings of the health risk assessment related to PAHs and their metabolites among different artisanal mechanical workers.

Summaries, suggestions, and conclusions are included in Chapter 5. A broad conclusion based on the primary purpose of the research was reached after findings based on its goals were made. Finally, some more research and institutional initiatives were suggested.

CHAPTER TWO

LITERATURE REVIEW

Introduction

This chapter examines some of the contaminants that are discharged at artisanal auto-mechanical workshops, such as PAHs and their metabolites, and the risks they pose to the artisanal auto-mechanical workers in Cape Coast Metropolis, Ghana. In addition, analytical methods (solid phase extraction (SPE) approach), HPLC-UV/RF instruments, and the health and safety aspects of artisanal auto-mechanical workers will also be reviewed.

Artisanal Mechanical Workers and their Poor Safety Culture

Spray painters, panel beaters, auto electricians, and mechanics all fall under the category of artisanal auto-mechanical employees. Their professions expose them to a range of dangers, much as many other occupational groups. An estimated 5000 people lose their lives to work-related accidents or diseases every day; there are an estimated 270 million occupational accidents (both fatal and non-fatal); 160 million incidents of occupational diseases occur; in addition, 340,000 workers worldwide are killed by hazardous substances like PAHs each year (ILO, 2022). Poor safety culture refers to a workplace environment where safety is not prioritized, risks are ignored, accidents and near-misses are frequent, employees feel uncomfortable reporting hazards and management shows little commitment to safety. Suction of gasoline is one of the dangerous practices that

Artisanal Auto-mechanical Workers in Ghana engage in, and gasoline-based hand and car part washing is another risky practice (Johnson & Bassey, 2016).

Numerous artisanal auto-mechanical workers engage in a number of other dangerous behaviours as part of their work, including applying diesel to injured body parts, working, eating, and sleeping in unhygienic settings, and not wearing personal protective equipment (PPE) like overcoats, gloves, and safety boots. These practices are known as poor safety culture (Afolabi et al., 2021). The direct exposure of artisanal auto-mechanical workers to phthalates and polycyclic aromatic hydrocarbons causes toxicity and increases their chances of developing skin, lung, urinary tract, and other cancers (Teixeira et al., 2017). In Ghana, a sizable portion of people who practice vocational trades are employed in the artisanal mechanical repair sector (Johnson & Bassey, 2016). Their occupation exposes them to a number of risks that increase their likelihood of developing health problems, some of which could be serious and incapacitating.

Health and Safety of Auto-mechanical Workers on the use of PPE

Many employments are created by the artisanal auto-mechanical industry, which is also vital to the growth and success of most countries' economies. Nonetheless, employment security and safety are often inadequate (Balkhyour et al., 2018). Artisanal auto-mechanical shops are characterized by their autonomous operation and ownership, tight supervision by masters who provide the majority of the operational capital, and composition of masters and apprentices who serve as the primary decision-makers (Balkhyour et al., 2018). Employees in the

artisanal auto-mechanical business are particularly susceptible since they are often exposed to a variety of physical, chemical, and unintentional risks. Their vulnerability is mostly brought on by a lack of education, insufficient information, ignorance of OSH risks, and a refusal to wear or get personal protective equipment (PPE) (Apreko et al., 2015). Workers in the artisan auto-mechanical sector are the least aware of the risks to their health and safety that arise from the materials, activities, and exposures they encounter at work (Ahmad et al., 2017). Studies have shown that these labourers are not well-versed in the correct use of personal protective equipment (PPE) and that there is a very low rate of PPE use in artisanal auto-mechanical industries, especially among Ghanaian artisanal auto-mechanical workers in their workshops (Afolabi et al., 2021).

Additionally, artisanal auto-workers with low levels of education may not utilize personal protective equipment (PPE) because they are unaware of its importance. Even yet, PPEs are only employed as a last resort to reduce occupational dangers when management and engineering controls have already been implemented (Monney et al., 2014). For workers in artisanal auto-mechanical industries where traditional programs and hazard management methods are still difficult to apply, personal protective equipment (PPE) is the most effective form of protection. When personal protective equipment (PPE) is not used, workers may be subjected to a variety of dangers and hazards that might have a major negative impact on their health (Ahmad et al., 2016).

Personal protective equipment is crucial in lowering workplace accidents and injuries, which may otherwise result in severe discomfort for workers as well

as monetary losses from missed work, insurance and medical claims, and absence from workshops. Artisanal auto-mechanical workers often operate in unsanitary circumstances, are regularly exposed to fuels, and are not always wearing personal protective equipment (PPE) or other types of protection. Examples of these industries include welding, car repair, and body paint businesses. These variables may put artisans', especially those working in Ghanaian mechanical workshops, at higher risk for respiratory ailments, skin cancer, and lung cancer (Kamal, Cincinelli, Martellini, Palchetti, Malik, et al., 2016).

According to Ahmad et al., 2016, among the many risks associated with artisans' labour in the workshops are objects that fall or fly, sharp objects that pierce, dust, fumes from the exhaust, chemical odours, intense heat, and noise. The use of personal protective equipment (PPE) is a crucial aspect of workplace health and safety protocols, as it guarantees the general well-being and security of employees (Apreko et al., 2015). When using the proper PPE, workers' health may be effectively protected against hazards to their well-being (Apreko et al., 2015).

All appropriate measures must be taken to safeguard workers' health and safety against risks and hazards at work, according to regulations enforced by the Occupational Safety and Health Administration (OSHA). Depending on the kind and degree of hazards, OSHA recommends the use of a variety of control strategies (elimination, substitution, engineering, administrative, and personal protective equipment) to eliminate or restrict them as much as is practical (ILO, 2022). When administrative and technological controls fail to adequately protect

artisans, workers should be outfitted with personal protective equipment (PPE) and trained in its use by stakeholders to guarantee their safety in the workshops, particularly for Ghanaian artisanal auto-mechanical workers.

Polycyclic Aromatic Hydrocarbons (PAHs)

Two or more fused aromatic rings make up the large family of chemical compounds known as polycyclic aromatic hydrocarbons (Djinovic et al., 2008b; Kim et al., 2013; Tongo et al., 2017). According to Djinovic et al.(2008a), PAHs are mildly volatile and soluble in water; their solubility declines as the number of aromatic rings rises. According to Abdel-Shafy & Mansou (2016), PAHs are lipophilic and readily dissolve in organic solvents. All PAHs have high melting and boiling temperatures and are solid substances. Although chemically inert, PAHs are adsorbed at the dust's surface, and they might attach themselves to particulate matter. Persistent organic pollutants (POPs) are the category to which PAHs belong (Guo et al., 2019). These are organic pollutants that have the capacity to harm the ecosystem, are resistant to degradation, and may linger in the environment for extended periods of time (Guo et al., 2019). When introduced into the environment, because of their greater chemical stability and resistance to biodegradation, PAHs have a longer half-life. (El-shahawi et al., 2010). According to reports by Manisalidis et al. (2020), Roberts (2021), and Sun et al.(2021), exposure of the human body to PAH-containing environments may result in a number of deadly illnesses, including lung and skin cancer. Because of their

ability to cause cancer and mutation in animals, PAHs have been the subject of substantial investigation (Anyakora & Coker, 2006).

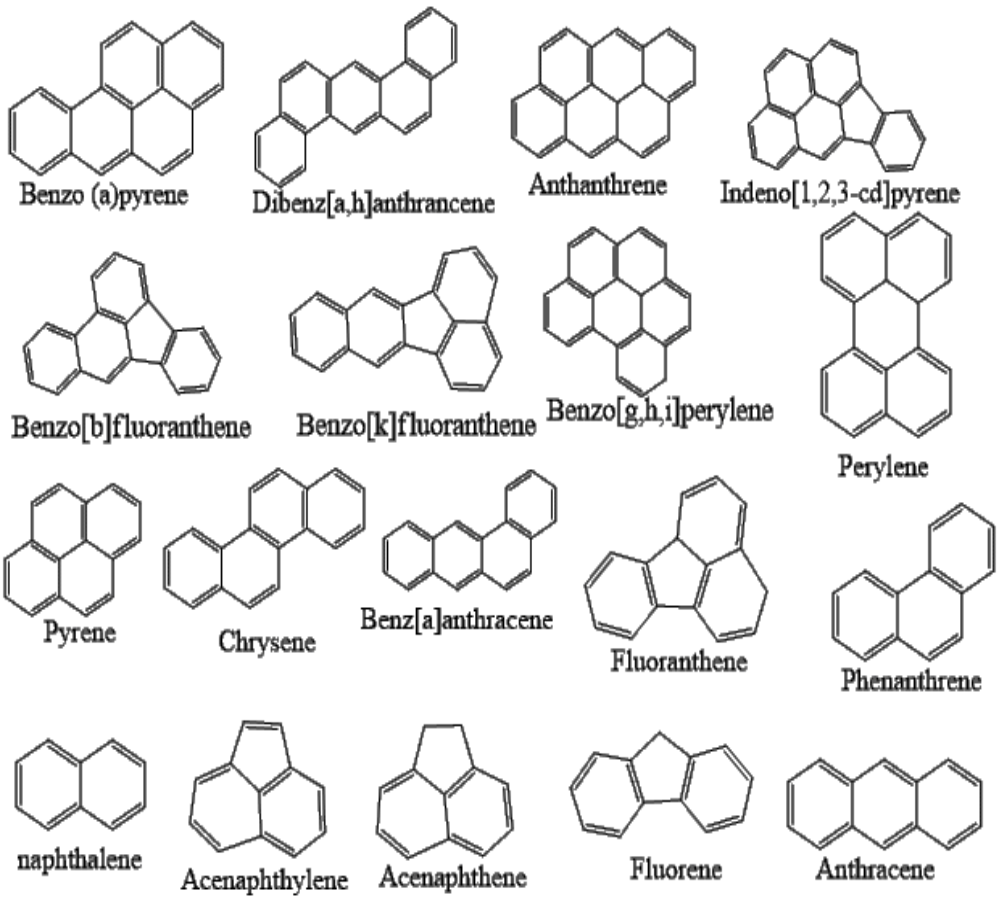


Figure 1: Molecular Structures of the 18 Prioritized PAHs
(Hussain et al., 2018)

Classes of PAHs

Based on their structural makeup, PAHs may be broadly classified into two groups: those that have a "bay region" and those that do not. (Kumar et al., 2016). According to Kumar et al. (2016), the structure, their metabolic activity, and their toxicity inside the body are significantly correlated. An example compares the less carcinogenic PAH anthracene with the dangerous PAH Dibenzo

(a, h) Anthracene (Dib(ah)A) with two bay regions (Abdel-Shafy & Mansour, 2016). Low-molecular-weight PAHs are light PAHs, which are defined as having up to four benzene rings fused (Kumar et al., 2016). Heavy PAHs are defined as compounds with four or more benzene rings. As stated by Abdel-Shafy and Mansour (2016), compared to light PAHs, larger PAHs are both more stable and harmful. Heavy PAHs are both more dangerous and stable than light PAHs in reference to (Figure 1).

Environmental Sources of PAHs

According to Wang et al. (2013), polycyclic aromatic hydrocarbons, often known as polyarenes, are ubiquitous environmental contaminants that may have natural or human origins. Anthropogenic sources of PAHs include wood, creosote discharges, burning of fossil fuels (coal, oil, and natural gas), fuel oil or gasoline spills, and natural seeps (Dowaidar et al., 2007). According to Hussain et al. (2018), the primary sources of PAHs are incomplete combustion of coal, oil, and gasoline; they may also originate from wood preservation facilities or petrochemical sector operations. They naturally arise in the environment during events such as spontaneous fires and thermal geological processes. In addition, PAHs are found naturally in peat, lignite, coal, and crude oil. Biogenic PAHs may originate from forest fires and volcanoes (Sun et al., 2021).

Because PAHs are produced in all processes that involve incomplete combustion of organic molecules, human activity is a significant source of PAHs in the environment (Sun et al., 2021). The durability, hydrophobicity,

bioaccumulation, and carcinogenicity of various individual polyarenes are what make these chemicals hazardous (Dowaidar et al., 2007; Guo et al., 2019; Sun et al., 2021). Environmental chemistry continues to be interested in PAHs due to their widespread distribution and frequent detection in sediments and soils. Guo et al. (2019) and Sun et al. (2021) asserted that one kind of persistent organic pollutant (POP) that is common in both regional and global cycles is PAHs. According to Aryee (2016), PAHs are primarily released into the atmosphere, where particles absorb them and may subsequently travel great distances before being discovered. Accordingly, PAHs are pervasive environmental contaminants that are typically present in high concentrations close to emission sources (Yebra-Pimentel et al., 2015).

Sources of PAHs and Exposure Routes in Human

When exposed to polycyclic aromatic hydrocarbons, people can suffer negative health effects (Ding et al., 2013). As a result, numerous studies have been done to determine how humans are exposed to it. People are primarily exposed to PAHs through their diets rather than by drinking water or the air (Ding et al., 2013). Regardless of whether they are inside or outside at their home or place of work, humans are exposed to PAH vapor or PAHs contained in dust and other particulate matter in ambient air (Kumar et al., 2016). Cigarette smoke, car exhaust, home heating, agricultural waste, waste incineration, and emissions from industrial activities are all sources of PAH exposure for humans (Yebra-Pimentel et al., 2015).

According to Kumar et al. (2016), exposure to polluted soil or dust can result in cutaneous (skin) exposure, ingestion, or inhalation of PAHs. Living or working close to a business that recycles used mineral-based crankcase oil puts them at risk of breathing in nearby fumes or coming into contact with polluted soil, sludge, or sediment (Xia et al., 2013).

Toxicity of PAHs in Humans

Human exposure to PAHs has been associated with an increased risk of developing cancer in a variety of organs, including the lung, bladder, stomach, and skin (especially the scrotum). This risk varies depending on the kind of PAH and the exposure route (Abdel-Shafy & Mansour, 2016; Roberts, 2021). Lung cancer risk has been associated with exposure to PAHs in a variety of occupational contexts, including coke manufacture, artisanal mechanical shops, coal gasification, paving and roofing, and many occupations involving exhaust emissions (Rengarajan et al., 2015). As stated by Rengarajan et al. (2015), PAHs have varying degrees of toxicity depending on their structure, from harmless isomers to very hazardous ones.

PAHs are recognized for their mutagenic, teratogenic, and carcinogenic qualities to humans. IARC has categorized PAHs according to their carcinogenicity as follows: for class 3 [Anthracene, Benzo(ghi)perylene, Fluoranthene, Fluorene, Phenanthrene, pyrene, Acenaphthene], class 2A [Dibenz(a,h)anthracene], class 2B [Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Naphthalene, Indeno(1,2,3-cd)pyrene, 1-

methylnaphthalene] and for class 1 [benzo(a)pyrene] (IARC, 2016). Benzo[a]pyrene (BaP) is the most studied polycyclic aromatic hydrocarbon (PAH) and is also often used as a marker for carcinogenic PAH levels in health risk assessments. (Rengarajan et al., 2015; Sun et al., 2021).

Health Effects of PAHs

The effects of PAHs as an environmental contaminant on human health have mostly been split into two categories: acute effects and chronic effects, depending on the exposure amount (Manisalidis et al., 2020; Sun et al., 2021). According to Kim et al. (2013) and Rengarajan et al. (2015), acute health impacts of occupational exposure to PAH chemicals include skin irritation, eye irritation, nausea, vomiting, inflammation, diarrhoea, and disorientation. Long-term exposure to PAHs may also have chronic impacts such as infertility and miscarriages (Ramesh et al., 2011), atherosclerosis, cataracts (Abdel-Shafy & Mansour, 2016; Adjei et al., 2021), cardiopulmonary mortality, lung, skin, bladder, liver, and other malignancies, breathing issues, asthma-like symptoms, and kidney and liver damage (such as jaundice) (Markiewicz et al., 2020; Sun et al., 2021).

Biomonitoring of PAHs

Tracking the internal dosage of PAHs may also be accomplished by identifying the exposure markers in the blood and urine. Measuring PAH metabolites in urine and intermediate indicators of impact (such as DNA and

haemoglobin adducts) are two instances of analytes used as biomarkers of PAH exposure (Klotz, 2021). For the most precise findings, urinary metabolites are employed. The primary purpose of the metabolites of phenanthrene and pyrene in the literature is to describe the internal occupational exposure of people to PAHs (Klotz, 2021).

Mammals use 1-hydroxypyrene as a key metabolite in the metabolism of pyrene (Hansen et al., 2008). The majority of 1-hydroxypyrene in people combines to generate the equivalent 1-hydroxypyrene glucuronide. During pyrene metabolism, 1,6- and 1,8-dihydroxypyrene may be produced by further oxidizing 1-hydroxypyrene enzymatically. Human urine may also include these metabolites, which are in a steady state with the corresponding pyrene quinones (Taylor et al., 2008). It may be shown that 1,8-dihydroxypyrene is eliminated in the general population at concentrations equal to or greater than those of 1-hydroxypyrene (Figure 2). Extremely high levels of PAH exposure at work cause pyrene metabolism to shift in favor of 1-hydroxypyrene (Förster et al., 2024).

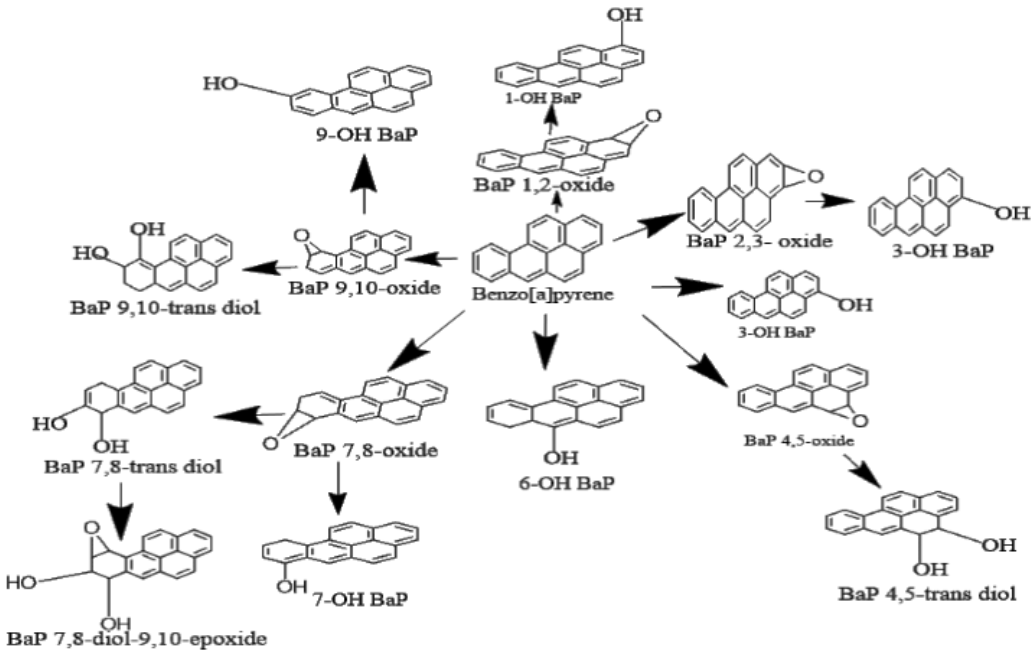


Figure 2: Metabolism Profile of Benzo(a)Pyrene to its Metabolites (Zhong et al., 2011)

Additionally, studies on human urine have examined the metabolites of phenanthrene, 1, 2, 3, and 9-hydroxyphenanthrene. Furthermore, it was possible to find phenanthrene tetrol and dihydrodiols (Taylor et al., 2008). While the removal of the non-carcinogenic phenanthrene's mono-hydroxylated metabolites signifies a detoxification process, the synthesis of phenanthrene quinone (Figure 3) can be thought of as a stand-in for the metabolic activation of PAHs because the enzyme reactions occur similarly to those with carcinogenic PAHs like benzo[a]pyrene (Zhong et al., 2011).

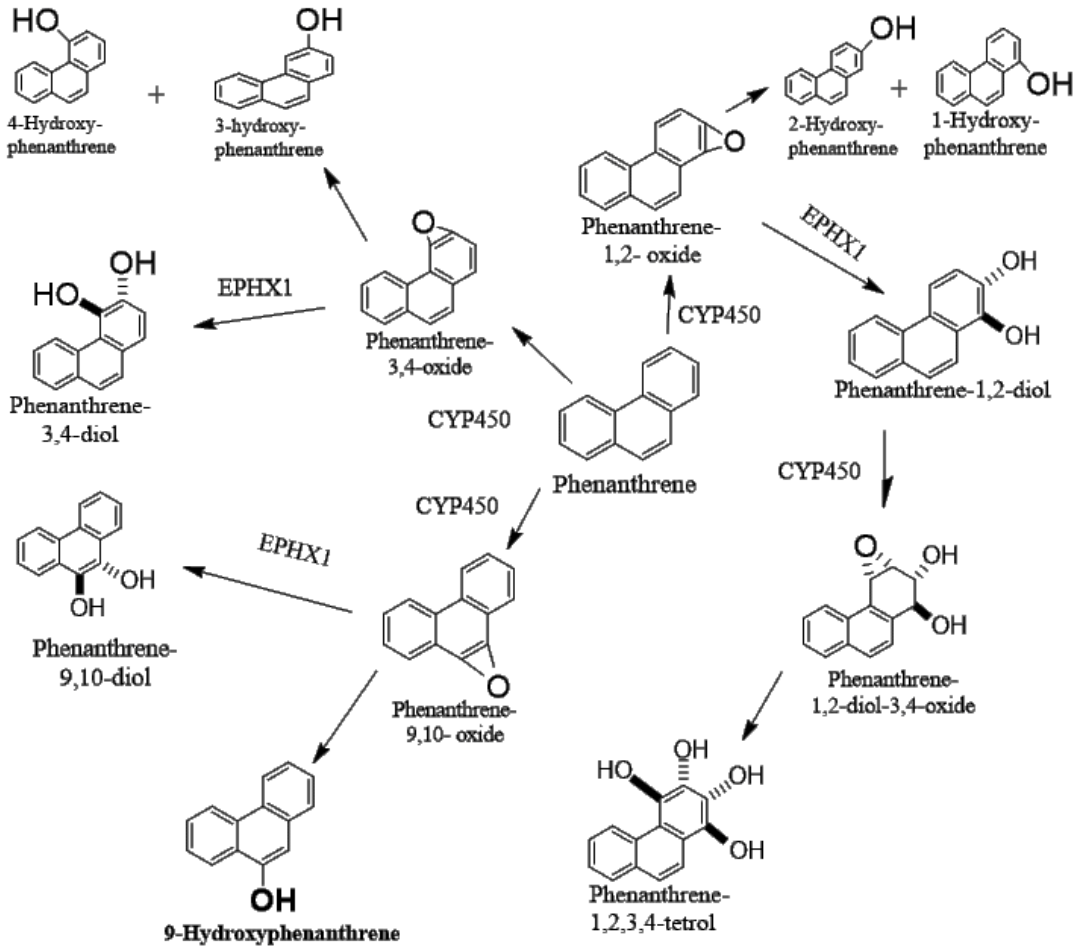


Figure 3: Metabolism of Phenanthrene to its Metabolite (Taylor et al., 2008)

The hydroxylated metabolites of benzo[a]pyrene, benzo[a]anthracene, chrysene, and naphthalene were analyzed to ascertain exposure to carcinogenic PAHs. Three-hydroxybenzo[a]pyrene is a metabolite of benzo[a]pyrene that has been found in the urine of both the general public and those who have been exposed to PAHs at work (Barbeau et al., 2011; Leroyer et al., 2010; Zhong et al., 2011). Dihydroxy-9,10-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene is the ultimate carcinogen, and benzo[a]pyrene tetrols are the metabolic by-products of this compound. Benzo[a]pyrene tetrols were found in the urine of non-smokers as well

as in those who were exposed to PAHs at work, using sensitive GC-MS techniques (Zhong et al., 2011).

Human Health Risk Assessment

As stated by the WHO (World Health Organization, 2021), the definition of human health risk assessment is the description of the possible negative effects that environmental threats may have on human health. According to the Edwin & Furtaw (2001), it is also referred to as the process of identifying the sort and probability of adverse health outcomes in individuals who may be exposed to chemicals in polluted environmental media at some point in the future or in the present. This method combines science, engineering, and statistics to quantify risk, find likely exposure pathways, and finally provide a number that represents the possible danger (WHO, 2021).

Hazard Identification

Hazard identification determines whether or not a chemical is incidentally linked to a certain health consequence (Chartres et al., 2019). It intentionally assesses the strength of evidence for harmful effects on people by analysing all available toxicity and mechanism of action data (Chartres et al., 2019). Two key concerns about danger identification are addressed.

1. Whether a substance might be harmful to people's health
2. In what situations might a recognized danger be expressed? Many outcomes are often seen after being exposed to a particular chemical. With

an increasing dosage, the crucial effect, typically the first notable side effect, is identified (Chartres et al., 2019).

Dose-Response

Dose-response analysis establishes the relationship between the level of exposure and the probability of the relevant health outcomes. It is a method for drawing a link between the administration or receipt of an agent's dosage and the development of a harmful health consequence (OECD, 2018). Organ-specific, neurological, behavioural, carcinogenic, reproductive, immunological, non-genotoxic, and developmental impacts are among the most common toxic consequences. It is thought that there is a threshold, or concentration, beyond which harmful effects do not occur. It is believed that individuals may suffer harm at any exposure level due to additional harmful consequences, often known as non-threshold effects. The non-threshold assumption is frequently used in the context of genotoxic carcinogenesis and mutagenesis (USEPA, 1989).

Exposure Assessment

Similar to the hazard detection and dose-response assessment phases, the exposure assessment analyses the kind and intensity of chemical substance interactions that are seen or anticipated in a variety of contexts (WHO, 2021). The cumulative volume of a dangerous agent that enters the body by oral, inhalation, or dermal modes of exposure determines the risk of the toxic agent in an exposure assessment (WHO, 2021). Assess the amount to which populations of people or

the environment (air, water, and soil) may be exposed. Depending on the evaluation's goal, the numerical performance of an exposure assessment might represent an estimate of the degree, pace, duration, or frequency of contact exposure or dosage (OECD, 2018).

In exposure evaluation, three primary exposure pathways oral, cutaneous, and respiratory are identified (OECD, 2018). An estimate of the dosage is often included in the result of risk assessments that are based on dose-response relationships. It is critical to stress that the toxicological outcome of a given exposure is determined by the internal dosage rather than the external exposure level (WHO, 2021). The phrase "worst-case exposure" indicates "the maximum possible exposure, or where everything that can plausibly happen to maximize exposure happens (Chartres et al., 2019)".

General Overview of Solid-Phase Extraction (SPE)

Solid-phase extraction (SPE) is a sample preparation method that finds widespread use across several application industries due to its numerous benefits over other traditional processes (Biziuk, 2006). SPE was developed as a replacement for liquid/liquid extraction and addressed a number of drawbacks, including the need for a significant amount of solvent, lengthy operating times and procedure stages, error-proneness and high expense (Biziuk, 2006). Additionally, SPE may be used with other analytical techniques and optional sample preparation methods (Semih & Kartal, 2016). The SPE technique is a helpful tool for a wide range of applications because of its versatility. The basic

techniques used in this extraction process include isolation, concentration, purification, and cleanup (Semih & Kartal, 2016).

According to Taylor et al. (2012), the partitioning of the analyte between a solid phase, typically a sorbent within a column and a liquid phase, either the sample matrix or a solvent containing analytes, is the basis of solid-phase extraction. Because of the distribution caused by molecule adsorption or penetration, the analyte is kept on a solid surface in line with the distribution coefficient (Taylor et al., 2012). By giving the analyte a more hospitable environment than solid-phase, it is possible to collect analytes from the SPE system. The analytes' entry into the liquid phase and escape from the SPE system may be used for additional advanced techniques, including a supercritical gas stream, to achieve the desorption of compounds with favoured liquids (Taylor et al., 2012). One or more washing or rinsing procedures can be used to get rid of unwanted chemicals that were kept alongside the analytes between the retention and elution phases or in the solid phase or eluted phase after this elution step (Semih & Kartal, 2016).

SPE sorbents typically come in the form of cartridges, discs, pipettes, or syringe barrels, with particle sizes ranging from 10 to 60 microns. There are many different sorbent types, and the decision may be made in light of the food matrix, relevant analytes, and substances that interfere (Semih & Kartal, 2016). The extraction of related analytes from samples involves a variety of methods that are based on various contacts, such as hydrogen bonds, dipole-dipole interactions,

van der Waals contacts, or electrostatic (ion exchange) interactions (Semih & Kartal, 2016).

According to Semih and Kartal (2016), in normal-phase, the polar functional groups of the analyte interact with polar groups on the sorbent surface to produce a polar stationary phase and retention in SPE. Van der Waals forces are the main method of interaction between the polar or moderately polar mobile phase and the nonpolar stationary phase in the reversed-phase, which is often used with aqueous materials (Semih & Kartal, 2016). For substances that are charged in a solution, ion exchange SPE can be employed. Finally, mixed-mode SPE makes use of two different functional groups on the same sorbent. Isolation is a common example of this kind of SPE as it involves both cation exchange and reversed-phase (Taylor et al., 2012). Because of its adaptability to alteration and stability, silica is the most popular sorbent type (along with alumina, magnesium silicate, and graphitized carbon) (Taylor et al., 2012). Silica bound with nonpolar chains like C18 (octadecyl), C8 (octyl) or sorbents often include cyclohexyl groups or polar chains such as hydroxyl, cyano, and diol groups.

Furthermore, polymeric resins, Florisil, polar sorbents (alumina, charcoal), and carboxylic acid or amino groups attached to silica for ionic functional groups are examples of the second kind of support materials (Semih & Kartal, 2016; Taylor et al., 2012). Due to special needs for improving specificity, several enhanced extraction media, such as affinity columns, restricted access media (RAM), or molecularly imprinted polymers (MIPs), are available to capture particular chemicals (Semih & Kartal, 2016).

Solid-phase extraction is a useful technique for applications involving isolation and separation. Additionally, one of the objectives in its field of application is concentration. In a tiny volume of solvent, the analyte exits the pre-treated column or cartridge that has been filled with the necessary sorbent (Semih & Kartal, 2016). The major reasons for using the SPE method for the concentration approach are the relatively small surface of the solid phase, the high volume of sample that may allow complete retention, and the use of volatile organic solvents (Biziuk, 2006). SPE may also be a useful technique for clean-up, which is necessary to remove contaminants that interfere with chromatographic analysis and take distinct signals (Semih & Kartal, 2016).

SPE is frequently used to extract the following substances from biological fluids: pharmaceutical chemicals and metabolites, drugs of abuse, environmental contaminants in drinking water and wastewater, and more. Antibiotics and pesticides in agricultural and food systems Protein and peptide desalination, lipid fractionation, and water- and fat-soluble vitamins are all examples of this process (Semih & Kartal, 2016). When processing water containing suspended solids, such as surface water or wastewater, packed SPE cartridge limitations include limited flow rates and blockage of the top frit (Biziuk, 2006).

General Overview of High-Performance Liquid Chromatography (HPLC)

Introduction on HPLC

High-performance liquid chromatography (HPLC) is a chromatographic technique used in analytical, biochemical, and industrial chemistry fields to separate mixtures of compounds (Sadapha & Dhamak, 2022). The main applications of HPLC are in the identification, measurement, and purification of particular chemical mixtures. Most drugs and other chemicals may be examined using the HPLC method because of its numerous benefits, which include speed, specificity, accuracy, precision, and ease of automation (Sadapha & Dhamak, 2022). The phrase chromatography originated from the Greek words chroma, which means color, and graphene, which means to write. Russian botanist Mikhail Tsvet coined the term chromatography in 1930.

Pharmaceutical products have long been analysed using high-performance liquid chromatography (HPLC), which has shown to be a more accurate analytical approach, both quantitatively and subjectively (Khatmode et al., 2022). The fundamental concept involves filling a porous material column with a sample compound (stationary phase) and forcing a liquid (mobile phase) through the column at high pressure (Shine & Janardhanan, 2019). Qualitative analysis provides information on the identity of the sample and whether or not certain components are present. Strong information is provided by a quantitative study, such as the relative quantity of one or more components (Khatmode et al., 2022).

Principle of HPLC

The concept of high-performance liquid chromatography (HPLC) involves injecting the sample solution into a porous material column (known as the stationary phase) and then pumping the liquid phase (known as the mobile phase) through the column at a higher pressure (Khatmode et al., 2022). The solute is adsorbed on the stationary phase according to its affinity for the stationary phase, which is the separation principle that is used (Thammana, 2016).

Chromatographic Techniques

The chromatographic techniques include the following:

Size Exclusion Chromatography, Ion Exchange Chromatography, Normal Phase Chromatography, Reverse-phase Chromatography, Bio Affinity, and Mode of Separation Chromatography.

1. Normal phase chromatography: This kind of chromatography uses a non-polar mobile phase together with a stationary polar phase. There, the combination of components that need to be separated and the analytes have a longer polar stationary phase compared to those that are less polar. Analytes are separated using this approach according to their polarity (Khatmode et al., 2022).

2. Reverse-phase chromatography: An aqueous, somewhat polar mobile phase and a non-polar stationary phase make up the Reversed-Phase HPLC, also known as RPC. There, the nonpolar solvents lingered for a longer period, whereas the polar solvents eluted first (Thammana, 2016).

3. Size Exclusion Chromatography: Also referred to as gel filtration chromatography, size exclusion chromatography (SEC) uses gels to separate particles primarily according to size. Particles are sorted based on molecular size and the columns are filled with materials having a regulated pore size. Stearic and diffusion effects are the separation mechanisms. Additionally, it may be used to determine the amino acid composition of proteins as well as their tertiary and quaternary structures (Thammana, 2016).

4. Ion Exchange Chromatography: Ion-exchange chromatography, or the reversible interchange of functional groups, is the separation principle. Retention in ion exchange chromatography is determined by the attraction between charged sites attached to the stationary phase and solute ions. The only samples for which this method works well are ionic or ionizable ones (Kumar et al., 2018).

5. Bio Affinity: The unique, reversible interaction between proteins and ligands provides the basis for the separation. The proteins that have interacted with the ligands that are attached to the column are retained. Common molecular forces, including hydrogen bonds, dipole-dipole interactions, van der Waals interactions, and electrostatic interactions, all play a role in the development of these complexes (Kumar et al., 2018).

HPLC Mode of Separation

Based on the makeup of the eluent, HPLC has two modalities of separation: I) Isocratic elution: This method of separation relies on a constant

eluent composition, which maintains both the column's equilibrium conditions and the compounds' real velocities as they pass through it (Khatmode et al., 2022)

II) Gradient elution: This method of separation uses a variable composition of eluent. This method greatly boosts a system's separation power mostly by boosting perceived efficiency (a reduction in peak width). The rate of the eluent's composition determines the peak's breadth (Khatmode et al., 2022).

Instrumentation of HPLC

The HPLC instrumentation involves an injector, column, detector, pump, integrator and display system.

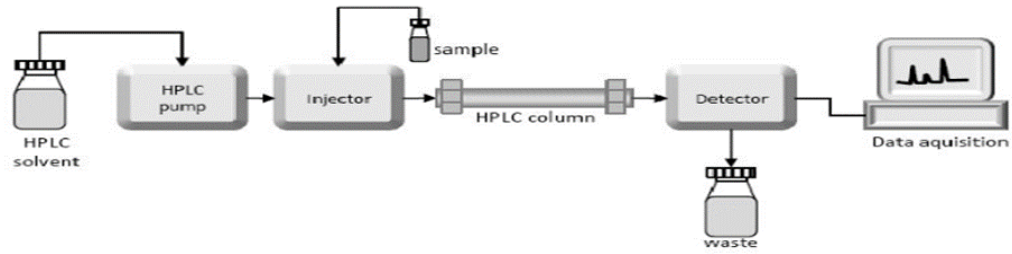


Figure 4: HPLC Instrumentation Diagram
(Rejakumar et al., 2022)

Solvent reservoir: Liquid components that are both polar and non-polar are combined to form the mobile phase, also known as the solvent, in HPLC. The choice of polar and non-polar solvents will depend on the sample's makeup.

Pump: The mobile phase is forced into the column by the pump, which also draws it out of the solvent reservoir and sends it to the detector. The pump's operating pressure is 42000 KPa. The dimensions of the column, the size of the particles, the flow rate, and the makeup of the mobile phase all affect this operating pressure (Rejakumar et al., 2022).

Sample Injector: An HPLC framework injector should provide a high-reproducibility, high-pressure infusion of the fluid specimen within the range of 0.1 mL to 100 mL of volume (up to 4000 psi) (Rejakumar et al., 2022).

Columns: Stainless steel that has been cleaned is usually used to make columns, which range in length from 50 to 300 mm and have an inward spacing of 2 to 5 mm. Typically, a stationary phase consisting of molecules ranging in size from 3 μm to 10 μm is placed into them. The many kinds of columns are:

A guard column is added before the analytical column in order to prolong its life. These are achieved by eliminating from the solvents any particles and impurities as well as sample components that bond permanently to the stationary phase.

The core of high-performance liquid chromatography is analytical columns. The length of liquid chromatographic columns varies from 10 to 30 cm. Typically, the columns are straight, with the ability to join two or more columns together to enhance length when necessary. Liquid columns usually have an inner diameter of 4 to 10 mm, while packing particles typically have a size of 5 or 10 m. Right now, the most often used column is 25 cm in length, has an inner diameter of 4.6 mm, and is filled with 5 mm particles. These columns hold between 40,000 and 60,000 plates per meter (Rejakumar et al., 2022).

Detector: Analytes elute from the chromatographic column and are identified by the HPLC detector, which is positioned toward the end of the column. The following are the detectors that are often used:

Ultraviolet Visible detector: It is the HPLC detector that is most often used. The majority of organic molecules absorb light between 400 and 750 nm in the visible and UV spectrums (190-400 nm). It is based on Beer-Lambert law; the UV is produced by deuterium and high-pressure xenon lamps. Among its benefits are its high sensitivity, temperature robustness, and compatibility with gradient elution. The drawbacks consist of: Only substances that absorbed light or ultraviolet light could be found (Swartz, 2010).

Fluorescence Detector: Among all the HPLC detectors now in use, it is the most selective and sensitive detector. The presence of a single analyte molecule in the flow cell may be identified. Compared to the UV detector, this detector has a sensitivity that is 10-1000 times greater. There are many different kinds of fluorescence detectors, including laser-induced, multi-wavelength, and single-wavelength excitation models (Swartz, 2010).

Some benefits are as follows: selectivity is high due to comparatively few chemicals fluorescing, sensitivity is greater than UV-Vis detector, and it is compatible with gradient elution.

Among the drawbacks are the following: Fluorescence is difficult to anticipate and is highly influenced by the environment, solvent, pH, temperature, viscosity, ionic strength, and dissolved gas (Swartz, 2010).

Data Collection Devices or Integrator: The detector's signals may be recorded on electronic integrators or graph recorders, which vary in terms of their multifaceted quality and ability to analyse, store, and reprocess chromatographic data. The analysis of this chromatogram may be done manually or with the aid of

specialist software in processes meant to separate a particular chemical from a mixture (Swartz, 2010).

Advantages of HPLC

High Sensitivity (ppm-ppb), excellent reproducibility, and ongoing column effluent monitoring are the benefits of HPLC. It can separate and analyse exceedingly complex mixtures without the need to evaporate the sample, as does gas chromatography (GC). Its great efficiency, high accuracy, high-resolution speed, versatility, and exceptional precision in identifying and measuring chemical components make it an excellent choice (Kumar et al., 2018).

Disadvantages of HPLC

HPLC disadvantages are regular maintenance is required, high cost and complex to operate (Patel & Dalwadi, 2023).

Applications of High Performances Liquid chromatography

In a variety of industries, including forensics, life sciences, food science, pharmaceuticals, and the environment, HPLC has helped with analytical solutions.

Pharmaceutical applications include active component identification, pharmaceutical quality control, and tablet-dissolving studies of the pharmaceutical dosage form to regulate medication stability and shelf-life determination (Patel & Dalwadi, 2023).

Food applications are: HPLC is often used in food analysis for specific product research and quality assurance. It is appropriate for analysing natural chemicals (sugar, lipids, protein, and amino acids), food additives, and multi-residue testing of pollutants and pesticides. It is also suitable for evaluating the labile compound for a complex matrix (Varhadi et al., 2020).

Forensic applications consist of measuring the drug's concentration in a biological sample, identifying anabolic steroids in sweat, serum, urine, and hair, analysing textile colours, and testing blood for cocaine and its metabolites (Varhadi et al., 2020).

Clinical Applications are routine clinical analysis, clinical research, and glycated haemoglobin measurement. Additionally, it is often used to determine the source of poisoning and drug metabolism, which may be crucial in deciding drug toxicity (Varhadi et al., 2020).

Chapter Summary

Artisanal auto-mechanical workers' exposure to environmental pollutants such as PAHs and their metabolites at their workshops is a challenge among auto-artisanal workers in Ghana because of their bad working habits. Exposure to those pollutants poses dangerous health effects on artisanal auto-mechanical workers, such as cancer diseases, asthma, and other health effects. This chapter has encapsulated the necessity to examine and evaluate these difficulties. This chapter also included a health risk assessment and HPLC instrumentation used in this study.

CHAPTER THREE

RESEARCH METHODS

Introduction

In this chapter, the research design and analytical methodology, such as the solid phase extraction technique (SPE) and HPLC – UV/RF detection, were discussed. Also, a questionnaire to ascertain the health and safety knowledge of artisanal auto-mechanical workers at their workshops was highlighted. Furthermore, the statistical instruments used for data analysis were examined.

Research Design

This study followed a positivist worldview of research design, which seeks an objective reality based on careful observations and measurements. The EPA method 8310, which is an International Standard method, was used in this quantitative study (EPA method 8310, 2016). Therefore, the US EPA method 8310 sampling and sample extraction protocol, quality control, instrumental analysis, and data analysis using HPLC – UV/RF detection were employed for this research.

Study Area

The study area was Swidu Auto-mechanical Shops, located in Cape Coast Metropolis. The total population of the artisans in Swidu workshop was about one-thousands (1000) workers (Figure 5).

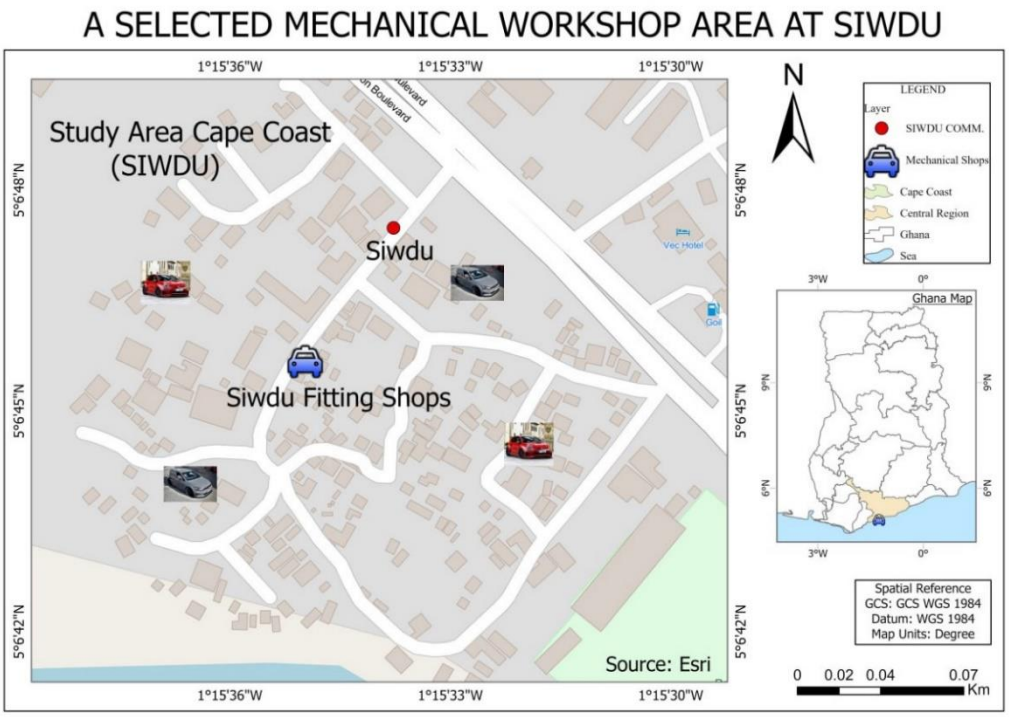


Figure 5: Study Area Map for Siwdu Auto-mechanical Shops
(Google construct, 2023)

Figure 6: Study Area Image for Siwdu Auto-mechanical Shops
(Google satellite image, 2023)

Study Participants

Three different auto mechanical workers, namely auto-mechanics, auto-sprayers, and plastic welders, constituted the study participants. The approach of purposeful random sampling was used for the selection of sixty (60) study participants for the study based on the strategic positioning. Thirty-two (32) participants were selected from 20 auto-mechanic shops, twenty-one (21) participants were chosen from 15 auto-sprayers shops, and seven (7) participants were selected from 5 selected plastic welders' shops, making a total of 60 study participants among the artisanal auto-mechanical workers who agreed to partake in the research work.

Eligibility Criteria

The study's inclusion criteria required participants to meet the following conditions: be employed as either an auto-mechanic, auto-sprayer, and plastic welder, have a minimum of 2 years of work experience in their respective role and maintain regular working hours at the workshop, and vice versa were the exclusion criteria for this study.

Ethical Clearance

Auto-mechanical workshop entry: the leaders in the Swidu auto-mechanical workshop located in Cape Coast were contacted to seek permission to enter the artisanal auto-mechanical workshop. A meeting was also held with the entire artisanal auto-mechanical workforce in the Cape Coast mechanical

workshop to explain the procedure and importance of the study to them for their acceptance. Also, the University of Cape Coast Institutional Review Board granted ethical approval (UCCIRB/CANS/2023/05).

Administration of Questionnaire to Participants in the Swidu Auto-mechanical Workshop

At the Swidu mechanical workshop located in Siwdu-Cape Coast, the studied group members, namely auto-mechanics, auto-sprayers, and plastic welders, a total of sixty (60) were administered with structured questionnaires to complete for participation. The study was conducted from the period of January 2023 to December 2023.

A Quantitative research method was applied in the form of a field survey for the evaluation of knowledge levels of artisanal auto-mechanical workers on occupational health and safety measures related to their work. Demographically, the connection between the number of years spent practicing the artisanal work and the experience of health effects was also assessed.

Urine Sample Collection

Fifty-nine (59) early morning urine samples: 32 from auto-mechanics, 21 from auto-sprayers, and 6 from plastic welders were respectively collected. Sterile, metal-free, high-density plastic sample containers were used to collect urine samples from study participants. They were instructed to avoid the first portion of the urine stream before collecting 15- 20 mL of mid-stream urine into

the plastic containers. The urine samples were then collected from the participants and kept in cool containers containing ice packs at 4-8 °C, transported to the laboratory, and then stored in the lab refrigerator at the Department of Laboratory Technology, University of Cape Coast, for analysis. Note one sample was lost due to storage challenges.

Chemicals and Standards

High-purity standards and reagents were used. The EPA method 8310 PAHs standards mixture and PAH metabolites standards were purchased from Restek. Dichloromethane (purity ≥ 99.8 %), Methanol (purity ≥ 99.8%), Ammonium phosphate dibasic (purity ≥ 98.5%), Formic acid (purity ≥ 98.5) and Acetonitrile (ACN) (purity ≥ 99.8%) all HPLC grade, solvents were purchased from Millipore Corporation, Germany, and MilliQ ultrapure deionized water (18.2 MΩ) filtered through MilliQ polisher (DI water).

Preparation of 0.1M $(NH_4)_2HPO_4$ Buffer in 100 ml Flask of pH 5.5

A 1.3206 g of $(NH_4)_2HPO_4$ was weighed using an analytical balance with the aid of a weighing dish and quantitatively transferred into a beaker and dissolved using DI water in a beaker by stirring it with a glass rod. The 100 mL volumetric flask was filled with some level of DI water, and the dissolved solution in the beaker was quantitatively transferred into the flask with the aid of a funnel. The beaker was rinsed four times with DI water and transferred back to the flask. After the buffer's pH was adjusted to 5.5 using 0.68 mL of Conc. H_3PO_4,

it was labelled. The pH of the buffer was then confirmed to be 5.5 using a pH meter (EPA method 8310, 2016).

Urine Sample Preparation and Extraction

The EPA Method 8310 sample preparation and extraction protocol with slight modification for optimization was employed (EPA Method 8310, 2016). The pH of the urine sample was adjusted to 6.0 using ammonium phosphate buffer. The Supelcean ultra SPE C18 cartridges were conditioned with 3.0 ml of ACN followed by 3.0 ml of MilliQ ultrapure type 1 deionized water (18.2 M) before samples were loaded (EPA method 8310, 2016). About 10 mL of each of the homogenized urine samples were loaded onto the cartridges by gravity. The cartridges were washed with 3 mL of 10% methanol and allowed to dry with the aid of a manifold at a flow rate of 0.2 mL/min for 5 minutes. This was followed by three successive elutions with 3.0 mL of ACN and DCM each. The eluent was collected, concentrated to about 1.0 mL, and dried further using a stream of pure nitrogen gas. The final eluent was reconstituted to 0.3 mL using ACN into 0.5 mL glass insert in 1.5 mL glass sample vials for HPLC – UV/RF instrumental analysis (EPA method 8310, 2016). Spiked samples (1 ppb, 5 ppb, and 10 ppb) were also extracted in like manner and reconstituted to 0.3 mL using ACN into 0.5mL glass insert in 1.5 mL glass sample vials for HPLC – UV/RF instrumental analysis for method recovery checks.

Preparation of Standard for PAH Metabolites and Native PAHs

Standard solution concentrations of 100, 1000, 2000, 5000, 10000, and 15000 ppb for 9-phenanthrol and 10, 50, 100, 200, 300, and 500 ppb for 1-hydroxypyrene were respectively prepared into the same vials and top-up to 1.5 ml from their respective stock concentration of 1000 ppm.

The standard solution concentrations of 1, 10, 20, 50,100, and 200 ppb were prepared from a stock concentration of 1000 ppm of EPA method 8310 18 PAH standards mixture into 1.5 mL glass vials.

HPLC-UV/RF Instrumental Analysis

The Shimadzu prominence UFLC 20AD (Ultra-Fast Liquid Chromatography) series coupled to UV/RF detectors was used for the analysis of the samples.

Analytical Conditions for PAH-metabolites

The EPA method 550.1, with slight modification to improve selectivity and sensitivity, was used for the HPLC-UV/RF instrumental analysis of PAH metabolites 9-phenanthrol and 1-hydroxypyrene (EPA method 550.1, 1990).

The injected sample volume of 5µL was eluted through a Luna 3µm C18 100A° (Phenomenex) column (150 x 4.6 mm) with the following mobile phases (solvent A: 50:50% [methanol: 0.1% formic acid in water] and solvent B 100% ACN). The elution was done at a flow rate of 1.0 mL/min. The column oven temperature was maintained at 30 ^{0}C. A gradient elution method of separation was performed using solvents A and B. The gradient conditions were as follows:

0.10 – 1.00 min (solvent A 60%: solvent B 40%), 6.80 – 8.80 min (solvent A 5%: solvent B 95%), and 8.90 min (solvent A 60%: solvent B 40%). Detection of analytes was done using the UV detector at 282 nm and the fluorescence detector with optimum excitation at 350 nm and emission at 450 nm with a flow cell temperature of 30 ^{0}C.

Analytical Conditions for Parent PAHs

The EPA method 610, with slight adjustments to improve sensitivity, accuracy, and selectivity, was employed for the HPLC -UV/RF detection analysis of 18 PAHs (EPA method 610, 2008).

The injected sample volume of 2µL was eluted through a Shimadzu C18 column (3µm, 50 x 4.6 mm) with the following mobile phases (Solvent A: 0.1% formic acid in water and solvent B: 100% acetonitrile). The elution was started at an initial flow rate of 0.60 mL/min. The column oven temperature was maintained at 30 ^{0}C. A gradient elution method system was employed using eluents A and B.

The gradient conditions were as follows: 0.01 - 0.50 min (solvent A 32%: solvent B 68%), 1- 5 min (flow rate: 0.6 – 0.65 mL/min), 6.00 min (solvent A 30%: solvent B 70%), 7.10 – 8.00 min (solvent A 0%: solvent B 100%), 8.5 min (solvent A 35%: solvent B 65%), 13-13.5 min (flow rate: 1.00mL/min), 13.6 min (flow rate: 0.6mL/min), 14.00 min (solvent A 40%: solvent B 60%) and 14.10 min (solvent A 32%: solvent B 68%). Detection of analytes was done using the fluorescence detector with four channels at different optimum excitation (Ex) and emission (Em.). The optimum excitation and emission used for each PAH were as

follows: channel 1: Ex. 230 nm – Em. 330 nm (Acy, Phe, 1-methylnap, 2-methylnap, Chr). For channel 2: Ex. 260 – Em. 352 nm (Nap, Ace, Flu, Ant), for channel 3: Ex. 260 – Em. 420 nm (I [1,2,3-cd] Pyr, BghiPer, BahA, BkFlt, B(a)P, B(a)A, FlT and for channel 4: Ex. 260 – Em. 460 nm (BbFlt, Pyr) for selective detection of individual PAHs in the samples analysed (EPA method 610, 2008).

Analytical Quality Control for PAH-Metabolites and Parent PAHs

A quantitative external standard calibration method was used in this study for the quantification of analytes. System suitability was conducted for each batch using US EPA pharmacopeia criteria. A new batch of solvent A was made before every batch analysis every day. Spiked and unspiked samples were analysed in replicates (n = 3). Reagent blank was prepared and analysed in a similar manner to the samples used. Spiked reagent blanks at levels of (1 ppb, 5 ppb, and 10 ppb) were analysed to ascertain the method's limits of detection, quantitation, and recoveries. Inter-day and intraday analyses were also done to check for the robustness of the method using the lower and highest concentrations (EPA method 8310, 2016).

Risk Assessment of Parent PAHs

Carcinogenic risk assessment was done using toxicity the equivalency factor (TEF) risk base approach.

The toxicity equivalency factors (TEFs) risk assessment protocol employed by (Essumang et al., 2013) were employed for the risk assessment.

That is;

$$TEQ_{BaP} = \Sigma\ (TEF_i \times C_i) \quad (1)$$

Where *Ci* is the measured individual PAH concentrations for the 'sample analysed' compound with the assigned TEF_i.

This approach has also been adopted because PAHs usually exist as a mixture of compounds that can exert synergistic effects on human health.

The calculated TEQ_{BaP} for the seven USEPA-classified carcinogens was used to estimate the carcinogenic risk involved upon exposure to the occupational PAHs by the artisanal auto-mechanical workers for an adult's lifetime of 70.0 years.

For compounds with carcinogenic effects as classified by IARC, the cancer risk is calculated by using the following equations (Adjei et al., 2019)

The total risk due to exposure to mixtures of carcinogenic PAHs is:

$$\text{Risk (carcinogenic)} = \text{Dose} \times \text{oral slope factor} \quad (2)$$

Where oral slope factor (SF_o) [7.3 $(\text{mg/kg-day})^{-1}$]

Estimated daily doses of exposure to PAH mixture for artisanal auto-mechanical workers from the respective mechanical workshop were calculated using the following equation (Adjei et al., 2019).

$$\text{DD} = \frac{C \times TEF \times P \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

Where DD is the daily dose of PAHs mixture (mg / kg-day), "C is the urinary PAHs concentration (ng /L) obtained in this study for each artisanal worker, EF is the exposure frequency (350-day $year^{-1}$), ED is the exposure duration (30 years), Adults average body weight (BW) of 70 kg, P is the expected urinary output per

day of adult man of average 1.65 L/day, CF is conversion factor that is 10^{-6} and a lifetime (AT) of 70 years were used.

Mutagenic risk assessment was done using the mutagenicity equivalency factor (MEF)

Mutagenicity equivalency factors (MEFs) risk assessment protocol employed by (Essumang et al., 2013) was employed for the risk assessment.

That is;

$$MEQ_{BaP} = \Sigma\ (MEF_i \times C_i) \quad (4)$$

Where *Ci* is the measured individual PAH concentrations for the 'sample analysed' compound with the assigned MEF_i.

This approach has also been adopted because PAHs usually exist as a mixture of compounds that can exert synergistic effects on human health.

The calculated MEQ_{BaP} for the seven USEPA-classified mutagens was used to estimate the mutagenic risk involved upon exposure to occupational PAHs of artisanal auto-mechanical workers for an adult's lifetime of 70.0 years.

For compounds of mutagenic effects as classified by IARC the mutagenic risk is calculated by using the equation (Adjei et al., 2019).

The total risk due to exposure to mixtures of mutagenic PAHs is:

Risk (mutagenic) = Dose × oral slope factor (5)

Where SF_o [7.3 $(mg/kg\text{-}day)^{-1}$]

Estimated daily intake doses of pyrene for artisanal auto-mechanical workers from the respective mechanical workshop were calculated using the following equation (Adjei et al., 2019).

$$DD = \frac{C \times MEF \times P \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

Where DD is the daily dose of PAHs mixture (mg / kg-day), "C is the urinary PAHs concentration (ng /L) obtained in this study for each artisanal worker, EF is the exposure frequency (350-day year^{-1}), ED is the exposure duration (30 years), Adults average body weight (BW) of 70 kg, P is the expected urinary output per day of adult man of average 1.65 L/day, CF is conversion factor that is 10^{-6} and a lifetime (AT) of 70 years were used.

Risk Assessment of PAH metabolites

Cancer risk assessment was done for 1-hydroxypyrene level concentrations in the urinary samples using the earlier equations (1, 2, and 3) used for parent PAHs cancer risk calculations.

Mutagenic risk assessment was done for the PAH metabolites mixture using the earlier equations (4, 5, and 6) for parent PAHs mutagenic risk analysis.

Note: toxicity and mutagenicity equivalent factors used for 1-hydroxypyrene risks calculation was B(a)P factors since 1-OHP is the metabolite form of benzo(a)pyrene. Also, benzo(a)anthracene mutagenicity equivalent factor was used for the 9-phenanthrol daily dose calculation.

Table 1: **Toxicity and Mutagenicity Equivalent Factors used for Risk Assessment**

PAHs	TEF (EPA, 1993)	MEF(Durant et al., 1999)
Chrysene	0.001	0.017
Benzo(a) anthracene	0.100	0.082
Benzo(b)fluoranthene	0.100	0.250
Benzo(k)fluoranthene	0.010	0.110
Benzo(a)pyrene	1.000	1.000
Indeno[1,2,3-cd] pyrene	0.100	0.310
Dibenz[a,h]anthracene	1.000	0.290

Source:(Durant et al., 1999)

Data Analysis

The ANOVA descriptive statistics analysis on the questionnaire was done using the Statistical Package for Social Sciences version 22 (SPSS). The Shimadzu labsolution browser was also employed in the calculations of LOD, MDL, LOQ, and other statistics of the instrumental analytical data. The multivariate analysis of variance on the data was conducted using excel toolpak software.

Chapter Summary

The study area, population, sampling procedure, instrumental analysis conditions, data collection, and data processing for PAHs and their metabolites in urine samples of auto-artisanal mechanical workers have been captured in this section.

CHAPTER FOUR

RESULTS AND DISCUSSION

Introduction

This section highlights the result and discusses the levels of urinary-PAHs and their metabolites in artisanal auto-mechanical workers' urine samples from the Siwdu workshop in Cape Coast Metropolis. The health risk assessment results of PAHs and their metabolites among various artisanal auto-mechanical workers were also discussed. The health and safety perception of artisans was captured.

Table 2: **Demographic Information on Auto-mechanical Workers**

	Responses	Frequency (percentage)
Gender	Male	60 (100.0)
	Female	0 (0.0)
Age	Under 25 years	16 (26.7)
	26 -35 years	17 (28.3)
	36- 45 years	16(26.7)
	46 -55 years	8 (13.3)
	56 and above years	3 (5.0)
Level of education	Informal	2 (3.3)
	Basic	53 (88.3)
	Secondary/ Technical	4 (6.7)
	Tertiary	0 (0.0)
	None	1 (1.7)
Job specialization	Auto mechanics	32 (53.3)
	Plastic welders	7 (11.7)
	Auto sprayers	21 (35)
Position at workshop	Master	37 (61.7)
	Apprentice	23 (38.3)
Years of practicing artisanal work	Below 1	0 (0.0)
	2-5	17 (28.3)
	6-9	10 (16.7)
	10-19	15 (25.0)
	20 and above	18 (30.0)

Source: Field survey (2023)

Demographic Information on Auto-mechanical Workers

From Table 2, the study respondents were 100.0% males engaged in various aspects of artisan work at the workshops, whereas the females recorded 0.0%; this may be attributed to the fact that artisanal auto mechanical work is energy involving therefore, few females are engaged in auto artisan works at the Siwdu workshop, and those females were unwilling to take part in this study which accounted for the 0.0% recorded. Also, the study participants considered in this work were sixty (60) due to the unwillingness of most artisan workers to participate in the study at the Siwdu workshop, which limited the sample size to only sixty participants. Generally, about three out of every five respondents were between 25-45 years of age (55.0%); only 13.3% were between 46 -55 years old; and out of the 60 study respondents, only 5.0% were 56 and older. From the analysis of the respondent's level of education, the research discovered that the majority of the artisans (88.3%) entered into their various fields of work after a basic education level, and only 6.7% of artisans had a secondary or technical level of education. From Table 2, considering the artisans' low level of education, most of the artisanal auto-mechanical workers may not be that knowledgeable about the hazards associated with their work and the related health implications associated with their occupation, thus cause for occupational health and safety concerns.

With respect to the respondents' job specialization, auto-mechanics recorded the highest (53.3%), followed by auto-sprayers (35%) and plastic welders (11.7%) (Table 2). According to the survey, most artisanal auto-mechanical workers at the workshops were masters (61.7%), whereas the

remaining 38.3% were apprentices (Table 2). This correlated with the years of working experience. The majority of the artisans (30%) had 20 and above years of working experience at the workshop; only 28.3% of the artisans had 1–5 years of working experience, whereas the remaining artisans' length of work experience was as follows: 10–19 years represented 25% and 6–9 years (16.7%). The years of practicing regularly at the workshop may also be linked to the risk levels of exposure at the workshop since the effects of hazards, such as the effects of PAHs on human health, are contingent upon exposure duration, pace, concentration, and inherent toxicity of the individual PAHs on the artisans (Abdel-Shafy & Mansour, 2016).

The result of this study is comparable to similar work reported by Monney et al.(2014) on "occupational health and safety practices among vehicle repair artisans in an urban area in Ghana." From this existing work, the demographic information recorded on vehicle repair artisans includes: all the study respondents were 100% males engaged in various artisanal works. The majority of the artisans (81%) entered into their different fields of work at age 26 years or younger. Also, the larger portion of artisans (66%) in the Monney et al., 2014 study were basic school education graduates (Monney et al., 2014). Comparably the demographic information recorded in this study was somehow similar compared with what has been reported in the above literature.

Table 3: **Basic Knowledge on Occupational Health and Safety on Auto-mechanical Workers**

Questions	Response	Frequency(percentage)
Do you have any knowledge about safety equipment	Yes	45 (75.0)
	No	15 (25.0)
If yes, give one or two examples of safety equipment you know and use	Gloves	41 (68.3)
	Nose mask	34 (56.7)
	Safety boot	16 (26.7)
	Working gear	11 (18.3)
Multiple uses of Personal Protective Equipment	No PPE	15(25)
	One PPE	7 (11.7)
	Two PPE	22 (36.7)
	Three PPE	13(21.7)
	All PPE	3 (5.0)
Do you feel comfortable and protected when using Personal Protective Equipment	Very often	6 (10.0)
	Often	37 (61.7)
	Not often	2 (3.3)
	none	15 (25.0)
Do you Clean your hands or other body parts with fuel, for example, Petrol and other liquids other than water	Yes	53 (88.3)
	No	7 (11.7)
Washing hands with soap under running water before eating at break	Very regularly	0 (0.0)
	regularly	8 (13.3)
	sometimes	52 (86.7)
	None	0 (0.0)
How often do you wash your work attire	Everyday	0 (0.0)
	3 days	4 (6.7)

	1 week	48 (80.0)
	months	8 (13.3)
	Never	0 (0.0)
Do you have any health conditions?	Yes	3 (5.0)
	No	57 (95.0)
	Maybe	0 (0.0)
If yes, please state that health condition (s)	body itching	3 (5.0)
Do you smoke or drink alcohol?	Yes	8 (13.3)
	No	52 (86.7)
Do you know of one common disease workers usually suffer and die from as a result of their work practices?	Malaria	16 (26.7)
	Headache	21 (35.0)
	Body pain	15 (25.0)
	None	8(13.3)
How often do you visit the clinic or hospital	Very often	0(0.0)
	often	0 (0.0)
	not often	55 (91.7)
	None	5 (8.3)

Source: Field survey (2023)

Basic Knowledge on Occupational Health and Safety of Auto-mechanical Workers

Occupational safety encompasses all areas of health and safety concerns in the workplace, with a particular emphasis on preventing dangers. This study sought to know the perception of artisanal auto-mechanical workers towards health and safety at work. From Table 3, the analysis of results conducted on data collected from the study participants to know about their basic knowledge of safety equipment showed that 75.0% of artisans had low knowledge of safety

equipment. In contrast, the remaining 25% had no knowledge of safety equipment. This suggested that a significant number of artisans may not use safety equipment at the workshops, thereby exposing them directly to the numerous hazardous chemicals, especially PAHs, at the workshops. Despite the host of hazards present at the artisanal mechanical workshops, only 5.0% of the artisans interviewed were found to use PPE during work activities at the workshops (Table 3). Approximately 68.3% of artisans used gloves, 56.7% of artisans used nose masks, and 26.7% used safety boots, whereas the remaining 18.3% of artisans observed used working gear during work. However, this does not constitute adequate protection from the hazards artisans were exposed to since other parts of their bodies, such as the face, hands, eyes, and nose, were equally exposed to hazardous substances such as PAHs through inhalation, ingestion, and dermal contact (Fadel et al., 2022). Also, from Table 3, 61.7% of artisans often feel comfortable and protected when using personal protective equipment, whereas the remaining 25% of artisans clearly stated that they feel uncomfortable and unprotected when using PPE at the workshop. These suggested about 25% of artisans may end up not using PPE for their safety at the workshops during work activities. The artisan's poor usage and little knowledge of PPE suggested that artisans may be directly exposed to hazardous substances such as PAHs. These may have contributed to the increased health risk incidences among auto-artisans in Ghana, especially among people in Siwdu, Cape Coast.

From Table 3, it was found that 88.13% of artisanal auto-mechanical workers engaged in regular unsafe working practices at their workshops by

cleaning and washing their hands and other body parts with fuels such as petrol and other liquids other than normal water. These unhealthy practices suggested that a larger group of artisans would be directly exposed to hazardous chemicals at the workshops. Moreover, from the study, it was found that only 13.3% of artisans observed proper hand washing during break hours before eating, while the remaining 86.7% of artisans did not observe proper hand washing at their workshops before eating. This observation suggested that most of the artisans would be exposed to dangerous substances such as PAHs through ingestion (Yebra-Pimentel et al., 2015). This may have also contributed to the higher levels of PAH concentration in the artisans' body systems, which would, therefore, increase the health implications among the artisans in Cape Coast.

Furthermore, from Table 3, it was observed that most artisans (80.0%) washed their working gear once a week, whereas the remaining 13.3% of the artisans washed their working gear once a month. The latter may have contributed to the elevated risk of exposure to hazardous chemicals such as PAHs through the route of dermal contacts (Abdel-Shafy & Mansour, 2016) since most of the artisans' working gears were stained with the oils and fuels they used for work activities (Gamboa et al., 2008; Kim et al., 2013).

According to the research, it was found that only 5.0% of artisans had health conditions such as body itching. It was also found that only 13.3% of artisans smoke and drink alcohol, whereas the remaining 86.7% do not smoke or drink alcohol. The 13.3% of artisans' smoking practices would increase their risk of having cancer and other PAHs related ailments since smoking is already

associated with lung cancer (Hoseini et al., 2018). Considering the results, it was observed that the common disease the artisans suffered from at the workshop was headache (35.0%). This was an implication that the artisans were exposed to some higher levels of PAH concentrations at their workshops. Literature has reported that prolonged exposure to high concentrations of PAHs causes health effects such as acute and chronic headaches (Kamal et al., 2015; Kamal, Cincinelli, Martellini, Palchetti, Bettazzi, et al., 2016). Therefore, the elevated headache cases recorded among the artisans confirmed that the people were at risk of exposure to PAHs at their workshops, which also may contribute to other health issues such as cancer and non-cancer diseases among the artisans' workers (Abdel-Shafy & Mansour, 2016).

Finally, from Table 3, it was found that 91.7% of artisans hardly visited the hospital for regular examinations of their health conditions, which implies that most artisans would be practicing self-medication, which would worsen their health conditions. The responses from the respondents showed that artisanal auto-mechanical workers' knowledge about health and safety related to the work they practiced at the workshop was very low. These may have contributed to poor safety culture among the artisans and may have rendered them vulnerable to exposure to elevated levels of hazardous chemicals at the workshops. The current situation at the workshop calls for urgent attention from the Government of Ghana and other stakeholders to help alleviate it, in order to safeguard the health of these artisans.

Table 4: **Quality Control Parameters for PAH-Metabolites**

Parameters	9-Phenanthrol	1-Hydroxypyrene
Retention Time	4.83	6.44
Quantitation Limit (ng/L)	25 ng/L	3.7 ng/L
R^2	0.9996	0.9994
RF %RSD	12.89%	9.83%

Source: Laboratory work (2023)

Table 5: **Quality Control Parameters for Parent PAHs**

PAHs	RT (min)	DL (ng/L)	QL (ng/L)	R^2	Spiked Recovery (%)	RF %RSD
NAP	1.61	2.67	8.10	0.9998	109.50	11.59
ACY	1.62	4.69	14.20	0.9998	109.80	11.99
ACE	2.10	1.15	3.48	0.9987	93.60	9.19
FLU	2.36	9.16	27.75	0.9999	102.90	8.58
PHE	2.64	3.68	11.15	0.9997	91.20	14.97
1-MN	3.32	1.69	5.11	0.9998	71.10	6.72
2-MN	3.69	2.60	7.88	0.9997	71.20	8.78
ANT	4.01	3.99	12.10	0.9998	57.10	8.27
FLT	4.35	0.74	2.23	0.9998	92.70	7.97
PYR	5.09	2.21	6.70	0.9997	71.30	7.89
B(a)A	5.64	0.85	2.58	0.9998	69.80	7.74
CHR	6.80	1.74	5.26	0.9999	98.10	8.74
B(a)P	7.27	1.59	4.81	0.9997	108.20	12.84
BbFlt	9.59	7.15	21.67	0.9998	71.70	5.70
BkFlt	10.00	1.40	4.25	0.9999	71.70	10.25
BahA	10.66	3.90	11.81	0.9998	73.20	6.49
BghiPer	11.54	8.22	24.90	0.9999	91.90	10.19
I[1,2,3-cd]P	12.06	1.05	3.17	0.9998	90.80	17.99

Source: Laboratory work (2023)

Quality Control for PAHs and their Metabolites

The external standard method was used to establish the six-point calibration curve and to quantify the PAHs and their metabolite in the sample. A good linearity response was observed between the peak areas and the

concentration range of 100-15000 ppb for 9-phenanthrol and 10-500 ppb for 1-hydroxypyrene, respectively. The correlation coefficients of determination, recorded were $R^2 \geq 0.9996$ and 0.9994 for 9-phenanthrol and 1-hydroxypyrene, respectively, for each plot from instrumental analysis of the analytes. The RF %RSD for the calibration curves were 12.89% and 9.83%, and the retention time for the analytes were 4.830 and 6.437mins for 9-phenanthrol and 1-hydroxypyrene, respectively (Table 4).

The quantitation limits (QL) were found to be 25 ng/L and 3.7 ng/L for 9-phenanthrol and 1-hydroxypyrene, respectively, which is also a good indication of the method's sensitivity. Well-resolved peaks were achieved for this study, as shown in (Appendix B, figure B 3).

A good linear response was also observed between the peak areas and the concentration range of 1-200 ppb for native PAHs when the plot of the concentration versus the peak area was made. The correlation coefficients of determination, recorded was $R^2 \geq 0.9997$ for all the analytes for each plot from instrumental analysis (Table 5). Good response factors (RF) percent relative standard deviations (%RSD < 15) were obtained for all the analytes except one analyte that had a %RSD to be 17.988% (Table 5). These findings show that the technique used has extremely excellent linearity in its analytical response. The detection limits and the quantitative limits were in the ranges of 0.74–8.22 ng/L and 2.58–24.90 ng/L respectively (Table 5). These limits indicated that the method employed herein had improved sensitivity. The spiked recoveries of the PAHs were calculated to range between 57.10-109.80 % (Table 5). These are

suggestive of the efficiencies of the methodology employed. Well-resolved peaks were achieved for this study, as shown in (Appendix B, figure B 5).

The result in this study is comparable to similar work reported by EPA method 8310 on "solid phase extraction of PAHs in water," recorded spiked recoveries of the PAHs range between 62.10 – 123.5% and good response factors percent relative standard deviations (%RSD < 10) were obtained for all the analytes (EPA method 8310, 2016). This study is also in line with but more sensitive than that work reported by EPA method 610 on the "determination of PAHs in Municipal and Industrial wastewater," where the detection limits recorded ranged from 10.00 to 490.00 ng/L for the analytes (EPA method 610, 2008). Comparably, the quality control results in this study are somehow similar to what has been reported in the above literature on PAH determination. These imply that the methods used in this study were sensitive and efficient for the determination of all the analytes in the urine samples of this study.

Table 6: **Mean Concentrations of PAH-metabolites (n = 3) in AM urine**

	Compound /ng/L		
Sample Id	9 -Phenanthrol	1-Hydroxypyrene	Mean total metabolites
AM 1	10110.00±0.01	<LOQ	10110.00
AM 2	4350.00±0.00	90.00±0.00	4440.00
AM 3	24120.00±0.00	<LOQ	24120.00
AM 4	7603.50±0.01	15.00±0.00	7618.50
AM 5	17061.00±0.01	190.50±0.01	17251.50
AM 6	5731.50±0.00	<LOQ	5731.50
AM 7	23512.50±0.02	12.00±0.00	23524.50
AM 8	19954.50±0.01	<LOQ	19954.50
AM 9	30955.50±0.00	201.00±0.01	31156.50
AM 10	14598.00±0.01	57.00±0.00	14655.00
AM 11	8457.00±0.01	<LOQ	8457.00
AM 12	23508.00±0.02	138.00±0.01	23646.00
AM 13	6048.00±0.06	24.00±0.01	6072.00
AM 14	21108.00±0.01	<LOQ	21108.00
AM 15	16287.00±0.01	55.50±0.01	16342.50
AM 16	11898.00±0.00	<LOQ	11898.00
AM 17	29644.50±0.00	2106.00±0.01	31750.50
AM 18	10711.50±0.01	<LOQ	10711.50
AM 19	4836.00±0.07	<LOQ	4836.00
AM 20	10477.50±0.01	93.00±0.00	10570.50
AM 21	26145.00±0.00	<LOQ	26145.00
AM 22	254643.00±0.05	<LOQ	254643.00
AM 23	43810.50±0.01	133.50±0.01	43944.00
AM 24	25770.00±0.00	45.00±0.00	25815.00
AM 25	17598.00±0.00	310.50±0.00	17908.50
AM 26	490759.50±0.01	6.00±0.01	490765.50
AM 27	57783.00±0.01	615.00±0.02	58398.00
AM 28	11179.50±0.01	<LOQ	11179.50
AM 29	9441.00±0.00	18.00±0.01	9459.00
AM 30	6658.50±0.01	219.00±0.02	6877.50
AM 31	1869.00±0.02	21.00±0.01	1890.00
AM 32	9510.00±0.01	<LOQ	9510.00

Limit of quantitation for 9-phenanthrol = 25 ng/L and 1-hydroxypyrene = 3.7ng/L

Source: Laboratory work (2023)

Table 7: **Mean Concentrations of PAH-metabolites (n = 3) in AS urine**

	compound /ng/L		
Sample Id	9 -Phenanthrol	1-Hydroxypyrene	Mean total metabolites
AS 1	3111.00±0.00	<LOQ	3111.00
AS 2	20986.50±0.01	<LOQ	20986.50
AS 3	31569.00±0.01	12.00±0.01	31581.00
AS 4	1828.50±0.01	<LOQ	1884.50
AS 5	2001.00±0.01	18.00±0.01	2019.00
AS 6	4222.50±0.00	<LOQ	4222.50
AS 7	2131.50±0.00	<LOQ	2131.50
AS 8	25960.50±0.01	36.00±0.02	25996.50
AS 9	32445.00±0.01	34.50±0.01	32479.50
AS 10	129819.00±0.02	<LOQ	129819.00
AS 11	32974.50±0.06	<LOQ	32974.50
AS 12	6580.50±0.00	9.00±0.00	6589.50
AS 13	16947.00±0.00	<LOQ	16947.00
AS 14	32649.00±0.05	<LOQ	32649.00
AS 15	24100.50±0.00	<LOQ	24100.50
AS 16	25599.00±0.00	<LOQ	25599.00
AS 17	33808.50±0.01	120.00±0.03	33928.50
AS 18	37162.50±0.01	<LOQ	37162.50
AS 19	1659.00±0.00	93.00±0.00	1752.00
AS 20	23320.50±0.01	420.00±0.01	23740.50
AS 21	25810.50±0.00	519.00±0.01	26329.50

Limit of quantitation for 9-phenanthrol = 25 ng/L and 1-hydroxypyrene = 3.7ng/L

Source: Laboratory work (2023)

Table 8: **Mean Concentrations of PAH-metabolites (n = 3) in PW urine**

	Compound /ng/L		
Sample Id	9 -Phenanthrol	1-Hydroxypyrene	Mean total metabolites
PW 1	2020.50±0.02	<LOQ	2020.50
PW 2	13977.00±0.01	114.00±0.00	14091.00
PW 3	7308.00±0.03	468.00±0.00	7776.00
PW 4	16866.00±0.01	<LOQ	16866.00
PW 5	45613.50±0.00	<LOQ	45613.50
PW 6	3282.00±0.02	42.00±0.01	3324.00

Limit of quantitation for 9-phenanthrol = 25 ng/L and 1-hydroxypyrene = 3.7ng/L

Source: Laboratory work (2023)

PAH Metabolites

Both 9-phenanthrol and 1-hydroxypyrene are PAH-metabolites, which are often used as urine biomarkers of exposure to polycyclic aromatic hydrocarbons (Hoseini et al., 2018). From the results, it was evident that artisanal auto-mechanical workers were exposed to PAHs through various possible routes like inhalation, dermal, and oral exposure as a result of poor safety culture such as applying diesel to injured body parts, suctioning gasoline with the mouth, working, eating, and sleeping in unhygienic settings, and not wearing personal protective equipment (PPE) like overcoats, gloves, and safety boots at their workshops (Abdel-Shafy & Mansour, 2016).

From the results in Table 6, significant levels of metabolites were recorded for all the urine samples analyzed for auto-mechanics. The mean total PAH metabolites recorded ranged between 1890.00 ng/L (AM 31) and 490765.50 ng/L (AM 26). Among the thirty-two samples analyzed, sample AM 26 recorded the

highest mean total, and AM 31 recorded the lowest mean total PAH-metabolites, respectively. Among the individual metabolites analyzed, 9-Phenanthrol recorded concentration levels ranging between 1869.00 ng/L - 490759.50 ng/L. For the thirty-two samples analyzed, sample AM 26 recorded the highest mean total of 490759.50 ng/L for 9-Phenanthrol, and sample AM 31 recorded the lowest mean total of 1869.00 ng/L for 9-Phenanthrol. The results from the auto-mechanic urine samples from Siwdu auto-mechanical workshops in Cape Coast were found to be significantly higher ($P < 0.05$) compared to WHO-set maximum permissible limits of 660 ng/L for 9-Phenanthrol (Jongeneelen, 2001). The presence of elevated levels of 9-phenanthrol may be attributed to exposure to diesel fuel, which is the source of exposure to the contaminant at the workshop by the artisans (Abdel-Shafy & Mansour, 2016). The elevated levels recorded for 9-phenanthrol may have dire consequences, such as skin and eye irritation and chest pain (Guinamard et al., 2014; Kamal et al., 2016) on AM workers in Cape Coast. Elevated levels of 9-phenanthrol have been linked to the modulation of smooth muscle contraction in the bladder and cerebral arteries of humans (Guinamard et al., 2014; Kamal, Cincinelli, Martellini, Palchetti, Malik, et al., 2016) and the AM artisans may suffer from this health implication.

Also, from Table 6, the levels of 1-hydroxypyrene (1-OHP), a definite carcinogen, ranged between <LOQ - 2106.00 ng/L. Among the thirty-two samples analyzed, sample AM 17 recorded the highest mean total of 2106.00 ng/L of 1-hydroxypyrene. Inferring from Table 6, the individual 1-OHP metabolite results of AM workers, most of the recorded results from their urine samples were below

the limit of quantitation. Among the samples, only sample AM 17 was found to be significantly higher ($P < 0.05$) compared to the occupational exposure threshold value set by the American Conference of Governmental Industrial Hygienists (ACGIH) of 1000 ng/L of 1-hydroxypyrene (ACGIH, 2010; Jongeneelen, 2014). The remaining results were found to be significantly lower ($P > 0.05$) compared to the ACGIH-set occupational threshold limit of 1000 ng/L of 1-hydroxypyrene (ACGIH, 2010; Jongeneelen, 2014). These may be attributed to the fact that parent PAHs especially the heavy molecular weight get slowly metabolized to 1-OHP. Notwithstanding, 1-OHP can bioaccumulate and elevated levels may result overtime since there is continuous exposure to parent PAHs. According to Hen et al. (2006), only about 6.7% of total parent PAHs get converted to 1-OH pyrene since they are slow to metabolize.

These low levels recorded for 1-OHP in the AM workers' samples may not have dire consequences on the health of AM workers. However, the metabolites are known to bioaccumulate, which implies that if more PAHs enter the system, metabolite levels may rise to a level that may initiate carcinogenesis and cause issues such as liver, skin, gastric, and lung cancer (Kim et al., 2013). The elevated level of 1-OHP recorded for AM 17 suggested that such an individual may possibly suffer from cancer and non-cancer health effects and needs immediate attention to help subvert the possible health risk.

From Table 7, elevated levels of total metabolites were recorded for all the urine samples analyzed for auto sprayers. The mean total PAH metabolites recorded ranged between 1752.00 ng/L -129819.00 ng/L. Among the twenty-one

samples analyzed, sample AS 10 recorded the highest mean total of 129819.00 ng/L, and sample AS 19 recorded the lowest mean total of 1752.00 ng/L of PAH metabolites, respectively. Among the individual metabolites analyzed, 9-Phenanthrol recorded concentration levels ranging between 1659.00 ng/L - 129819.00 ng/L. The results from auto-sprayer urine samples were found to be significantly higher ($P < 0.05$) compared to WHO-set maximum permissible limits of 660 ng/L for 9-Phenanthrol (Jongeneelen, 2001). The presence of high levels of 9-phenanthrol may be attributed to exposure to diesel fuel exhaust fumes sources at the workshop. The elevated levels recorded for 9-phenanthrol may pose health challenges such as skin and eye irritation, chest pain, and other diseases on the health of AS workers in Ghana, specifically among the AS artisans in Cape Coast (Guinamard et al., 2014; Kamal, Cincinelli, Martellini, Palchetti, Malik, et al., 2016).

Also, from Table 7, the levels of 1-hydroxypyrene (1-OHP), a biomarker, ranged between <LOQ to 519.00 ng/L. Among the twenty-one samples analyzed, sample AS 21 recorded the highest mean total of 519.00 ng/L of 1-hydroxypyrene. Inferring from Table 7, the majority of 1-OHP metabolite results for auto-sprayers were below the LOQ. The remaining results were found to be significantly lower ($P > 0.05$) compared to the ACGIH-set occupational threshold limit of 1000 ng/L of 1-hydroxypyrene (ACGIH, 2010; Jongeneelen, 2014). These may be attributed to the fact possibly 1-OHP still exist in the P-PAHs form rather than in 1-OHP form since the parent PAHs are slowly metabolised.

These low concentrations recorded for 1-OHP in the AS workers' samples may not have immediate consequences on the health of AS workers. However, since the 1-OHP tends to bioaccumulate, there is still a cause by concern.

From the results in Table 8, elevated levels of total metabolites were recorded for all the urine samples of plastic welders analyzed. The mean total PAH metabolites recorded ranged between 2020.50 ng/L - 45613.50 ng/L. For the six samples analyzed, sample PW 5 recorded the highest mean total of 45613.50 ng/L, and sample PW 1 recorded the lowest mean total of 2020.50 ng/L of PAH metabolites, respectively. For the individual metabolite analyzed, 9-Phenanthrol recorded elevated levels ranging between 2020.50 ng/L - 45613.50 ng/L. The results from plastic welder's urine samples were found to be significantly higher ($P < 0.05$) compared to WHO-set maximum permissible limits of 660 ng/L for 9-Phenanthrol (Jongeneelen, 2001). The presence of high levels of 9-phenanthrol may be attributed to exposure to diesel fuel exhaust fumes, which is the source of exposure to the contaminant at the workshop. These elevated levels recorded for 9-phenanthrol may pose health implications such as skin and eye irritation, chest pain, and other diseases on the health of PW workers in Ghana, specifically among the PW artisans in Cape Coast (Abdel-Shafy & Mansour, 2016; Guinamard et al., 2014; Kamal, Cincinelli, Martellini, Palchetti, Malik, et al., 2016).

Also, from the results in Table 8, the levels of 1-hydroxypyrene, 1-OHP, ranged between <LOQ to 468.00 ng/L. For the six samples analyzed, sample 3(PW 3) recorded the highest mean total of 468.00 ng/L of 1-hydroxypyrene.

Inferring from Table 8, the individual 1-OHP metabolite results of PW workers, half of the sample's registered results were found below the limit of quantitation. The remaining results were found to be significantly lower ($P > 0.05$) compared to the ACGIH-set occupational threshold limit of 1000 ng/L of 1-hydroxypyrene (ACGIH, 2010; Jongeneelen, 2014). The low concentrations recorded for 1-OHP in the PW workers' samples may not pose significant health implications to the PW workers.

Considering the trend of the metabolite levels recorded in this study for the three different working artisans' groups, statistically, at a 95% confidence level, there was a significant difference among the artisans' group samples analysed ($p = 0.04198$). That is AM > AS > PW respectively. The elevated levels of PAH metabolites recorded for the auto-mechanics may be attributed to the fact that the auto-mechanics were exposed to very high concentrations of PAHs as a result of the frequent direct exposure to fuels, oils and more vehicular exhaust fumes and dust particles that contain PAHs at their workshops due to poor usage of PPE.

The results of this study are comparable to results on the analysis of occupational exposure level of PAH metabolites reported by Pérez-Maldonado et al. (2019), where they recorded mean total levels for 1-hydroxypyrene range between 100000.00-3500000.00 ng/L for children living in Mexican communities (Pérez-Maldonado et al., 2019). The work is also in line with other work reported in literature by McClean et al. (2004) on-air concentrations and urinary metabolites of PAHs among paving and remixing workers where they recorded

mean total results for 9-phenanthrol ranged between 200.00 – 4400.00 ng/L and for 1-hydroxypyrene ranged from 10.00 to 1200.00 ng/L for the workers (by McClean et al.,2004). Comparably, the mean total PAH-metabolite levels recorded in this study were slightly higher ($p < 0.05$) compared with what has been reported in the by McClean et al. (2004) but lower than that reported by Pérez-Maldonado et al. (2019). These elevated levels recorded communicated that those Ghanaian artisans in Swidu auto-mechanical workshops in Cape Coast were highly exposed to PAHs since the metabolites served as biomarkers for occupational exposure to parent PAHs.

Table 9: **Mean Concentrations in ng/L of PAHs (n = 3) in AM urine**

	SAMPLE ID / ng/L										
PAHs	AM 1	AM 2	AM 3	AM 4	AM 5	AM 6	AM 7	AM 8	AM 9	AM 10	AM 11
NAP	< LOQ	5223.45	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
ACY	< LOQ	< LOQ	704.64	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	86.22
ACE	< LOQ	< LOQ	< LOQ	237.66	<LOQ	652.83	<LOQ	<LOQ	<LOQ	<LOQ	25.38
FLU	< LOQ	< LOQ	179.46	<LOQ	<LOQ	473.88	168.57	<LOQ	<LOQ	87.96	<LOQ
PHE	3187.62	3172.92	2901.39	6528.09	3369.09	3736.92	3396.66	2592.99	2644.38	3776.19	3006.39
1-MN	87.36	16.65	26.04	242.79	21.36	16.65	51.12	20.19	24.33	33.93	23.43
2-MN	67.53	<LOQ	80.31	83.55	39.00	35.97	51.30	40.65	37.56	100.62	31.86
ANT	<LOQ	14.94	<LOQ	<LOQ	24.6	<LOQ	24.72	<LOQ	<LOQ	21.30	44.85
FLT	<LOQ	75.6	54.93	411.54	<LOQ	15.15	48.96	103.38	<LOQ	30.69	117.84
PYR	50.28	85.47	70.05	97.98	212.43	47.76	137.37	51.57	65.19	36.63	92.28
BaA	111.24	102.39	102.09	96.00	114.99	117.45	46.38	100.89	295.86	87.33	126.12
CHR	1226.61	4007.73	3707.55	2230.50	8024.25	2803.86	427.44	3911.46	529.05	420.96	4330.08
BaP	20.85	9.51	19.05	18.03	19.20	26.61	6.06	5.07	11.91	2.07	19.32
BbFlt	<LOQ	<LOQ	48.87	3.45	4.80	3.21	3.78	7.02	2.34	3.90	3.84
BkFlt	5.43	6.33	6.87	6.06	6.60	5.04	8.67	6.36	6.57	5.16	5.52
BahA	<LOQ	<LOQ	<LOQ	0.90	2.40	<LOQ	0.39	<LOQ	<LOQ	2.46	<LOQ
BghiPer	34.53	24.33	43.35	89.28	54.27	32.16	22.47	32.31	26.13	<LOQ	45.21
I[1,2,3-cd] PYR	59.10	19.62	18.39	15.78	101.67	48.93	9.12	52.02	17.79	123.24	90.75
Mean Total PAHs	4850.55	12758.94	7962.99	10061.61	11994.66	8016.42	4403.01	6923.91	3661.11	4732.44	8049.09

Source: Laboratory work (2023)

Continuation of Table 9: **Mean Concentrations in ng/L of PAHs (n = 3) in AM urine**

	SAMPLE ID / ng/L										
PAHs	AM 12	AM 13	AM 14	AM 15	AM 16	AM 17	AM 18	AM 19	AM 20	AM 21	AM 22
NAP	11975.5	24182.9	<LOQ	<LOQ	23061.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
ACY	5659.86	5964.75	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
ACE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	322.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
FLU	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	240.54	<LOQ
PHE	2638.56	1770.21	3344.70	1052.97	3041.40	772.89	1600.86	2929.38	2376.39	3213.00	1207.08
1-MN	24.51	25.77	171.51	32.16	27.03	18.48	45.36	32.97	16.62	20.64	26.04
2-MN	92.19	33.9	<LOQ	50.55	366.75	28.77	39.81	<LOQ	26.07	448.32	46.35
ANT	52.56	19.71	30.93	33.06	36.87	49.71	20.37	17.37	<LOQ	37.05	31.56
FLT	<LOQ	151.47	70.50	59.85	<LOQ	<LOQ	50.46	<LOQ	33.93	<LOQ	<LOQ
PYR	44.04	83.07	46.92	89.10	147.99	78.30	59.37	31.62	35.16	36.45	29.31
BaA	96.12	71.07	44.01	95.46	471.60	61.53	230.01	82.86	96.39	61.32	50.40
CHR	2262.51	1917.84	1337.22	1824.93	2045.16	3284.58	274.62	2039.70	814.47	268.77	1379.46
BaP	8.10	16.53	11.61	17.79	7.29	9.00	9.72	4.26	11.19	8.76	0.66
BbFlt	3.75	10.80	4.77	6.12	3.54	2.22	<LOQ	4.23	<LOQ	<LOQ	<LOQ
BkFlt	5.76	9.09	5.97	8.88	5.43	5.49	5.22	5.25	5.19	<LOQ	5.31
BahA	0.69	3.30	<LOQ	<LOQ	0.66	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiPer	<LOQ	33.54	32.97	26.31	80.64	30.51	50.76	<LOQ	42.66	<LOQ	31.17
I[1,2,3-cd] PYR	135.60	59.73	29.97	61.38	77.58	19.56	70.11	31.32	14.16	<LOQ	33.57
Mean Total PAHs	22999.71	34353.69	5131.08	3358.56	29373.45	4683.84	2456.67	5178.96	3472.23	4334.85	2840.91

Source: Laboratory work (2023)

Continuation of Table 9: **Mean Concentrations in ng/L of PAHs (n = 3) in AM urine**

	SAMPLE ID / ng/L									
PAHs	AM 23	AM 24	AM 25	AM 26	AM 27	AM 28	AM 29	AM 30	AM 31	AM 32
NAP	<LOQ	6682.56	8118.24	15490.8	<LOQ	<LOQ	9122.58	<LOQ	<LOQ	<LOQ
ACY	<LOQ	<LOQ	60259.80	<LOQ	1685.88	<LOQ	<LOQ	<LOQ	1579.23	1391.73
ACE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	36.87	63.90	<LOQ	<LOQ
FLU	<LOQ	780.81	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	69.06
PHE	2079.54	2305.11	2655.42	2439.24	2922.09	1070.25	1057.17	1512.78	997.17	677.04
1-MN	23.64	87.09	16.86	31.80	20.34	15.69	18.24	15.51	16.5	27.57
2-MN	245.79	<LOQ	85.71	348.12	<LOQ	20.79	28.26	21.96	23.97	16.98
ANT	16.23	14.67	16.38	11.40	18.27	40.17	12.30	14.16	15.18	19.14
FLT	<LOQ	<LOQ	<LOQ	41.16	<LOQ	45.27	<LOQ	<LOQ	<LOQ	<LOQ
PYR	26.91	36.15	48.93	25.53	29.79	27.24	127.41	110.28	83.28	38.7
BaA	72.54	72.42	41.61	97.47	143.25	65.07	37.26	47.34	110.13	39.42
CHR	<LOQ	<LOQ	597.54	<LOQ	3.06	<LOQ	86.31	994.65	1045.62	53.34
BaP	3.00	4.26	1.41	6.93	35.10	6.60	48.45	60.57	0.93	<LOQ
BbFlt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BkFlt	<LOQ	5.28	5.31	5.43	5.01	5.82	6.96	7.77	5.64	6.12
BahA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiPer	37.53	<LOQ	69.15	<LOQ	<LOQ	33.24	25.65	106.65	44.01	<LOQ
I[1,2,3-cd] PYR	27.99	7.86	<LOQ	22.71	<LOQ	52.59	0.90	40.20	46.14	<LOQ
Mean Total PAHs	2533.17	9996.21	71916.36	18520.59	4862.79	1382.73	10608.36	2995.77	3967.80	2339.10

Source: Laboratory work (2023)

Table 10: **Mean Concentrations in ng/L of PAHs (n = 3) in AS urine**

	SAMPLE ID / ng/L										
PAHs	AS 1	AS 2	AS 3	AS 4	AS 5	AS 6	AS 7	AS 8	AS 9	AS 10	AS 11
NAP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6726.18	<LOQ	<LOQ
ACY	610.08	190.95	370.86	254.55	572.76	587.25	<LOQ	<LOQ	<LOQ	<LOQ	1602.48
ACE	47.49	18.21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	57.99
FLU	97.77	122.34	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PHE	2333.46	2424.81	2621.58	1787.61	3080.64	2546.79	1582.47	3155.55	1436.67	1972.08	2844.15
1-MN	<LOQ	<LOQ	99.75	61.59	69.30	<LOQ	20.67	<LOQ	32.82	<LOQ	<LOQ
2-MN	<LOQ	114.78	33.69	<LOQ	20.07	129.03	45.81	120.60	16.80	127.08	129.18
ANT	<LOQ	15.42	<LOQ	14.16	35.40	<LOQ	<LOQ	15.12	13.08	11.58	<LOQ
FLT	<LOQ	<LOQ	195.42	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	18.15
PYR	<LOQ	<LOQ	100.08	<LOQ	<LOQ	<LOQ	<LOQ	86.61	66.18	<LOQ	<LOQ
BaA	<LOQ	<LOQ	35.97	27.18	<LOQ	<LOQ	23.79	24.84	49.77	<LOQ	<LOQ
CHR	<LOQ	<LOQ	1722.48	<LOQ	<LOQ	<LOQ	<LOQ	261.6	926.31	412.35	234.75
BaP	<LOQ	66.15	200.37	<LOQ	1.62	2.01	3.21	162.51	<LOQ	135.27	38.73
BbFlt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BkFlt	<LOQ	<LOQ	5.58	6.12	4.98	5.13	5.04	5.16	5.07	5.49	<LOQ
BahA	<LOQ	<LOQ	<LOQ	1.59	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiPer	<LOQ	<LOQ	25.23	22.59	21.93	21.54	22.05	25.59	24.90	27.42	<LOQ
I[1,2,3-cd] PYR	<LOQ	<LOQ	5.13	6.42	<LOQ	<LOQ	<LOQ	8.31	51.33	7.05	3.51
Mean Total PAHs	3088.80	2952.66	5416.14	2181.81	3806.70	3291.75	1703.04	3865.89	9349.11	2698.32	4928.94

Source: Laboratory work (2023)

Continuation of Table 10: **Mean Concentrations in ng/L of PAHs (n = 3) in AS urine**

	SAMPLE ID / ng/L									
PAHs	AS 12	AS 13	AS 14	AS 15	AS 16	AS 17	AS 18	AS 19	AS 20	AS 21
NAP	<LOQ	<LOQ	10471.68	<LOQ	<LOQ	<LOQ	3640.68	<LOQ	<LOQ	<LOQ
ACY	<LOQ	<LOQ	<LOQ	301.23	<LOQ	<LOQ	<LOQ	584.28	574.44	614.85
ACE	35.13	<LOQ	<LOQ	21.30	112.02	<LOQ	<LOQ	<LOQ	35.94	<LOQ
FLU	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PHE	2959.20	2873.79	1217.94	2176.77	2165.16	2251.20	2524.80	2796.84	1999.65	2837.25
1-MN	26.82	<LOQ	71.55	<LOQ	<LOQ	43.02	<LOQ	<LOQ	37.80	114.39
2-MN	42.87	146.10	37.41	110.94	85.02	50.97	398.94	117.03	33.81	<LOQ
ANT	<LOQ	16.89	20.01	<LOQ	12.93	<LOQ	<LOQ	<LOQ	14.46	13.71
FLT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PYR	26.88	<LOQ	<LOQ	109.95	23.64	132.30	<LOQ	69.24	176.37	<LOQ
BaA	48.63	<LOQ	<LOQ	35.64	25.05	57.81	<LOQ	<LOQ	117.45	35.31
CHR	1194.39	<LOQ	363.75	<LOQ	347.07	628.95	<LOQ	1448.13	606.51	310.29
BaP	<LOQ	<LOQ	61.23	1.68	<LOQ	126.00	<LOQ	<LOQ	<LOQ	10.77
BbFlt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.04	<LOQ	<LOQ	4.32	<LOQ
BkFlt	5.13	5.04	<LOQ	<LOQ	<LOQ	6.06	<LOQ	6.03	6.12	<LOQ
BahA	2.01	<LOQ	<LOQ	<LOQ	<LOQ	1.71	<LOQ	3.54	6.69	<LOQ
BghiPer	<LOQ	24.90	22.41	<LOQ	27.48	22.41	<LOQ	25.38	27.30	24.84
I[1,2,3-cd] PYR	1.23	3.00	2.82	<LOQ	8.16	21.12	<LOQ	0.48	16.47	<LOQ
Mean Total PAHs	4342.29	3069.72	12268.8	2757.51	2806.53	3343.59	6564.42	5050.95	3657.33	3961.41

Source: Laboratory work (2023)

Table 11: **Mean Concentrations in ng/L of PAHs (n = 3) in PW urine**

	SAMPLE ID / ng/L					
PAHs	PW1	PW2	PW3	PW4	PW5	PW6
NAP	12027.84	<LOQ	26328.33	<LOQ	58064.64	<LOQ
ACY	865.83	<LOQ	<LOQ	848.31	936.30	<LOQ
ACE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
FLU	65.55	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PHE	2500.68	2320.23	1454.19	1697.85	2242.38	2283.51
1-MN	23.13	27.24	30.63	15.18	15.21	21.00
2-MN	40.17	22.47	13.89	17.13	24.24	23.01
ANT	14.67	<LOQ	<LOQ	12.09	12.51	12.60
FLT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PYR	<LOQ	67.50	48.96	34.59	<LOQ	29.28
BaA	45.27	45.30	219.00	58.29	52.92	55.95
CHR	689.85	2139.84	<LOQ	1631.64	1582.53	1380.00
BaP	70.77	1.26	74.01	2.28	0.66	5.19
BbFlt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BkFlt	5.04	6.72	5.43	5.52	5.46	7.35
BahA	1.23	1.41	<LOQ	<LOQ	<LOQ	<LOQ
BghiPer	24.78	<LOQ	29.43	22.08	<LOQ	26.34
I[1,2,3-cd] PYR	7.53	<LOQ	25.74	17.07	<LOQ	20.22
Mean Total PAHs	16382.34	4631.97	28229.61	4362.03	62936.85	3864.45

Source: Laboratory work (2023)

Parent PAHs

Occupational exposure to PAHs is of significant concern because of the cancer and non-cancer-related effects of PAHs on human health.

From the results in Table 9, the mean total PAHs recorded ranged between 1382.73 ng/L -71916.36 ng/L. Among the thirty-two samples analysed, sample AM 25 recorded the highest mean total of 71916.36 ng/L of PAH mixture,

and sample AM 28 recorded the lowest result of 1382.73 ng/L of PAHs. Statistically, at a 95% confidence level, there was no significant difference among the individual auto-mechanic samples analysed ($p = 0.2559$). The levels of PAHs in the urine samples of AM were found to be significantly higher ($p < 0.05$) compared to the set occupational threshold value of 200 ng/L of PAHs by the National Institute for Occupational Safety and Health (NIOSH, 2010). These elevated PAH levels recorded may significantly pose health effects such as skin, lung, bladder, and kidney cancers (Kim et al., 2013); chest pain; severe abdominal pain; reproductive issues; eye and skin irritation; respiratory problems; fever; chronic headaches; liver diseases; endocrine disruption (Abdel-Shafy & Mansour, 2016); and other related diseases associated with occupational exposure to PAHs on AM workers.

The levels of B(a)P, a definite carcinogen, ranged between <LOQ - 60.57 ng/L (Table 9) in the auto-mechanics urine samples analysed. The AM workers' B(a)P levels were found to be significantly higher ($p < 0.05$) compared to the set existing limit (4.00 ng/L) set by the California Public Health Goal (PHG) (PHG, 2010), except for six samples (AM 10, 22, 23, 25, 31 and 32), which were slightly lower than the threshold limit. Elevated levels of pyrene and benzo(a)pyrene have been linked to certain cancers in humans such as liver cancer, gastric cancer, lung cancer, and bladder cancer (Kim et al., 2013). Considering the B(a)P mean concentrations for AM workers, which were significantly higher compared to the PHG set threshold limit of B(a)P, these elevated levels recorded may pose serious carcinogenic and non-carcinogenic risks to AM artisans. But for those six

samples, which recorded mean concentrations a little lower compared to the PHG set limit of B(a)P, levels recorded may not pose serious health challenges on those six AM artisans.

From the results in Table 10, elevated levels of PAHs were recorded for all the auto-sprayers urine samples analysed. The mean total PAHs recorded ranged between 1703.04 ng/L - 12268.80 ng/L. Statistically, there was no significant difference among the individual auto-sprayer samples analysed ($p = 0.7807$) at the 95% CL. For the twenty-one samples analysed, sample AS 14 recorded the highest mean total of 12268.80 ng/L of PAH mixture, and sample AS 7 recorded the lowest mean total of 1703.04 ng/L of PAHs. The recorded mean concentrations of PAHs in the urine samples of AS were found to be significantly higher ($P < 0.05$) compared to the set occupational threshold value of 200 ng/L of PAHs set by the National Institute for Occupational Safety and Health (NIOSH, 2010). These elevated concentrations recorded may pose health challenges to AS workers, both carcinogenic and non-carcinogenic risks.

The levels of B(a)P ranged between <LOQ - 200.37 ng/L (Table 10) in the auto-sprayer urine samples analysed. The AS workers' B(a)P levels were found to be significantly lower ($p > 0.05$) compared to the existing limit (4.00 ng/L) set by the California Public Health Goal (PHG) (PHG, 2010). Exception of the following eight samples: (AS 2, 3, 8, 10, 11, 14, 17 and 21), which recorded significantly higher ($p < 0.05$) concentrations compared to the set limit (4.00ng/L) by the PHG. The levels recorded showed that auto-sprayers may have low health risk as far as exposure to B(a)P was concerned since the level of concentrations

recorded for B(a)P fell below the threshold limit. But those eight AS artisans whose samples recorded elevated levels, may suffer from health effects associated with B(a)P exposure, both carcinogenic and non-carcinogenic diseases.

Also, inferring from Table 11, the mean total PAHs recorded for plastic welders ranged between 3864.45 - 62936.85 ng/L. Statistically, there was no significant difference among the individual plastic welder samples analysed ($p = 0.4227$). For the six samples analysed, sample PW 5 recorded the highest mean total of 62936. 85 ng/L and sample PW 6 recorded the lowest result of 3864.45 ng/L of PAHs, respectively. The levels of PAHs in the urine samples for PW were found to be significantly higher ($p < 0.05$) compared to the set occupational threshold value of 200 ng/L for total PAHs set by the National Institute for Occupational Safety and Health (NIOSH, 2010). These elevated concentrations recorded may pose health issues on PW workers, both carcinogenic and non-carcinogenic risks (Kim et al., 2013).

The levels of B(a)P ranged between 0.66 to 74.01ng/L (Table 11) in the plastic welder's urine samples analysed. The samples (PW 1, 3 and 6) for PW workers' B(a)P results were found to be averagely higher ($p < 0.05$) compared to the existing limit (4.00 ng/L) set by the California Public Health Goal (PHG) (PHG, 2010). The remaining samples recorded mean concentrations lower than the set limit by PHG. The B(a)P results recorded for plastic welders may pose slight health effects on PW workers.

Considering the trend of the PAH levels recorded in this study for the three different working artisans, statistically, there was a significant difference

among the artisan group samples analysed (p = 0. 01368). The trend in the hierarchical order was AM > AS > PW, respectively (Tables 9, 10 and 11). The significantly high levels of PAHs in the auto-mechanics from the Siwdu auto-mechanical workshop may be attributed to the fact that the auto-mechanic workers were directly exposed to high concentrations of PAH contaminants from fuels and oils, exhaust fumes and dust particles that contain PAHs at their workshops due to poor usage of PPE and poor safety culture. There is, thus, a cause for concern about the safety measures in the various auto-mechanical shops in Ghana, especially among artisanal auto-mechanical workers in Siwdu, Cape Coast.

In general, the levels of PAHs absorbed and the OH-P all present in the urine of individual artisanal recorded a significantly poor correlation (r = < 0.2), which suggests that the metabolism of parent PAHs is independent of the amount of P-PAHs absorbed but may depend on individual's metabolic system.

Also, the levels of PAHs absorbed and the metabolites (OH-P) all present in the urine of individual artisanal recorded a moderate significantly correlation (r = 0.4) which suggests that the elevated levels of PAHs and OH-P concentrations were somehow dependent on the number of duration (age) of exposure to PAHs sources at workshop.

Furthermore, the results of this study are comparable to that of similar work in literature where Dhananjayan & Narayana (2023) reported (20.00 to 184710.00 ng/L) values on occupational exposure to PAHs (Dhananjayan & Narayana, 2023). This study is also comparable to similar work conducted by

Burstyn et al.(2002) in Norway for asphalt workers, where the levels recorded ranged from 3.00 to 150000.00 ng/L PAHs (Burstyn et al., 2002). Again, the study was in line with other work reported in literature by Järvholm et al.(1999) on the level of total PAHs observed among Swedish road paving workers, which ranged between 200.00 - 23800 ng/L (Järvholm et al., 1999) and the results reported by McClean et al.(2004) where values ranging from 2800 to 43000.00 ng/L among asphalt paver workers were found (Mcclean et al., 2004). Comparably, the mean total PAH levels recorded in this study were somehow significantly higher ($p < 0.05$) compared with what has been reported in the above studies.

The elevated levels in this study for Ghana's auto-mechanical artisans in Siwdu, Cape Coast, may be attributed to the fact that the PAHs may have gotten into their system through dermal routes as a result of poor usage of PPE and poor safety culture of the artisans at the workshops. Therefore, long term exposure to hazardous PAHs may result in adverse health effects on auto-mechanical workers. These may increase cancers and other related diseases among Ghana's auto-mechanical workers if the necessary measures on occupational health and safety are not put in place at artisans' workshops by stakeholders to safeguard their health. These may result in reduced productivity among Ghana's artisans in Cape Coast since most of these working forces are youths with strong energy for maximum productivity in the mechanical sector. These may affect the country's economy if care is not taken to minimize exposure levels of hazardous PAHs at various mechanical workshops across the country.

Table 12: **Carcinogenic and Mutagenic Risk levels for PAH-metabolites in urine of AM (n = 3)**

SAMPLE ID	$DD_{1\text{-}OHP}$, (mg/kg-day) for cancer	Carcinogenic risk	DD_{OHP}, (mg/kg-day) for Mutagenic	Mutagenic risk
AM 1	5.4E-07	4E-06	2.2E-06	2E-05
AM 2	8.7E-07	6E-06	1.6E-06	1E-05
AM 3	5.4E-07	4E-06	4.5E-06	3E-05
AM 4	1.5E-07	1E-06	1.4E-06	1E-05
AM 5	1.8E-06	1E-05	4.7E-06	3E-05
AM 6	5.4E-07	4E-06	1.5E-06	1E-05
AM 7	1.2E-07	8E-07	4.0-06	3E-05
AM 8	5.4E-07	4E-06	3.8E-06	3E-05
AM 9	1.9E-06	1E-05	7.0E-06	5E-05
AM 10	5.5E-07	4E-06	3.0E-06	2E-05
AM 11	5.4E-07	4E-06	1.9E-06	1E-05
AM 12	1.3E-06	1E-05	5.2E-06	4E-05
AM 13	2.3E-07	2E-06	1.2E-06	9E-06
AM 14	5.4E-07	4E-06	4.0E-06	3E-05
AM 15	5.4E-07	4E-06	3.2E-06	2E-05
AM 16	5.4E-07	4E-06	2.5E-06	2E-05
AM 17	2.0E-05	1E-04	2.5E-05	2E-04
AM 18	5.4E-07	4E-06	2.3E-06	2E-05
AM 19	5.4E-07	4E-06	1.3E-06	1E-05
AM 20	9.0E-07	7E-06	2.6E-06	2E-05
AM 21	5.4E-07	4E-06	4.9E-06	4E-05
AM 22	5.4E-07	4E-06	4.3E-05	3E-04
AM 23	1.3E-06	9E-06	8.5E-06	6E-05
AM 24	4.4E-07	3E-06	4.7E-06	3E-05
AM 25	3.0E-06	2E-05	5.9E-06	4E-05
AM 26	5.8E-08	4E-07	8.1E-05	6E-04
AM 27	6.0E-06	4E-05	1.6E-05	1E-04
AM 28	5.4E-07	4E-06	2.4E-06	2E-05
AM 29	1.7E-07	1E-06	1.7E-06	1E-05
AM 30	2.1E-06	2E-05	3.2E-06	2E-05
AM 31	2.0E-07	1E-06	5.1E-07	4E-06
AM 32	5.4E-07	4E-06	2.1E-06	2E-05

Source: Laboratory work (2023)

Table 13: **Carcinogenic and Mutagenic Risk levels for PAH-metabolites in urine of AS (n = 3)**

SAMPLE ID	$DD_{1\text{-}OHP}$, (mg/kg-day) for cancer	Carcinogenic risk	DD_{OHP}, (mg/kg-day) for Mutagenic	Mutagenic risk
AS 1	5.4E-07	4E-06	1.1E-06	8E-06
AS 2	5.4E-07	4E-06	4.0E-06	3E-05
AS 3	1.2E-07	8E-07	5.3E-06	4E-05
AS 4	5.4E-07	4E-06	8.4E-07	6E-06
AS 5	1.7E-07	1E-06	5.0E-07	4E-06
AS 6	5.4E-07	4E-06	1.2E-06	9E-06
AS 7	5.4E-07	4E-06	8.9E-07	7E-06
AS 8	3.5E-07	3E-06	4.6E-06	3E-05
AS 9	3.3E-07	2E-06	5.7E-06	4E-05
AS 10	5.4E-07	4E-06	2.2E-05	2E-04
AS 11	5.4E-07	4E-06	6.0E-06	4E-05
AS 12	8.7E-08	6E-07	1.2E-06	9E-06
AS 13	5.4E-07	4E-06	3.3E-06	2E-05
AS 14	5.4E-07	4E-06	5.9E-06	4E-05
AS 15	5.4E-07	4E-06	4.5E-06	3E-05
AS 16	5.4E-07	4E-06	4.8E-06	3E-05
AS 17	1.2E-06	8E-06	6.7E-06	5E-05
AS 18	5.4E-07	4E-06	6.7E-06	5E-05
AS 19	9.0E-07	7E-06	1.2E-06	9E-06
AS 20	4.1E-06	3E-05	7.9E-06	6E-05
AS 21	5.0E-06	4E-05	9.3E-06	7E-05

Source: Laboratory work (2023)

Table 14: **Carcinogenic and Mutagenic Risk levels for PAH-metabolites in urine of PW (n = 3)**

SAMPLE ID	$DD_{1\text{-}OHP}$ (mg/kg-day) for cancer	Carcinogenic risk	DD_{OHP}, (mg/kg-day) for mutagenic	Mutagenic risk
PW 1	5.4E-07	4E-06	8.8E-07	6E-06
PW 2	1.1E-06	8E-06	3.4E-06	2E-05
PW 3	4.5E-06	3E-05	5.7E-06	4E-05
PW 4	5.4E-07	4E-06	3.3E-06	2E-05
PW 5	5.4E-07	4E-06	8.1E-06	6E-05
PW 6	4.1E-07	3E-06	9.5E-07	7E-06

Source: Laboratory work (2023)

Human Health Risk Assessment

Cancer Risk on PAH-metabolite (1-hydroxypyrene)

From Table 12, the daily dose for PAH metabolite (1-OHP) for an adult upon 70 years of lifetime exposure to PAHs per the levels in the urine of auto-mechanics ranged between 5.8×10^{-8} - 2.0×10^{-5} mg/kg-day, and their respective cancer risks recorded to be between 4.0×10^{-7} - 1.0×10^{-4}. The sample AM 17 had an elevated cancer risk value of 1.0×10^{-4}, which was the same as the USEPA upper bound value of 10^{-4} for cancer risk, and the samples AM 5, 9, 12, 25, 27, and AM 30 had elevated risk levels that were all, above the USEPA moderate-bound cancer risk level of 10^{-5}. The remaining samples had cancer risk levels ranging from 1.0×10^{-6} to 9.0×10^{-6}, respectively, which were above the EPA lower bound value of 10^{-6} (EPA, 2004), with the exception of AM 7 and AM 26, which had cancer risks below the USEPA lower bound value of 10^{-6}, which is considered negligible cancer risk (Table 12).

These elevated risk levels imply that there is more than 1 chance in 10,000 (in the case of sample AM 7) and 1 to 4 chances in 100,000 (in the case of samples AM 5, 9, 12, 25, 27, and AM 30) of increased cancer risk for cases such as lung, stomach, bladder, prostate, kidney, and other cancers (Kumar et al., 2016; Moorthy et al., 2015) in a 70-year lifetime exposure to the PAHs at their workshops. The risk levels for the remaining samples also suggest that there are more than 1 to 9 chances in 10^6 of increased cancer risks in an adult's lifetime of 70 years of exposure to the PAHs. The levels are suggestive of a possible increase in cancer incidences in Ghana as a result of exposure to elevated PAH concentrations, especially among artisanal auto-mechanics workers.

Also, inferring from Table 13, the daily dose for 1-OHP for an adult upon 70 years of lifetime exposure to PAHs per the levels in the urine of auto-sprayers ranged from 8.7×10^{-8} to 5.0×10^{-6} mg/kg-day, and their respective cancer risk levels recorded were between 6.0×10^{-7} - 4.0×10^{-5}. The samples AS 20 and AS 21 had risk levels that were all, respectively, above the USEPA moderate-bound excess cancer risk levels of 10^{-5}. The remaining samples had cancer risk levels ranging from 1.0×10^{-6} to 8.0×10^{-6}, respectively, which were above the EPA lower bound value of 10^{-6}, with the exception of AS 3 and AS 12, which had cancer risks below the USEPA acceptable lower bound value of 10^{-6}, which is regarded as negligible cancer risk (Table 13).

These cancer risk levels imply that there are more than 3 to 4 chances in 100,000 (in the case of samples AS 20 and AS 21) of increased carcinogenic health issues (Moorthy et al., 2015) in a 70-year lifetime exposure to the PAHs at

their workshops. The risk levels for the remaining samples also suggest that there are more than 1 to 8 chances in 10^6 of increased cancer incidences in an adult's lifetime of 70 years of exposure to the PAHs. The levels imply there may be a possible increase in cancer cases in Ghana, especially among the auto-sprayer artisans in Cape Coast. There is a cause for concern by stakeholders for the safety of these working groups in the country.

Furthermore, considering Table 14, the cancer risks for PAH metabolite (1-OHP) in the urine samples computed for an adult upon 70 years of lifetime exposure to PAHs for plastic welders ranged from 3.0×10^{-6} to 3.0×10^{-5}, and their respective daily dose recorded between 4.07×10^{-7} - 4.53×10^{-6} mg/kg/day. The PW 3 sample had a cancer risk value of 3.0×10^{-5}, which was above the USEPA and WHO moderate-bound excess cancer risk level of 10^{-5}. The remaining samples had cancer risk levels ranging from 3.0×10^{-6} to 8.0×10^{-6}, respectively, which were above the EPA lower bound value of 10^{-6} (Table 14). The cancer risk level implies that there are more than 3 chances in 100,000 (in the case of the sample PW 3) of increased cancer incidence for a 70-year lifetime exposure to the PAHs at their workshops. The risk levels for the remaining samples also suggested that there are more than 3 to 8 chances in 10^6 of increased cancer incidences in an adult's lifetime of 70 years of exposure to the PAHs. The risk levels are suggestive of possible increased cancer cases in Ghana among plastic welders in Cape Coast as a result of exposure to PAHs.

Furthermore, considering the trend of the 1-hydroxyprene cancer risk level results in this study among the three different artisans, statistically, there was a

significant difference among the artisans' group samples analysed, hierarchically on the average, the trend is as follows AM > AS > PW, respectively (Tables 12, 13, and 14). The results imply that there may be more possible cancer cases reported among the auto-mechanic artisans in Cape Coast than the remaining different groups of artisans at the workshop. It is thus imperative that all stakeholders take urgent action in the auto-mechanical sector to amend the situation to safeguard the health of the mechanics.

Mutagenic Risks on PAH Metabolites

From Table 12, the mutagenic risk levels computed for PAH metabolites (OH-PAHs) in the urine of AM upon 70 years of lifetime exposure to PAHs ranged between 4.0×10^{-6} - 6.0×10^{-4}, and their respective daily doses for PAH recorded were between 5.11×10^{-7} - 8.09×10^{-5} mg/kg-day. The samples AM 17, 22, 26, and AM 27 had associated elevated mutagenic risk values ranging between 1.0×10^{-4} - 6.0×10^{-4} (Table 12). These risk levels were above the USEPA acceptable upper bound value of 10^{-4}. The remaining samples had elevated risk levels ($> 10^{-5}$), with the exception of AM 13 and AM 31, which had 9.0×10^{-6} and 4.0×10^{-6} mutagenic risk levels that were respectively above the EPA acceptable lower bound value of 10^{-6} (EPA, 2004). These elevated risk levels imply that there is more than 1 chance in 10,000 (in the case of samples AM 17, 22, 26, and AM 27) and 1 chance in 100,000 (in the case of the remaining samples, with the exception of AM 13 and AM 31), of increased mutagenic issues such as liver and kidney damage, severe headache, body pain, severe body

itching, eye issues, and other non-cancer related diseases in a 70-year lifetime exposure to the PAHs at the workshops. The elevated risk levels for AM 13 and AM 31 also suggest that there are more than 4 to 9 chances in 10^6 of developing mutagenic effects in an adult's lifetime of 70 years of exposure to the PAHs. These may be linked to the severe headaches frequently experienced by the workers as found from the questionnaire. These elevated levels are suggestive of a possible increase in non-cancer issues in Ghana among auto-mechanic workers, especially in Cape Coast, upon exposure to PAHs. There is cause for concern by the stakeholders.

Also, from Table 13, the daily dose computed for OH-PAHs in the urine of AS upon 70 years of lifetime exposure to PAHs ranged between 5.04×10^{-7} - 2.19×10^{-5} mg/kg-day, and their respective mutagenic risk levels recorded were between 4.0×10^{-6} - 2.0×10^{-4}. The sample AS 10 had a very high mutagenic risk value of 2.0×10^{-4}, which was significantly above the USEPA acceptable upper bound value of 10^{-4}. The remaining samples had elevated risk levels that were all respectively above the USEPA moderate-bound excess mutagenic risk level of 10^{-5}. Except for the following samples: AS 1, 4, 5, 6, 7, 12, and AS 19, which recorded mutagenic risk levels ranging from 4.0×10^{-6} to 9.0×10^{-6}, respectively. These risk levels recorded were above the EPA acceptable lower bound value of 10^{-6} (EPA, 2004) (Table 13).

These elevated risk levels imply that there is more than 1 chance in 10,000 (in the case of sample AS 10) and 3 to 7 chances in 100,000 (in the case of the remaining samples, with the exception of AS 1, 4, 5, 6, 7, 12, and AS 19) of

developing the mutagenic incidences mentioned above in a 70-year lifetime exposure to the PAHs at their workshops. The elevated risk levels for AS 1, 4, 5, 6, 7, 12, and AS 19 also suggest that there are more than 4 to 9 chances in 10^6 of developing mutagenic effects in an adult's lifetime of 70 years of exposure to the PAHs. These elevated results are suggestive of a possible increase in non-cancer related cases in Ghana among auto-sprayer workers in Ghana as a result of exposure to elevated PAH concentrations. Some of the risk levels are quite alarming and call for urgent attention to help safeguard the health of such workers.

Moreover, the daily dose for PAH metabolites (OH-PAHs) in the urine of PW for 70 years of lifetime exposure to PAHs ranged from 8.75×10^{-7} to 8.05×10^{-5} mg/kg-day, and their respective mutagenic risks were found to be between 6.0×10^{-6} - 6.0×10^{-5} for PW 1 to PW 6, respectively (Table 14). The samples PW 2 to PW 5 had elevated risk levels, which were all above the USEPA moderate-bound excess mutagenic risk level of 10^{-5}. Samples PW 1 and PW 6 also had risk values of 6.0×10^{-6} and $7.0 \times 10^{-6,}$ respectively, which were above the EPA acceptable lower bound value of 10^{-6} (Table 14).

These elevated mutagenic risk levels imply that there are more than 2 to 6 chances in 100,000 (in the case of samples PW 2 to PW 5) and 6 to 7 chances in 10^6 (in the case of samples PW 1 and PW 6) of increased mutagenic incidences in a 70-years lifetime exposure to the hazardous PAHs at the workshops. These elevated levels imply that there may be a possible elevation of mutagenic cases in

Ghana among the plastic welders, especially in Cape Coast, as a result of exposure to PAH mixtures.

Also, considering the trend of the mutagenic risk level results in this work among the three different auto-artisans studied, statistically, there was a significant difference among the artisanal mechanical workers' group samples analysed. The average hierarchical order of trend is as follows AM > AS > PW (Tables12, 13, and 14). The levels are suggestive that there may be increased mutagenic incidences reported among the auto-mechanic artisans than the other different groups of artisans at workshops, which is attributed to the fact that the AM workers are exposed to a very high concentration of PAHs at the workshops.

Table 15: **Carcinogenic and Mutagenic Risk levels for P-PAHs in urine of AM (n=3)**

SAMPLE ID	DD_{BaP}, (mg/kg-day) for cancer	Carcinogenic risk	DD_{BaP}, (mg/kg-day) for Mutagenic	Mutagenic risk
AM 1	4.47E-07	3E-06	7.18E-07	5E-06
AM 2	3.17E-07	2E-06	9.42E-07	7E-06
AM 3	4.42E-07	3E-06	1.07E-06	8E-06
AM 4	3.17E-07	2E-06	6.83E-07	5E-06
AM 5	5.02E-07	4E-06	1.93E-06	1E-05
AM 6	5.07E-07	4E-06	9.89E-07	7E-06
AM 7	1.78E-07	1E-06	2.28E-07	2E-06
AM 8	3.00E-07	2E-06	9.70E-07	7E-06
AM 9	4.84E-07	4E-06	5.20E-07	4E-06
AM 10	2.56E-07	2E-06	5.51E-07	4E-06
AM 11	4.47E-07	3E-06	1.29E-06	9E-06
AM 12	3.36E-07	2E-06	9.52E-07	7E-06
AM 13	3.49E-07	3E-06	7.57E-07	6E-06
AM 14	2.59E-07	2E-06	4.92E-07	4E-06
AM 15	4.06E-07	3E-06	7.74E-07	6E-06
AM 16	6.33E-07	5E-06	1.03E-06	8E-06
AM 17	2.57E-07	2E-06	7.63E-07	6E-06
AM 18	4.56E-07	3E-06	5.81E-07	4E-06
AM 19	2.33E-07	2E-06	5.69E-07	4E-06
AM 20	2.92E-07	2E-06	4.10E-07	3E-06
AM 21	2.72E-07	2E-06	4.54E-07	3E-06
AM 22	1.69E-07	1E-06	4.23E-07	3E-06
AM 23	2.09E-07	2E-06	4.32E-07	3E-06
AM 24	1.96E-07	1E-06	3.14E-07	2E-06
AM 25	1.79E-07	1E-06	3.52E-07	3E-06
AM 26	2.60E-07	2E-06	4.05E-07	3E-06
AM 27	5.98E-07	4E-06	6.61E-07	5E-06
AM 28	2.55E-07	2E-06	4.66E-07	3E-06
AM 29	6.26E-07	5E-06	7.22E-07	5E-06
AM 30	7.50E-07	5E-06	9.60E-07	7E-06
AM 31	1.00E-06	7E-06	1.22E-06	9E-06
AM 32	9.33E-07	7E-06	1.02E-06	7E-06

Source: Laboratory work (2023)

Table 16: **Carcinogenic and Mutagenic Risk levels for P-PAHs in urine of AS (n = 3)**

SAMPLE ID	DD_{BaP}, (mg/kg-day) for cancer	Carcinogenic risk	DD_{BaP}, (mg/kg-day) for Mutagenic	Mutagenic risk
AS 1	9.51E-07	7E-06	1.23E-06	9E-06
AS 2	8.16E-07	6E-06	1.09E-06	8E-06
AS 3	2.07E-06	2E-05	2.32E-06	2E-05
AS 4	8.42E-07	6E-06	9.96E-07	7E-06
AS 5	1.85E-07	1E-06	4.00E-07	3E-06
AS 6	1.50E-07	1E-06	3.92E-07	3E-06
AS 7	1.82E-07	1E-06	4.00E-07	3E-06
AS 8	1.68E-06	1E-05	1.71E-06	1E-05
AS 9	9.50E-07	7E-06	1.17E-06	9E-06
AS 10	1.43E-06	1E-05	1.48E-06	1E-05
AS 11	4.97E-07	4E-06	5.77E-07	4E-06
AS 12	8.65E-07	6E-06	1.05E-06	8E-06
AS 13	8.96E-07	7E-06	1.01E-06	7E-06
AS 14	7.15E-07	5E-06	8.14E-07	6E-06
AS 15	1.85E-07	1E-06	4.65E-07	3E-06
AS 16	8.85E-07	6E-06	9.95E-07	7E-06
AS 17	1.32E-06	1E-05	1.45E-06	1E-05
AS 18	9.51E-07	7E-06	1.23E-06	9E-06
AS 19	8.76E-07	6E-06	1.09E-06	8E-06
AS 20	9.80E-07	7E-06	1.05E-06	8E-06
AS 21	2.17E-07	2E-06	3.03E-07	2E-06

Source: Laboratory work (2023)

Table 17: **Carcinogenic and Mutagenic Risk levels for P-PAHs in urine of PW (n = 3)**

SAMPLE ID	DD_{BaP}, (mg/kg-day) for cancer	Carcinogenic risk	DD_{BaP} (mg/kg-day) for mutagenic	Mutagenic risk
PW 1	7.66E-07	6E-06	1.74E-06	1E-05
PW 2	1.53E-07	1E-06	1.44E-06	1E-05
PW 3	1.03E-06	8E-06	2.01E-06	1E-05
PW 4	1.79E-07	1E-06	1.29E-06	9E-06
PW 5	9.61E-07	7E-06	2.13E-06	2E-05
PW 6	2.06E-07	2E-06	1.28E-06	9E-06

Source: Laboratory work (2023)

Cancer Risks for Parent-PAHs in urine samples

The estimated daily dose (DD) for PAH mixture in the urine samples of auto-mechanics ranged from 1.69×10^{-7} to 1.00×10^{-6} mg/kg-day. Sample AM 31 recorded the highest daily dose of 1.00×10^{-6} mg/kg-day, and sample AM 22 recorded the lowest daily dose of 1.69×10^{-7} mg/kg-day. The respective cancer risk levels for adults' lifetime of 70 years were also found to range from 1.0×10^{-6} to 7.0×10^{-6} for AM workers (Table 15). From the risk levels, it was found that auto-mechanics have lower risk compared to the acceptable reference value of 1.0×10^{-6} to 1.0×10^{-4} for cancer (EPA, 2004). The risk levels for AM workers recorded suggest that the AM workers have more than 1.0 to 7 chances in 10^6 of developing cancer in an adult's lifetime of 70 years of occupational exposure to high levels of PAHs at their workshops. The recorded risk levels for AM workers are considered to be low cancer risk according to the USEPA set reference value for low-bound risk units. The results on the cancer risk levels for auto-mechanic

artisans imply that there may be a slight upsurge in cancer incidences in Ghana, especially among the AM people in Cape Coast.

From Table 16, the cancer risk levels in the urine of AS upon 70 years of lifetime exposure to PAHs ranged from 1.0×10^{-6} to 2.0×10^{-5}, and their respective daily doses for the PAH mixture were recorded to be between 1.50×10^{-7} - 2.07×10^{-6} mg/kg/day. Comparing the risk levels found for AS workers to that USEPA reference value of 1.0×10^{-6} to 1.0×10^{-4} (EPA, 2004) showed that almost all the people were at relatively low risk of cancer, with the exception of AS 8, 10, and 17, who recorded cancer levels of 1.0×10^{-5}, and sample AS 3, which recorded a mid-cancer risk level of 2.0×10^{-5} among the samples analysed for auto-sprayers. These elevated risk levels imply that there are more than 2 chances in 100,000 (in the case of sample AS 3) and 1 chance in 100,000 (in the case of samples AS 8, 10, and 17, respectively) of increased cancer cases such as lung, skin cancer, and other cancers in a 70-year lifetime exposure to the hazardous PAHs at the workshops (Abdel-Shafy & Mansour, 2016). The remaining cancer risk levels recorded for AS workers also suggest that those people have more than 1.0 to 7 chances in 10^6 of developing cancer in an adult's lifetime of 70 years of exposure to PAHs at their various workshops, which is considered to be relatively low cancer risk according to USEPA reference value for lower-bound risk units. The results on the cancer risk levels for artisanal auto-sprayers imply that those groups of AS workers may contribute moderately to an upsurge in cancer incidences in Ghana.

The daily dose (DD) for PAH mixture in the urine samples of plastic welders was found to range from 1.53×10^{-7} to 1.03×10^{-6} mg/kg/day, and the respective cancer risk levels for adults' lifetime of 70 years were also found to be between 1.0×10^{-6} - 8.0×10^{-6} for plastic welders (Table 17). Considering the risk levels recorded for PW, it was found that upon their exposure to PAHs, cancer risk levels were lower ($p > 0.05$) compared to the acceptable reference value of 1.0×10^{-6} to 1.0×10^{-4} for cancer (EPA, 2004). The risk levels for PW workers recorded suggest that the people may have more than 1.0 to 8 chances in 10^6 of developing cancer in an adult's lifetime of 70 years of occupational exposure to elevated levels of PAHs at the workshops, which is considered to be low cancer risk according to USEPA reference value for lower-bound risk units. Therefore, the cancer risk levels for PW artisans imply that those groups of PW workers may contribute to the very low rate of an upsurge in cancer incidences in Ghana, especially among the plastic welder workers in Cape Coast.

Also, comparing the parent PAHs cancer risk level results in this study among the three different artisans studied, the levels were recorded as follows: for AM (1.0×10^{-6} to 7.0×10^{-6}), AS (1.0×10^{-6} to 2.0×10^{-5}) and PW (1.0×10^{-6} to 8.0×10^{-6}) as their respective cancer risk levels of PAHs. Inferring from Table 16, the individual risk levels analysed for AS workers were averagely highly significant ($P < 0.05$) compared to AM and PW workers' cancer risk levels determined from their urine samples. On the other hand, the risk levels recorded for the respective auto-mechanics sample were higher compared to the individual sample risk levels determined for PW workers (Table 15). The results imply that

there may be more cancer cases recorded among the artisanal auto-sprayers than the other different groups of artisans at workshops.

These results, when combined with that of the metabolites, showed an increased risk of cancer among the artisans studied. This, therefore, calls for urgent attention by all stakeholders to help ameliorate the situation.

Mutagenic Risk for Parent-PAHs

The mutagenic daily dose (DD) for PAH mixture in the urine samples of auto-mechanics was found to range from 3.14×10^{-7} to 1.93×10^{-6} mg/kg/day, and the respective mutagenic risk levels for adults' lifetime of 70 years were also found to range from 2.0×10^{-6} to 1.0×10^{-5} for AM (Table 15). From the levels recorded for AM, it was found that for auto-mechanics upon their exposure to PAHs, mutagenic risk levels were considered to be low compared to the acceptable reference value of 1.0×10^{-6} to 1.0×10^{-4} for mutagenic risk (EPA, 2004). The risk levels for AM workers recorded imply that the people may have more than 2.0 to 9 chances in 10^6 of increased mutagenic risks in an adult's lifetime of 70 years of occupational exposure to PAHs at the workshops. The levels for AM workers are considered to be low mutagenic risk according to the USEPA set reference value for lower bound risk unit, with the exception of sample AM 5, which recorded the highest mutagenic risk of 1.0×10^{-5}, also implying that the individual is having more than 1 chance in 100,000 of developing non-carcinogenic effects such as eyes and skin irritation, severe headache (Dhananjayan & Narayana, 2023), chest and abdominal pain,

reproductive disorders, and other diseases (Kim et al., 2013). The results on the mutagenic risk levels for artisanal auto-mechanics imply that those groups of AM workers may contribute to an upsurge in non-carcinogenic incidences in Ghana.

From Table 16, the mutagenic risk levels involved upon 70 years of lifetime exposure to PAHs in the urine samples of auto-sprayers range between 2.0×10^{-6} and 2.0×10^{-5}, and their respective daily doses for the PAH mixture were recorded between 3.03×10^{-7} and 2.32×10^{-6} mg/kg/day. Comparing the mutagenic risk levels found for AS workers to the USEPA acceptable reference limit of 1.0×10^{-6} to 1.0×10^{-4} for mutagenic (EPA, 2004) showed that almost all the people were at low mutagenic risk, with the exception of AS 8, 10, and 17, which recorded mid-elevated mutagenic levels of 1.0×10^{-5}, and sample AS 3 recorded a high mutagenic risk level of 2.0×10^{-5} among the samples analysed for auto-sprayers. These elevated risk levels imply that there are more than 2 chances in 100,000 (in the case of sample AS 3) and 1 chance in 100,000 (in the case of samples AS 8, 10, and 17, respectively) of increased non-cancer effects such as nausea, vomiting, diarrhoea, liver, and kidney damage (Kumar et al., 2016), and other diseases in a 70-year lifetime exposure to hazardous PAHs at the workshops. The remaining mutagenic risk levels recorded from AS urine samples also suggest those people have more than 2 to 9 chances in 10^6 of developing mutagenic risks in an adult's lifetime of 70 years of exposure to PAHs at the various workshops, which is considered to be low mutagenic risk according to USEPA reference value for lower-bound risk units. Therefore, the results on the

mutagenic risk levels for auto-sprayer artisans imply that those AS workers may contribute moderately to an upsurge in mutagenic cases in Ghana.

Moreover, for Table 17, the mutagenic risk levels involved upon 70 years of lifetime exposure to PAHs per the levels in the urine of plastic welders ranged from 9.0×10^{-6} to 2.0×10^{-5}, and their respective daily doses for the PAH mixture range from 1.28×10^{-6} to 2.13×10^{-6} mg/kg/day. Comparing the mutagenic risk levels found for plastic welders to the acceptable reference limit of 1.0×10^{-6} to 1.0×10^{-4} for mutagenic showed that two of the people were at moderate mutagenic risk, and the remaining plastic welders in PW 1, 2, and 3 recorded mid-high elevated mutagenic levels of 1.0×10^{-5}, respectively, and sample PW 5 recorded a high mutagenic risk level of 2.0×10^{-5} among the samples analyzed for PW workers. The elevated risk levels imply that there are more than 2 chances in 100,000 (in the case of sample PW 5) and 1 chance in 100,000 (in the case of samples PW 1, 2, and 3, respectively) of developing non-carcinogenic health issues in a 70-year lifetime exposure to PAHs at the workshops. The remaining mutagenic risk levels recorded for PW also suggest that those individuals may have more than 9 chances in 10^6 of developing mutagenic risks in an adult's 70 years of exposure to high PAHs at the various workshops, which is considered to be low mutagenic risk according to reference value for low-bound risk units. The results on the mutagenic risk levels for plastic welder artisans imply that those groups of PW workers may contribute to an upsurge in non-carcinogenic incidences in Ghana.

Finally, comparing the mutagenic risk results in this study among the three different artisans studied, the levels were recorded as follows: for AM (2.0×10^{-6} to 1.0×10^{-5}), AS (2.0×10^{-6} to 2.0×10^{-5}) and PW (9.0×10^{-6} to 2.0×10^{-5}) as their respective mutagenic risk levels of PAH mixture. Inferring from Table 16, the individual levels analysed for AS workers were statistically highly significant ($P < 0.05$) compared to PW and AM workers' mutagenic risk levels found in their urine samples. On the other hand, the mutagenic risk levels recorded for individual samples of plastic welders were high compared to AM workers' sample levels (Table 17). The elevated levels suggest that there may be higher mutagenic issues recorded among the artisanal auto-sprayers than the other different groups of artisans at workshops.

These results, when combined with that of the metabolites mutagenic risk levels, showed an increased risk of non-cancer health effects among the artisans studied. This, therefore, calls for urgent attention by all stakeholders to help amend the situation.

Correlating the findings of the questionnaire to the risk analysis, was found from that the majority of the artisans (88.3%) entered into their various fields of work after basic education level. Considering the artisans' low level of education, most of the artisanal auto-mechanical workers may not be that knowledgeable about the hazards associated with direct exposure to exhaust fumes and other chemicals used at the workshop. Also, poor safety cultural practices, such as poor usage of PPE and siphoning diesel with the mouth, may have contributed to higher levels of exposure to PAHs of the artisans at the

workshops. These factors may be attributed to the higher risk levels obtained for the artisanal auto-mechanical workers from the instrumental analysis in this study. The situation seems alarming; there is a need for stakeholders and policymakers to devise interventions that may help the artisans work while safeguarding them at the workshop.

Chapter Summary

Levels of PAHs and metabolites determined in urine samples have been discussed. Health risk assessment and quality control results have been discussed. The occupational health and safety knowledge outcomes from the field studied have been discussed. This work has stated the need for stakeholders and policymakers to devise interventions that may help the artisans work while safety is assured.

CHAPTER FIVE

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Overview

This chapter of the study talks about conclusions, recommendations, and summaries. Conclusions were based on the objectives of this study and summarized in a general conclusion based on the main purpose of this study. Some further studies and institutional interventions were finally recommended.

Summary

The study was pinned on the health risk assessment of urinary-PAHs and their metabolites in the urine sample of artisanal auto-mechanical workers from the Siwdu auto-mechanical workshop in Cape Coast. It was observed that poor safety culture practices such as poor usage of appropriate personal protective equipment (PPE), working in an unclean environment, suction of gasoline with the mouth, gasoline-based hand washing, and applying diesel to injured body parts may contribute to the major factors of exposure to an elevated PAHs levels by auto artisanal mechanical workers through dermal contact at the workshops. These, therefore, contributed to the elevated results recorded in this study. The findings showed that poor knowledge in health and safety practices is the major contributor to the exposure levels of PAHs recorded.

Conclusions

Occupational safety addresses all facets of health and safety concerns in the workplace, with a particular emphasis on the main mitigation of risks. This study sought to identify the perception of artisanal auto-mechanical workers towards health and safety at work. From the survey, responses from the respondents showed that artisanal auto-mechanical workers' knowledge about health and safety related to their work was very low. These may have contributed to the high levels of exposure to PAHs as found with respect to the P-PAHs and their metabolites in the urine samples of the artisans.

Urinary-PAHs and their metabolites recorded in this study among auto-mechanical workers were above the occupational threshold limit of 200.00 ng/L set by the NIOSH, which may pose health effects on the artisanal auto-mechanical workers in Ghana, especially artisans in Swidu, Cape Coast.

Moreover, in this study, cancer and mutagenic risk assessment on the urinary PAHs and its metabolites upon exposure to the contaminants showed elevated risk ($> 10^{-6}$) for about 70% of the samples analysed, which may contribute to the upsurge of cancer and non-cancer cases in Ghana. The situation and the number of artisans involved were quite alarming and thus calls for immediate attention by stakeholders to help reduce the incidence.

Recommendations

Based on the above findings and the need to remedy the situation, the following recommendations were made:

1. The Occupational Health and Safety Board should come to the aid of the artisanal auto-mechanical workers to safeguard their health by formulating health and safety protocols for them at the artisanal mechanical workshops.
2. Non-governmental organizations should engage the auto-mechanical workers to provide appropriate personal protective equipment and training on proper usage of PPE at their workshops.
3. Policymakers should support researchers with funding to extend the research to a larger number of auto-mechanical workshops across the country. These would give a broader knowledge of the findings among auto-mechanical workers in Ghana to inform policies.
4. Some food vendors and children come to the workshops, so the effect of PAH exposure on those non-auto-mechanical workers should also be assessed to ascertain the impact of the environmental PAHs on their health.
5. Routine public health education should be provided to the auto-artisanal workers on occupational health and safety practices and dangers associated with direct exposure to hazardous chemicals at their workshops by Public Health Personnel and EPA Ghana.

REFERENCES

Abdel-Shafy, H. I., & Mansour, M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum, 25*(1), 107–123. https://doi.org/10.1016/j.ejpe.2015.03.011

ACGIH. (2010). *Documentation for a Recommended BEL of Polycyclic Aromatic Hydrocarbons. ACGIH, Cincinatti,OH, USA.*

Adjei, K. J., Ofori, A., Megbenu, K. H., Ahenguah, T., Boateng, K. A., Alimoh, G., Bentum, K. J., & Essumang, K. D. (2021). *Science of the Total Environment Health risk and source assessment of semi-volatile phenols , p-chloroaniline and plasticizers in plastic packaged (sachet) drinking water*. *797*. https://doi.org/10.1016/j.scitotenv.2021.149008

Adjei, K. J., Essumang , K. D., Twumasi, E., Nyame, E., & Muah, I. (2019). *Levels and risk assessment of residual phthalates , polycyclic aromatic hydrocarbons and semi-volatile chlorinated organic compounds in toilet tissue papers*. *6*(November), 1263–1272. https://doi.org/10.1016/j .toxrep .2019.11.013

Afolabi, F. J., Beer, P. De, & Haafkens, J. A. (2021). *Occupational Risk Perception and the Use of Personal Protective Equipment (PPE): A Study Among Informal Automobile Artisans in Osun*. https://doi.org/10 .1177/2158244021994585

Ahmad, I., Balkhyour, M., Ismail, I., & Rehan, M. (2017). *Workplace Safety and Health Conditions and Facilities in Small Industries in Jeddah , Saudi Arabia*. *June*. https://doi.org/10.5296/jss.v3i1.11104

Ahmad, I., Rehan, M., Balkhyour, M., & Abbas, M. (2016). *Review of Environmental Pollution and Health Risks at Motor Vehicle Repair Workshops : Challenges and Perspectives for Saudi Arabia REVIEW OF ENVIRONMENTAL POLLUTION AND HEALTH RISKS AT MOTOR VEHICLE REPAIR WORKSHOPS : CHALLENGES AND*. *May*.

Anyakora, C., & Coker, H. (2006). Determination of polynuclear aromatic hydrocarbons (PAHs) in selected water bodies in the Niger Delta Several water bodies in the Niger Delta region of Nigeria where extensive crude oil production activities take place were analyzed for the presence of 16. *African Journal of Biotechnology*, *5*(21), 2024–2031. http://www.academicjournals.org/AJB

Apreko, A. A., Danku, L. S., Selase, M., Adokou, A., & Apeletey, F. (2015). *Occupational Health and Safety Management : The Use of Personal Protective Equipment (Ppe) by Artisans in The Local Automotive Industry in Volta International Journal of Engineering Trends and Technology (IJETT) – Volume 19 Number 4 – Jan 2015 Occupat*. *December*. https://doi.org/10.14445/22315381/IJETT-V19P236

Aryee, A. A. (2016). *University of Ghana http://ugspace.ug.edu.gh LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS AND HEAVY METALS IN SURFACE SOIL AT AUTO-MECHANIC WORKSHOPS WITHIN*. *October*.

Balkhyour, M. A., Ahmad, I., & Rehan, M. (2018). Assessment of Personal Protective Equipment use and Occupational Exposures in Small Industries in Jeddah: Health Implications for Workers. *Saudi Journal of Biological Sciences*. https://doi.org/10.1016/j.sjbs.2018.06.011

Barbeau, D., Ma, A., & Marques, M. (2011). *quantitation using liquid chromatography-fluorescence detection and automated off-line solid phase extraction*. 1183–1191. https://doi.org/10.1039/c0an00428f

Biziuk, M. (2006). *Solid Phase Extraction Technique – Trends , Opportunities and Applications*. *15*(5), 677–690.

Burstyn, I., Ferrari, P., Wegh, H., Heederik, D., Kromhout, H., Burstyn, I., Ferrari, P., Wegh, H., Heederik, D., & Kromhout, H. (2002). *Characterizing Worker Exposure to Bitumen During Hot Mix Paving and Asphalt Mixing Operations. 8117*(September). https://doi.org/10.1080/15428110208984716

Chartres, N., Bero, L. A., & Norris, S. L. (2019). A review of methods used for hazard identi fi cation and risk assessment of environmental hazards. *Environment International*, *123*(October 2018), 231–239. https://doi.org/10.1016/j.envint.2018.11.060

Chhikara, B. S., Parang, K., & Etters, L. (2023). *Global Cancer Statistics 2022 : the trends projection analysis*. *10*(1), 1–16.

Dhananjayan, V., & Narayana, J. (2023). *Personal exposure to polyaromatic hydrocarbon and inhalation risk assessment among asphalt hot mixed plant and road paving workers*.

Ding, C., Ni, H. G., & Zeng, H. (2013). Human exposure to parent and halogenated polycyclic aromatic hydrocarbons via food consumption in Shenzhen, China. *Science of the Total Environment*, *443*, 857–863. https://doi.org/10.1016/j.scitotenv.2012.11.018

Djinovic, J., Popovic, A., & Jira, W. (2008a). *MEAT Polycyclic aromatic hydrocarbons (PAHs) in different types of smoked meat products from Serbia*. *80*, 449–456. https://doi.org/10.1016/j.meatsci.2008.01.008

Djinovic, J., Popovic, A., & Jira, W. (2008b). *Polycyclic aromatic hydrocarbons (PAHs) in traditional and industrial smoked beef and pork ham from Serbia*. 1191–1198. https://doi.org/10.1007/s00217-008-0836-8

Dowaidar, A. M., El-Shahawi, M. S., & Ashour, I. (2007). Adsorption of polycyclic aromatic hydrocarbons onto activated carbon from non-aqueous media: 1. the influence of the organic solvent polarity. *Separation Science and Technology*, *42*(16), 3609–3622. https://doi.org/10.1080/01496390701626537

Durant, J., Lafleur, A., Busby, W., Donhoffner, L., Penman, B., & Crespi, C. (1999). Mutagenicity of C24H14 PAH in human cells expressing CYP1A1. Mutat. Res. Genet. *Toxicol. E. M.*, *446*, 1–14.

Edwin, J., & Furtaw, J. (2001). An overview of human exposure modeling activities at the USEPA ' s National Exposure Research Laboratory y. *Toxicology and Industrial Health*, *17*, 302–314.

El-shahawi, M. S., Hamza, A., Bashammakh, A. S., & Al-saggaf, W. T. (2010). Talanta An overview on the accumulation , distribution , transformations , toxicity and analytical methods for the monitoring of persistent organic pollutants. *Talanta*, *80*(5), 1587–1597. https://doi.org/10.1016/j.talanta.2009.09.055

EPA. (1993). *Carcinogenic Polycyclic Aromatic Hydrocarbons. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons.* 28.

EPA. (2004). *Risk Assessment Guidance for Superfund: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment). 1*. EPA/540/R/99/005, OSWER 9285.7-02EP, PB99-9633, 12 July

EPA method 550.1. (1990). *Determination of Polycyclic Aromatic Hydrocarbons in Drinking water by Liquid-Solid Extraction and HPLC with Coupled Office of Research and Development. July*, 1–22.

EPA method 610. (2008). *Determination of Polyc ycl ic Aromat ic H y droc arbons (PAHs) in Municipal and Industrial Wastewater*. 17–18.

EPA method 8310. (2016). *EPA Method 8310 : Determination of Polynuclear Aromatic Hydrocarbons (PAHs) in Water and waste using HPLC-UV/RF*.

Essumang, K. D., Dodoo, D. K., & Adjei, K. J. (2013). Effect of smoke generation sources and smoke curing duration on the levels of polycyclic aromatic hydrocarbon (PAH) in different suites of fish. *Food and Chemical Toxicology*, *58*, 86–94. https://doi.org/10.1016/j.fct.2013.04.014

Fadel, M., Afif, C., & Courcot, D. (2022). *Human health risk assessment for PAHs , phthalates , elements , PCDD / Fs , and DL-PCBs in PM 2 . 5 and for NMVOCs in two East-Mediterranean urban sites under industrial influence*. *13*(November 2021). https://doi.org/10.1016/j.apr.2021.101261

Förster, A. K., Preuss, R., Roßbach, B., Brüning, T., Angerer, J., Simon, P., Occupational, S., Medicine, E., April, N., Förster, K., Preuss, R., Roßbach, B., Brüning, T., Angerer, J., & Simon, P. (2024). *polycyclic aromatic hydrocarbons in different industries Linked references are available on JSTOR for this article : 3-Hydroxybenzo [a] pyrene in the urine of workers with occupational exposure to polycyclic aromatic hydrocarbons in different industries*. *65*(4), 224–229. https://doi.org/10.1136/oem.2006.030809

Gamboa, R. T., Gamboa, A. R., Bravo, A. H., & Ostrosky, W. P. (2008). *Genotoxicity in child populations exposed to Polycyclic Aromatic Hydrocarbons (PAHs) in the air from Tabasco , Mexico*. *5*(5), 349–355.

Guinamard, R., Hof, T., & Negro, C. A. Del. (2014). *The TRPM4 channel inhibitor 9-phenanthrol*. https://doi.org/10.1111/bph.12582

Guo, W., Pan, B., Sakkiah, S., Yavas, G., Ge, W., & Zou, W. (2019). Persistent Organic Pollutants in Food : Contamination Sources , Health E ff ects and Detection Methods. *Environmental Research and Public Health*, 10–12. https://doi.org/10.3390/ijerph16224361

Hansen, M., Mathiesen, L., Pedersen, M., & Knudsen, L. E. (2008). *Urinary 1-hydroxypyrene (1-HP) in environmental and occupational studies — A review*. *211*, 471–503. https://doi.org/10.1016/j.ijheh.2007.09.012

Hoseini, M., Nabizadeh, R., & Delgado-saborit, J. M. (2018). *Environmental and lifestyle factors affecting exposure to polycyclic aromatic hydrocarbons in the general population in a Middle Eastern area*. *240*. https://doi.org/10.1016/j.envpol.2018.04.077

Hussain, K., Hoque, R. R., & Balachandran, S. (2018). *Monitoring and Risk Analysis of PAHs in the Environment Monitoring and Risk Analysis of PAHs in the Environment* (Issue January). https://doi.org/10.1007/978-3-319-58538-3

IARC. (2016). *Agents Classified by the IARC Monographs , Volumes 1 – 122*. *026148*, 1–36.

IARC. (2020). *Source: Globocan 2020*. *419*, 7–8.

IARC. (2022). *chemical agents and related occupations COAL-TAR PITCH*. *100*(October 2021).

ILO. (2022). *International Labour Organization Curriculum on Building Modern and Effective Labour Inspection Systems on Occupational safety and health*. *Module 8*.

Järvholm, B., Nordström, G., Högstedt, B., Levin, J., Scandinavian, S., Järvholm, B., Nordström, G., Högstedt, B., & Levin, J. (1999). *Exposure to polycyclic aromatic hydrocarbons and genotoxic effects on nonsmoking Swedish road pavement workers Wahlström , Conny Östman and Curt Bergendahl Published by : the Scandinavian Journal of Work , Environment & Health , the Finnish Institute of O*. *25*(April).

Johnson, O. E., & Bassey, E. A. (2016). *Work Habits and Health Problems of Automobile Technicians at Mechanic Village , Uyo , Nigeria*. *5*(5), 136–142.

Jongeneelen, F. J. (2001). *Benchmark Guideline for Urinary 1-Hydroxypyrene as Biomarker of Occupational Exposure to Polycyclic Aromatic Hydrocarbons*. *45*(1), 3–13.

Jongeneelen, F. J. (2014). *A guidance value of 1-hydroxypyrene in urine in view of acceptable occupational exposure to polycyclic aromatic hydrocarbons*. *231*, 239–248.

Kamal, A., Cincinelli, A., Martellini, T., Palchetti, I., Bettazzi, F., & Malik, R. N. (2016). Health and carcinogenic risk evaluation for cohorts exposed to PAHs in petrochemical workplaces in Rawalpindi city (Pakistan). *International Journal of Environmental Health Research*, *26*(1), 37–57. https://doi.org/10.1080/09603123.2015.1007843

Kamal, A., Cincinelli, A., Martellini, T., Palchetti, I., Malik, R. N., Kamal, A., Cincinelli, A., Martellini, T., & Palchetti, I. (2016). Health and carcinogenic risk evaluation for cohorts exposed to PAHs in petrochemical workplaces in Rawalpindi city (Pakistan). *International Journal of Environmental Health Research*, *26*(1), 37–57. https://doi.org/10.1080/09603123.2015.1007843

Kamal, A., Qamar, K., Gulfraz, M., Anwar, M. A., & Malik, R. N. (2015). PAH exposure and oxidative stress indicators of human cohorts exposed to traffic pollution in Lahore city (Pakistan). *Chemosphere*, *120*, 59–67. https://doi.org/10.1016/j.chemosphere.2014.05.021

Khatmode, R. B., Babar, R. P., & Giri, T. (2022). *A REVIEW ARTICLE ON HIGH- PERFORMANCE LIQUID*. *10*(5), 963–970.

Kim, K., Ara, S., Kabir, E., & Brown, R. J. C. (2013). Author ' s personal copy A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International*.

Klotz, K. (2021). *Polycyclic aromatic hydrocarbons (PAHs) – Evaluation of EKA and a BAR Assessment Values in Biological Material – Translation of the German version from 2013*. *2007*, 1–21.

Kumar, V., Kothiyal, N. C., Saruchi, Vikas, P., & Sharma, R. (2016). Sources, distribution, and health effect of carcinogenic polycyclic aromatic hydrocarbons (PAHs) – current knowledge and future directions. *Journal of the Chinese Advanced Materials Society*, *4*(4), 302–321. https://doi.org/10.1080/22243682.2016.1230475

Kumar, Y., Sayed, M. M., & Mustaq, A. (2018). *International Journal of Trend in Scientific Research and Development (IJTSRD) HPLC : Principle and Maintenance with Application*. 1618–1626.

León-martínez, L. D. De, Flores-ramírez, R., & Rodriguez-aguilar, M. (2021). *Analysis of urinary metabolites of polycyclic aromatic hydrocarbons in precarious workers of highly exposed occupational scenarios in Mexico*. 23087–23098.

Leroyer, A., Jeandel, F., Maitre, A., Howsam, M., Deplanque, D., Mazzuca, M., & Nisse, C. (2010). Science of the Total Environment 1-Hydroxypyrene and 3-hydroxybenzo [a] pyrene as biomarkers of exposure to PAH in various environmental exposure situations. *Science of the Total Environment, The*, *408*(5), 1166–1173. https://doi.org/10.1016/j. scitotenv. 2009.10.073

Manisalidis, I., Stavropoulou, E., Stavropoulos, A., & Bezirtzoglou, E. (2020). Environmental and Health Impacts of Air Pollution: A Review. *Frontiers in Public Health*, *8*(February), 1–13. https://doi.org/10.3389/fpubh .2020.00014

Markiewicz, A., Strömvall, A., & Björklund, K. (2020). Science of the Total Environment Alternative sorption fi lter materials effectively remove non-particulate organic pollutants from stormwater. *Science of the Total Environment*, *730*, 139059. https://doi.org/10.1016/j.scitoten v.2020.139 059

Mcclean, M. D., Rinehart, R. D., Ngo, L., & Eisen, E. A. (2004). *Inhalation and Dermal Exposure among Asphalt Paving Workers*. *48*(8), 663–671. https://doi.org/10.1093/annhyg/meh062

Monney, I., Bismark, D., & Isaac, O. (2014). *Occupational health and safety practices among vehicle repair artisans in an urban area in Ghana*. *October*. https://doi.org/10.5455/jeos.20140528072614

Moorthy, B., Chu, C., & Carlin, D. J. (2015). Polycyclic aromatic hydrocarbons: From metabolism to lung cancer. *Toxicological Sciences*, *145*(1), 5–15. https://doi.org/10.1093/toxsci/kfv040

NIOSH. (2010). *Occupational exposure limit of polycyclic aromatic hydrocarbons*. *National Institute for Occupational Safety and Health*.

OECD. (2018). *Considerations for assessing the risks of combined exposure to multiple chemicals*. *296*.

Patel, D. K., & Dalwadi, M. (2023). *A Review on High Performance Liquid Chromatography*. *8*(1), 2531–2536. https://doi.org/10.35629/7781-080125312536

Pérez-maldonado, I. N., Ochoa-martínez, Á. C., López-, M. L., Varela-silva, J. A., Ochoa-martínez, Á. C., & López-, M. L. (2019). Urinary levels of 1-hydroxypyrene and health risk assessment in children living in Mexican communities with a high risk of contamination by polycyclic aromatic hydrocarbons (PAHs). *International Journal of Environmental Health Research*, *29*(3), 348–357. https://doi.org/10.1080/09603123.2018.1549727

PHG. (2010). *CHEMICALS IN DRINKING WATER Public Health Goal for Benzo (a) pyrene in Drinking Water*. *September*, 1–68.

Ramesh, A., Archibong, A. E., Hood, D. B., Guo, Z., & Loganathan, B. G. (2011). Global environmental distribution and human health effects of polycyclic aromatic hydrocarbons. *Global Contamination Trends of Persistent Organic Chemicals*, *October 2016*, 97–126. https://doi .org/10.1201/b11098-10

Ravanbakhsh, M., Yousefi, H., Lak, E., Ansari, M. J., Suksatan, W., Qasim, Q. A., Asban, P., & Kianizadeh, M. (2023). Effect of Polycyclic Aromatic Hydrocarbons (PAHs) on Respiratory Diseases and the Risk Factors Related to Cancer Effect of Polycyclic Aromatic Hydrocarbons (PAHs) on Respiratory Diseases and the Risk Factors Related to Cancer. *Polycyclic Aromatic Compounds*, *43*(9), 8371–8387. https://doi.org/10. 1080/10406638.2022.2149569

Rejakumar, P., Subash, C. M. ., Prasoabh, G. ., Akhila, J. ., Renjini, A. S., & Sahishna, S. . (2022). *An Overview on High-Performance Liquid Chromatography*. *23*(4), 506–527.

Rengarajan, T., Rajendran, P., Nandakumar, N., Lokeshkumar, B., Rajendran, P., & Nishigaki, I. (2015). Asian Pacific Journal of Tropical Biomedicine. *Asian Pacific Journal of Tropical Biomedicine*, *5*(3), 182–189. https://doi. org/10.1016/S2221-1691(15)30003-4

Roberts, W. (2021). Air pollution and skin disorders. *International Journal of Women's Dermatology*, *7*(1), 91–97. https://doi.org/10.1016/j.ijwd.2020.11.001

Sadapha, P., & Dhamak, K. (2022). *Review Article Review Article on High-Performance Liquid Chromatography (HPLC) Method Development and Validation*. *74*(03), 23–29. https://doi.org/10.47583/ijpsrr.2022.v74i02.003

Semih, O., & Kartal, C. (2016). *SOLID-PHASE EXTRACTION (SPE): PRINCIPLES AND APPLICATIONS*. https://doi.org/10.17306/J.AFS.2016.1.1

Shine, S., & Janardhanan., V. and S. (2019). *Review Article Review on HPLC Method Development Validation and Optimization 1*. *56*(05), 28–43.

Sun, K., Song, Y., He, F., Jing, M., Tang, J., & Liu, R. (2021). A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics. *Science of the Total Environment*, *773*, 145403. https://doi.org/10.1016/j.scitotenv.2021.145403

Swartz, M. (2010). *Hplc detectors: a brief review*. 1130–1150. https://doi.org/10.1080/10826076.2010.484356

Taylor, P., Buszewski, B., & Szultka, M. (2012). *Critical Reviews in Analytical Chemistry Past , Present , and Future of Solid Phase Extraction : A Review*. *June*, 37–41. https://doi.org/10.1080/07373937.2011.645413

Taylor, P., Seidel, A., Spickenheuer, A., Straif, K., Rihs, H., Scherenberg, M., Dettbarn, G., Angerer, J., Brüning, T., Jacob, J., Pesch, B., Seidel, A., Spickenheuer, A., Straif, K., Rihs, H., Scherenberg, M., Dettbarn, G., Angerer, J., Wilhelm, M., … Pesch, B. (2008). *Journal of Toxicology and Environmental Health , Part A : Current Issues New Biomarkers of Occupational Exposure to Polycyclic Aromatic Hydrocarbons New Biomarkers of Occupational Exposure to Polycyclic*. *January 2015*, 37–41. https://doi.org/10.1080/15287390801985265

Teixeira, E. C., Schneider, I. L., Silva, L. F. O., & Rinc, S. (2017). *Exposure to polycyclic aromatic hydrocarbons in atmospheric PM 1 . 0 of urban environments : Carcinogenic and mutagenic respiratory health risk by age groups *. 224*, 158–170.

Thammana, M. (2016). *A Review on High Performance Liquid Chromatography (HPLC)*. *5*(2), 22–28.

Tongo, I., Ezemonye, L., & Akpeh, K. (2017). Distribution, characterization, and human health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in Ovia River, Southern Nigeria. *Environmental Monitoring and Assessment*, *189*(6). https://doi.org/10.1007/s10661-017-5931-5

Tuck, C. Z., Cooper, R., Aryeetey, R., Gray, L. A., & Akparibo, R. (2023). *A critical review and analysis of the context , current burden , and application of policy to improve cancer equity in Ghana*. *2*, 1–11.

USEPA. (1989). *Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)*. *I*(December).

Varhadi, S. D., Gaikwad, V. A., Sali, R. R., Chambalwar, K., & Kandekar, V. (2020). *A Short Review on : Definition , Principle and Applications of High Performance Liquid Chromatography*. *2*.

Wang, X. T., Miao, Y., Zhang, Y., Li, Y. C., Wu, M. H., & Yu, G. (2013). Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: Occurrence, source apportionment and potential human health risk. *Science of the Total Environment*, *447*, 80–89. https://doi.org/10 .1016/j.scitotenv.2012.12.086

WHO. (2021). *WHO Human Health Risk Assessment Toolkit* (Issue 8).

Xia, Z., Duan, X., Tao, S., Qiu, W., Liu, D., Wang, Y., Wei, S., Wang, B., Jiang, Q., Lu, B., Song, Y., & Hu, X. (2013). Pollution level, inhalation exposure and lung cancer risk of ambient atmospheric polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Environmental Pollution*, *173*, 150–156. https://doi.org/10.1016/j.envpol.2012.10.009

Yebra-Pimentel, I., Fernández-González, R., Martínez-Carballo, E., & Simal-Gándara, J. (2015). A critical review about the health risk assessment of pahs and their metabolites in foods. *Critical Reviews in Food Science and Nutrition*, *55*(10), 1383–1405. https://doi.org/10.1080/10408398.2012. 697497

Zhong, Y., Carmella, S. G., Hochalter, J. B., Balbo, S., & Hecht, S. S. (2011). *7 , 8 , 9 , 10-tetrahydrobenzo [a] pyrene in Human Urine : A Biomarker for Directly Assessing Carcinogenic Polycyclic Aromatic Hydrocarbon Exposure Plus Metabolic Activation*. 73–80.

APPENDICES

Appendix A

Questionnaire for Artisanal Auto-mechanical Workers in Siwdu Workshop

QUESTIONNAIRE

UNIVERSITY OF CAPE COAST

COLLEGE OF AGRICULTURE AND NATURAL SCIENCES

SCHOOL OF PHYSICAL SCIENCES

DEPARTMENT OF CHEMISTRY

Artisanal Mechanical Workers in Cape Coast Occupational Safety Research Survey

I am MPhil student in the department of chemistry, I will be very grateful if you could help us complete the following questionnaire below for academic purpose. No identity will be revealed for ethical purposes. Information provided will be kept confidential.

Please fill the questionnaires by ticking only one or more options in the bracket and also provide short answers in the empty spaces provided.

Section A: Personal information

1. What is your sex: Male ( ) Female ( )

2. What is your age (years):

Under 25 ( ) 26 -35 ( ) 36- 45 ( ) 46 -55 ( ) 56 and above ( )

3. What is your level of education?

Informal ( ) Basic ( ) Secondary / Technical ( ) Tertiary ( ) None ( )

4. What is your job of specialization?

Auto mechanics ( ) Auto electricians ( ) Welders ( ) Sprayer ( ) Vulcanizers ( )

5. What is your position at workshop? Master ( ) Apprentice ( )

6. How many years have you been practicing this work.

Below 1 ( ) 1-5 ( ) 6-9 ( ) 10-19 ( ) 20 and above ( )

Section B: General occupational safety information at workshop

7. Do you have any knowledge about safety equipment?

Yes ( ) No ( )

If yes give one or two example of safety equipment you know and use

…….

8. Do you often feel comfortable and protected when using safety equipment during working hours?

Very often ( ) often ( ) not often ( ) None ( )

9. Do you sometimes clean your hands or other parts of your body with fuel for example Petrol and other liquids other than water during work hours or when you close from work.

Yes ( ) No ( )

10. Do you wash your hands with soap under running water before eating at break hours or after closed from workplace?

Very regularly ( ) regularly ( ) sometimes ( ) None ( )

11. How often do you wash your work attire when dirty or change it when worn-out.

Everyday ( ) 3 days ( ) 1 week ( ) months ( ) Never ( )

Section C: Health issues at workshop

12. Do you have any health condition? Such as cancer, kidney diseases, liver diseases, body itching, birth issues etc. Yes ( ) No ( ) Maybe ( )

If yes please state that health condition (s)…….....

13. Do you smoke or drink alcohol. (Please for research purposes, no strings attacked thank you)

Yes ( ) No ( )

14.Do you know of one common diseases / illness workers in your field of work usually suffers and die from as a result of their work practices

……

15. How often you visit the clinic or hospital.

Very often ( ) often ( ) not often ( ) None ( )

Thank you for your participation and God richly bless you

APPENDIX B

Analytical Figure of Merits

FOR PAH METABOLITES

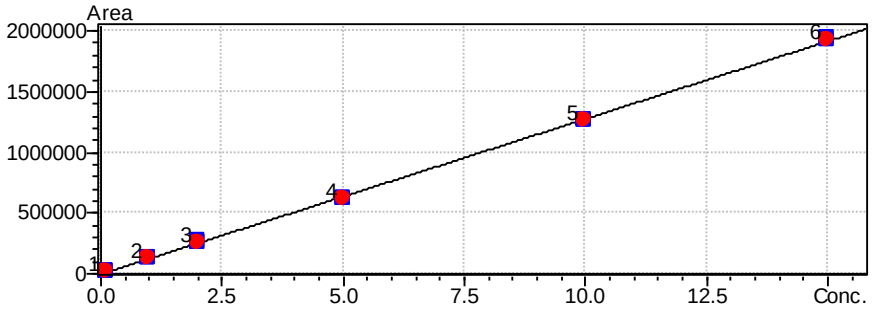


Figure B1: Six point calibration curve of 9-Phenanthrol

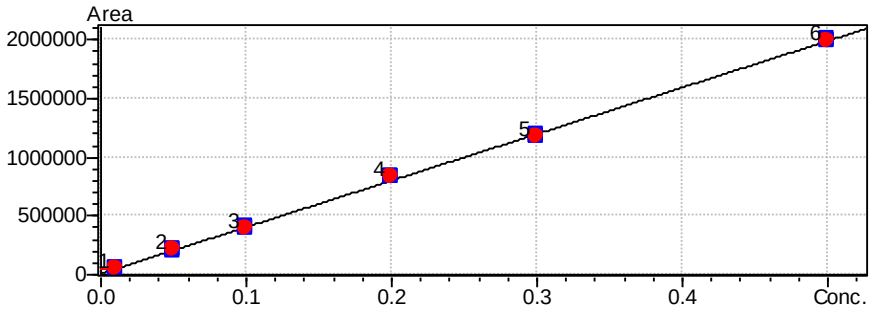


Figure B 2: Six-point calibration curve of 1-Hydroxypyrene

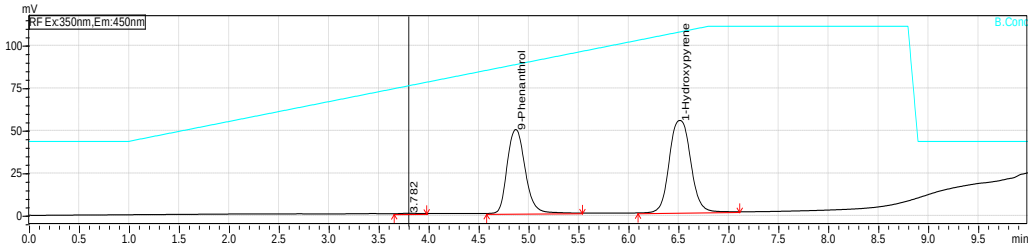


Figure B 3: A Chromatogram of 200 ppb of PAH metabolite

FOR PARENT PAHs

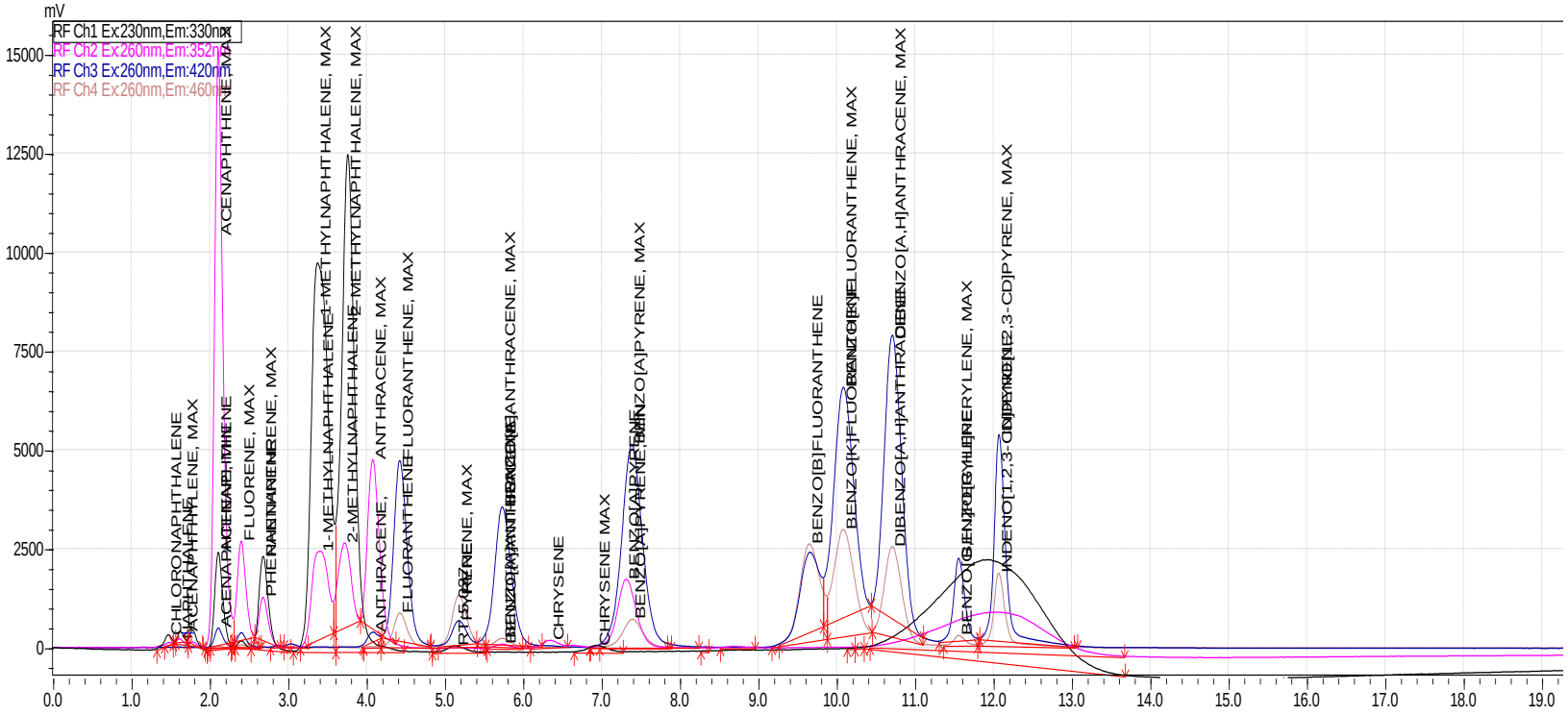


Figure B 4: A Chromatogram of 100 ppb of Parent PAHs

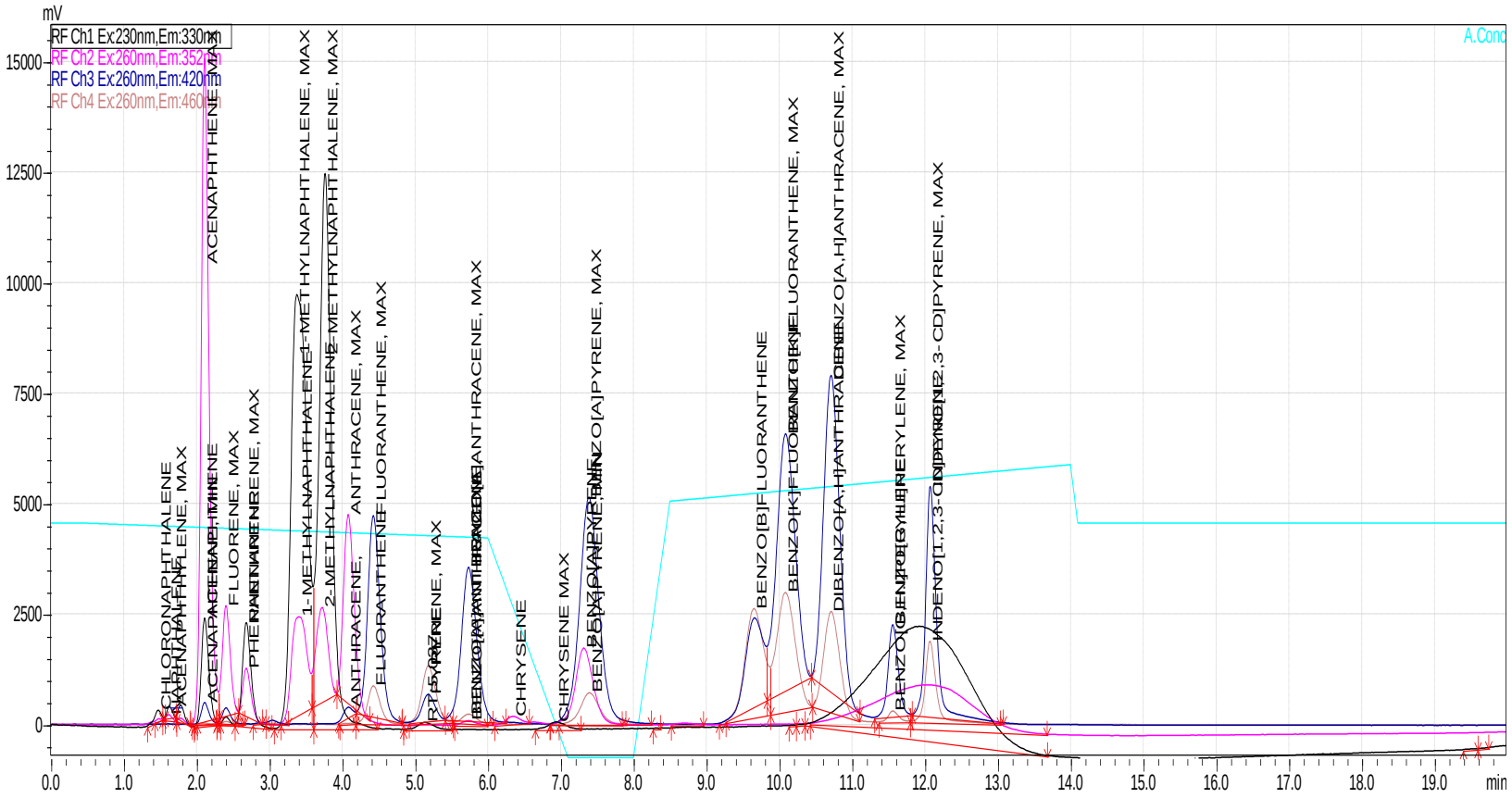


Figure B 5: A Chromatogram of 50 ppb of Parent PAHs

APPENDIX C

Two Anova Analysis for Artisanal Auto-mechanical Workers Samples

Table C 1: Two-Way Anova Analyis for Auto-Mechanics at 95.0% confidence level

Source of Variation	SS	df	MS	F	P-value	F crit
PAHs	6.19E+08	17	36414781	4.061933	1.13E-07	1.642183
AM samples	3.22E+08	31	10397625	1.159816	0.25587	1.473097
Error	4.72E+09	527	8964890			
Total	5.67E+09	575				

Table C 2: Two-Way Anova Analyis for Auto-Sprayers at 95.0% confidence level

Source of Variation	SS	df	MS	F	P-value	F crit
pahs	1.21E+08	17	7137859	15.59866	2.69E-33	1.652887
AS	6799540	20	339977	0.742966	0.780662	1.601537
Error	1.56E+08	340	457594.3			
Total	2.84E+08	377				

Table C 3: Two-Way Anova Analyis for Plastic welders at 95.0% confidence level

Source of Variation	SS	df	MS	F	P-value	F crit
PAHs	1.45E+09	17	85394487	2.884064	0.000685	1.744299
PW samples	1.48E+08	5	29615976	1.000233	0.422711	2.321812
Error	2.52E+09	85	29609083			
Total	4.12E+09	107				

Table C 4Two -Way Anova Analysis among three different artisans groups Parent PAHs

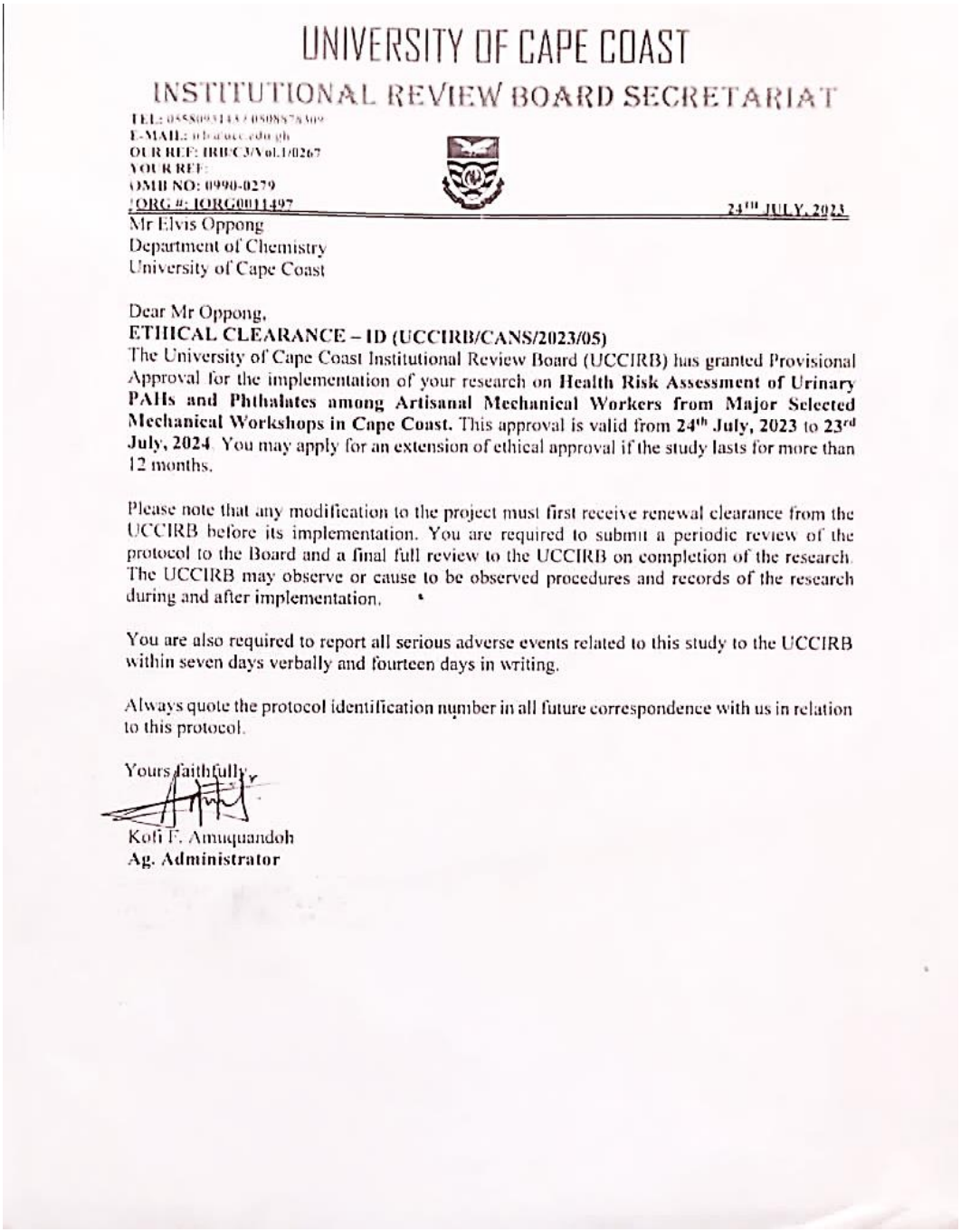
Source of Variation	SS	df	MS	F	P-value	F crit
AUTO-MECHANICAL WORKERS	1.07E+09	2	5.34E+08	4.60291	0.013682	3.145258
MEAN TOTAL PAHs	3.5E+09	31	1.13E+08	0.9727	0.521396	1.636151
Error	7.19E+09	62	1.16E+08			
Total	1.18E+10	95				

Table C 5:Two -Way Anova Analysis among three different artisans' groups for PAH metabolites

Source of Variation	SS	df	MS	F	P-value	F crit
Samples ID	8.73E+10	31	2.82E+09	0.85649	0.675823	1.636151
Mean total for auto-artisanal mechanical workers	2.19E+10	2	1.1E+10	3.338315	0.041982	3.145258
Error	2.04E+11	62	3.29E+09			
Total	3.13E+11	95				

APPENDIX D

Ethical Clearance



UNIVERSITY OF CAPE COAST

INSTITUTIONAL REVIEW BOARD SECRETARIAT

TEL: 0558093143 / 0508878309
E-MAIL: irb@ucc.edu.gh
OUR REF: IRB/CC3/Vol.1/0267
YOUR REF:
OMB NO: 0990-0279
IORG #: IORG0011497

24TH JULY, 2023

Mr Elvis Oppong
Department of Chemistry
University of Cape Coast

Dear Mr Oppong,

ETHICAL CLEARANCE – ID (UCCIRB/CANS/2023/05)

The University of Cape Coast Institutional Review Board (UCCIRB) has granted Provisional Approval for the implementation of your research on **Health Risk Assessment of Urinary PAHs and Phthalates among Artisanal Mechanical Workers from Major Selected Mechanical Workshops in Cape Coast.** This approval is valid from **24th July, 2023** to **23rd July, 2024**. You may apply for an extension of ethical approval if the study lasts for more than 12 months.

Please note that any modification to the project must first receive renewal clearance from the UCCIRB before its implementation. You are required to submit a periodic review of the protocol to the Board and a final full review to the UCCIRB on completion of the research. The UCCIRB may observe or cause to be observed procedures and records of the research during and after implementation.

You are also required to report all serious adverse events related to this study to the UCCIRB within seven days verbally and fourteen days in writing.

Always quote the protocol identification number in all future correspondence with us in relation to this protocol.

Yours faithfully,

Kofi F. Amuquandoh
Ag. Administrator