

**ATRAZINE LEVEL IN AIR PARTICULATE MATTER IN THE KUMASI  
METROPOLIS AND ITS ENVIRONS**

KNUST

**A thesis submitted to the Department of Chemistry, Kwame Nkrumah University of  
Science and Technology, Kumasi**

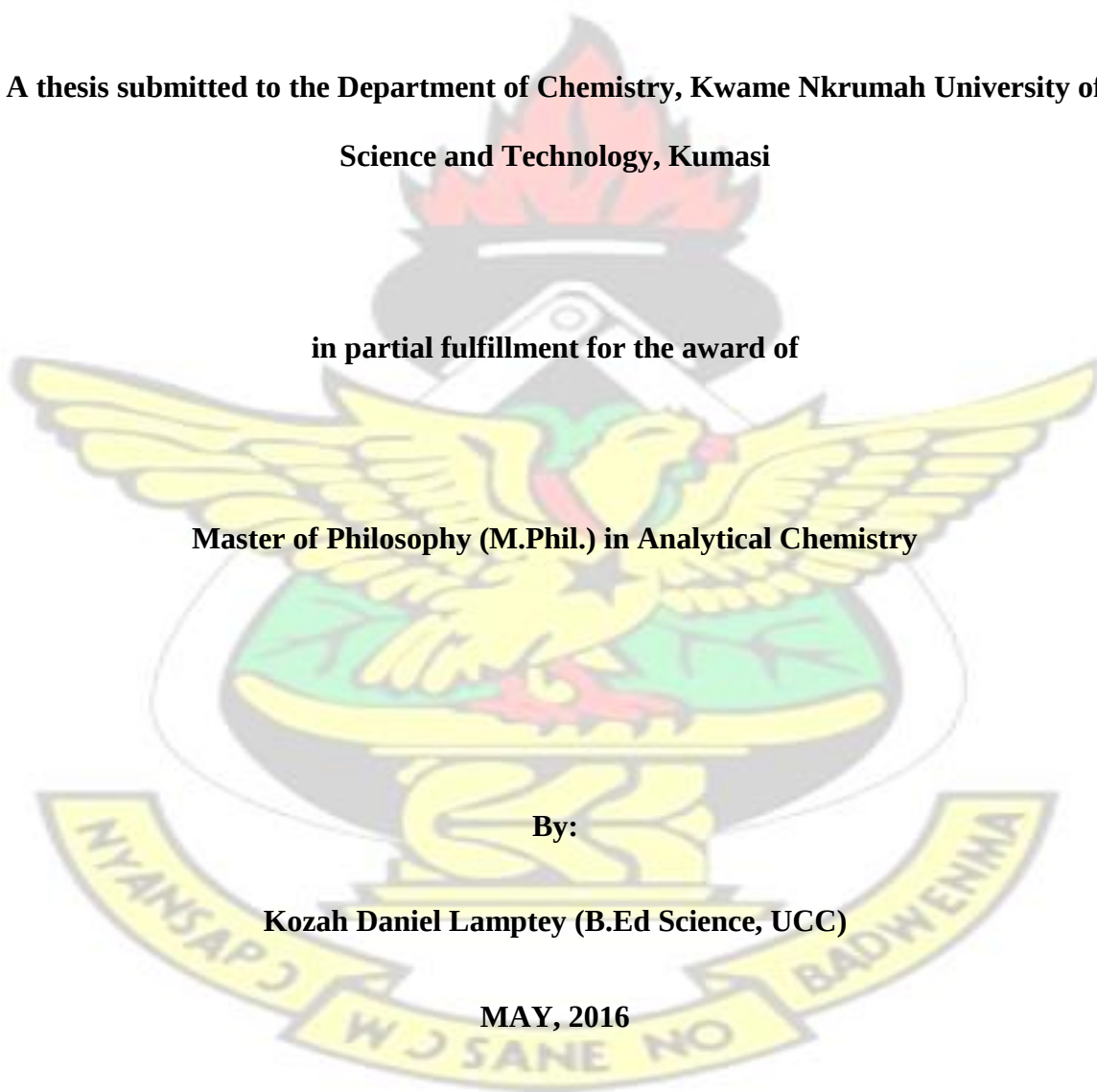
**in partial fulfillment for the award of**

**Master of Philosophy (M.Phil.) in Analytical Chemistry**

**By:**

**Kozah Daniel Lamptey (B.Ed Science, UCC)**

**MAY, 2016**



## DECLARATION

I, Kozah Daniel Lamptey, hereby declared that this thesis is a compilation of research results conducted by myself in the Department of Chemistry, KNUST, under the supervision of Dr. Osei Akoto. This work has not been presented to this university or another elsewhere to the best of my knowledge for an award of a degree. Cited literature has been duly acknowledged.

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## ACKNOWLEDGEMENT

I am grateful to Almighty God for His mercy, guidance and protection throughout this Master of Philosophy (M.Phil) programme. The retrieval of my stolen laptop computer containing my thesis, downloaded articles and other vital documents from a computer dealer at Kejetia was entirely miraculous working of God.

I am highly indebted, in thousand folds, to my seasoned and committed project supervisor, Dr. Osei Akoto, for his involvement in the selection and fine tuning of the topic for this project. Specially, I appreciate his unbridled in-depth knowledge in scientific research with which he offered excellent alternative suggestions to this work. Taking time off his busy academic schedule to read and correct mistakes in the script deserves special commendation and honour.

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## DEDICATION

I dedicate this project work to Kwao Kozah, Saint Sampson K. Ablenkwhah, Yaw Kozah, Yohana Pakada, Mawuvi Dzekle, Ador Gbedemah, Patrick K. Nyamedor and Ador Faustina from my nuclear and extended families.



## ABSTRACT

Atrazine is a widely used pre- and post-emergence herbicide to selectively control weed growth. A total of 40 air particulate samples were collected on filter papers from all the 8 urban and farming communities. A Sibata Low Volume pump (Model LV- 40) air sampler was mounted at a height of 1.5 m during sampling at each of the sites. Air samples were collected by continuously pumping air through a filter paper fixed in the sample inlet of the sampler for 8 hours at a flow rate of 30 L/min and a temperature of 25 °C. A total volume of 14.4 m<sup>3</sup> of air was sampled. In all, about 20 mL of acetonitrile was used to extract the air samples through 5-minute ultrasonication. High Performance Liquid Chromatograph (Varian Inc, USA) coupled with a UV detector (HPLC-UV) fitted to autosampler (model 410 Varian, USA) was used to analyse the samples based on modified Multi-Residue Method (MRM, GSA- T 24) by Ghana Standards Authority (GSA). The mobile phase involves acetonitrile/water (80:20 % v/v) for separation at a flow rate of 1.5 mL/min with a detection within 6 mins at a wavelength of 254 nm. The mean concentrations in the urban areas were found to be  $0.28 \pm 0.55$  pg/m<sup>3</sup> each for Suame and Gyinyase communities. Buokrom Estate had  $0.29 \pm 0.55$  pg/m<sup>3</sup> while  $0.53 \pm 1.05$  and  $1.05 \pm 2.10$  pg/m<sup>3</sup> was obtained for Tanoso and Kejetia communities respectively. The mean concentrations for farming communities include:  $12.72 \pm 7.69$ ,  $13.34 \pm 10.70$  and  $16.48 \pm 17.17$  pg/m<sup>3</sup> for Nkawie-Toase, Afari and Mpasatia respectively. All the mean concentrations were found to be less than WHO Threshold Risk Value (TRV) of 5.0 ng/m<sup>3</sup>. The health risk indices for children in the farming communities were more than one indicating potential atrazine hazards.

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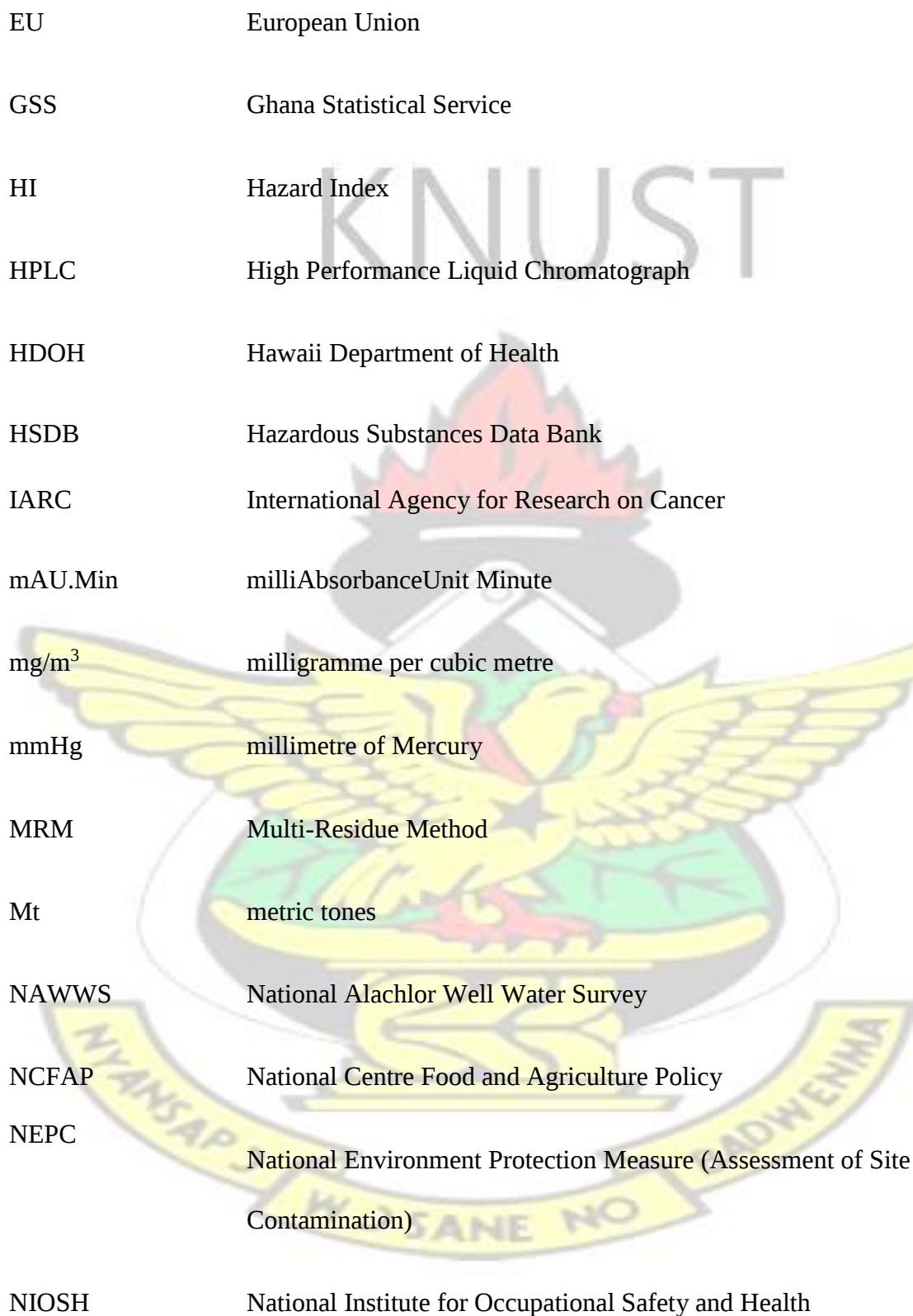
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## **LIST OF ABBREVIATION /SYMBOL**

|          |                                                           |
|----------|-----------------------------------------------------------|
| ACGIH    | American Conference of Governmental Industrial Hygienists |
| AI       | Active Ingredient                                         |
| ATS      | American Thoracic Society                                 |
| CDC      | Centers for Disease Control and Prevention                |
| CEC      | Cation Exchange Capacity                                  |
| CNS      | Central Nervous System                                    |
| DDT      | Dichlorodiphenyltrichloroethane                           |
| DEA      | Deethylatrazine                                           |
| US DHHS  | United States Department of Health and Human Services     |
| DIA      | Deisopropylatrazine                                       |
| enHealth | Environmental Health, Australia                           |
| EPA      | Environmental Protection Agency of Ghana and the USA      |



|                   |                                                                            |
|-------------------|----------------------------------------------------------------------------|
| EU                | European Union                                                             |
| GSS               | Ghana Statistical Service                                                  |
| HI                | Hazard Index                                                               |
| HPLC              | High Performance Liquid Chromatograph                                      |
| HDOH              | Hawaii Department of Health                                                |
| HSDB              | Hazardous Substances Data Bank                                             |
| IARC              | International Agency for Research on Cancer                                |
| mAU.Min           | milliAbsorbanceUnit Minute                                                 |
| mg/m <sup>3</sup> | milligramme per cubic metre                                                |
| mmHg              | millimetre of Mercury                                                      |
| MRM               | Multi-Residue Method                                                       |
| Mt                | metric tones                                                               |
| NAWWS             | National Alachlor Well Water Survey                                        |
| NCFAP             | National Centre Food and Agriculture Policy                                |
| NEPC              | National Environment Protection Measure (Assessment of Site Contamination) |
| NIOSH             | National Institute for Occupational Safety and Health                      |

|                   |                                               |
|-------------------|-----------------------------------------------|
| ng m-2s-1         | nanogramme per squared metre per second       |
| nm                | nanometres                                    |
| NPAS              | Northern Presbyterian Agriculture Services    |
| OSHA              | Occupational Safety and Health Administration |
| PEL               | Permissible Exposure Limit                    |
| pg/m <sup>3</sup> | picogramme per cubic metre                    |
| PGWDB             | Pesticide in Ground Water Data Base           |
| PM                | Particulate Matter                            |
| ppb               | parts per billion                             |
| ppm               | parts per million                             |
| PTS               | Persistent Toxic Substances                   |
| RUP               | Restricted-Use Pesticide                      |
| SC                | Soluble Concentrate                           |
| TRI               | Toxics Release Inventory                      |
| TSP               | Total Suspended Particles                     |
| TWA               | Time-Weighted Average                         |
| UNEP              | United Nations Environnent Programme          |

UV Ultra-Violet

V/V Volume by Volume

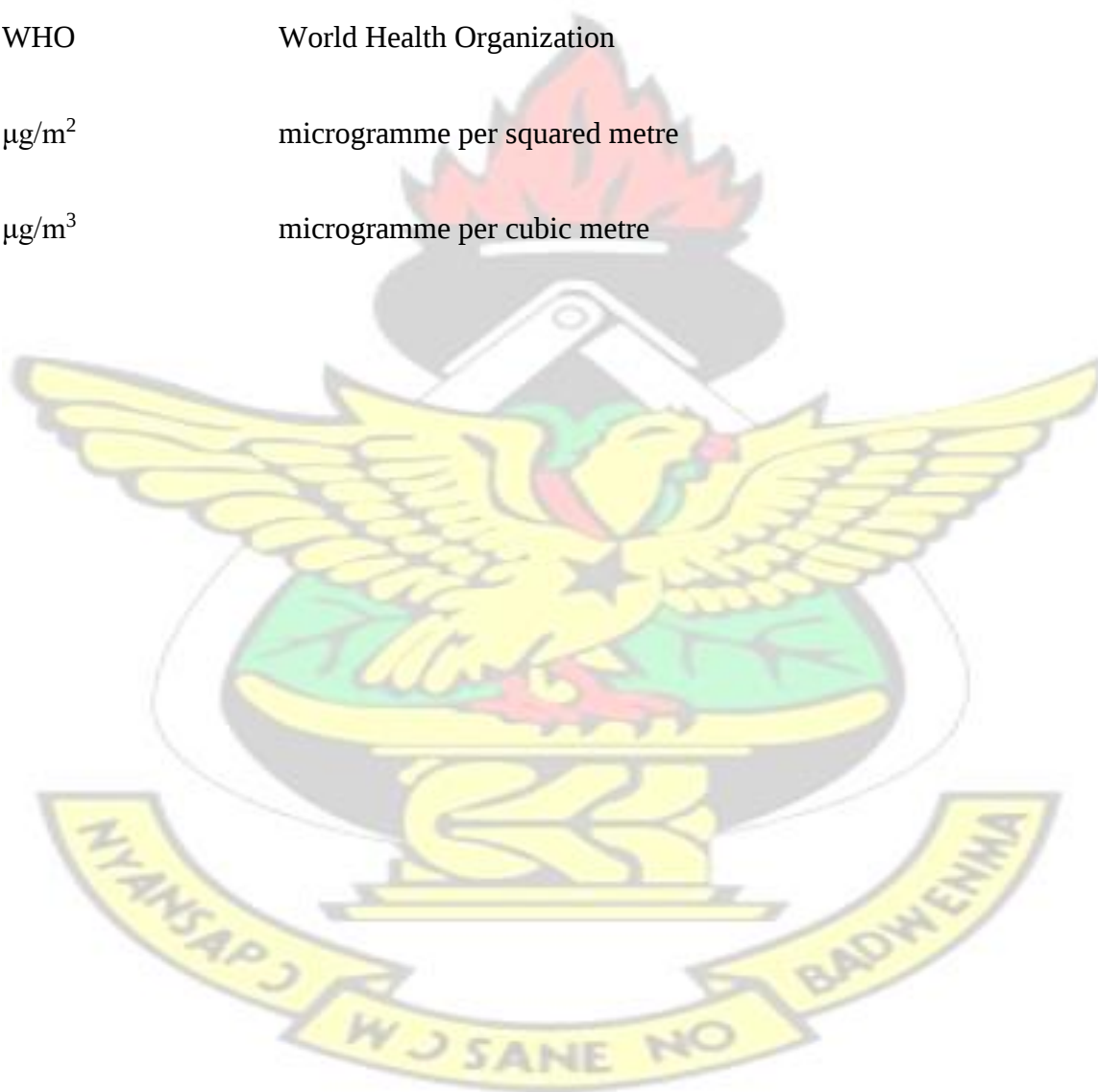
W/V Weight by Volume

WBCs White Blood Cells

WHO World Health Organization

$\mu\text{g}/\text{m}^2$  microgramme per squared metre

$\mu\text{g}/\text{m}^3$  microgramme per cubic metre



## CHAPTER ONE

### 1.0 INTRODUCTION

#### 1.1 Background

Hand weeding and hoeing are the oldest methods of weed control in many agricultural practices. However, they are tedious and time consuming. Pesticides are therefore a better and faster alternative to hand weeding (Ishaya et al, 2007). Atrazine is one of the commonest pesticides used to control pre- and post-emergence broadleaf and grassy weeds in major crops.

In the United States, atrazine is a Restricted-Use Pesticide (RUP) administered only by registered professionals because it is easily carried by air particulate matter and deposited in non-target areas including water bodies. Atrazine has also been banned by the European Union (EU) because it became a major contaminant in drinking water sources (Sass et al, 2006). However, in Ghana, particularly Kumasi and its environs, nonprofessionals rather apply this pesticide indiscriminately since there is no effective regulatory mechanism to check its safe use (Mensah et al, 2013).

The destruction of crops by weeds has made many farmers to apply atrazine to their farms in order to protect their crops. Atrazine is an inexpensive and a selective herbicide which is used to effectively control weeds by many small and large scale farmers (Frimpong et al, 2013). Farmers may over-apply atrazine in their farms without necessarily knowing the health and environmental consequences because most farmers cannot probably read and understand the specific instructions on the use of atrazine (Yeboah et al, 2004). About 2 to

25 % of atrazine volatilizes from treated areas and drifts across to untreated areas (Rice et al, 2002; Prueger et al, 2005).

Atrazine application to urban vegetation such as residential lawns, roadside grasses, golf course turf, football fields, backyard gardens, grasses on newly acquired lands and more particularly vegetation in marshy areas along water courses has become rampant in the Kumasi Metropolis. Atrazine may be blown off by wind or evaporate into the ambient air in the course of application (Tashkent, 1998). The chemical may also be evaporated into the atmosphere due to poor storage or improper disposal procedures (Tashkent, 1998). All these activities in and around the metropolis are exposing inhabitants to atrazine either by dermal contact or through inhalation from polluted air.

Volatilization of pesticides is influenced by factors such as high temperature, low relative humidity and air movement. The higher the vapour pressure of atrazine, the higher the rate of volatilization. The movement of atrazine from treated fields to untreated areas affects non-target species including humans (HDOH, 2013). In air, it can react with reactive species like hydroxyl radicals to form hydroxyatrazine or it can be adsorbed by particulate matter and can be transported far away from the closest application point (Thurman and Cromwell, 2000). The health effects of atrazine exposure include blisters on the skin, menstrual problems in women and birth deformities (Rogers and Kavlock, 2008).

## **1.2 PROBLEM STATEMENT**

Atrazine application constitutes an integral component in the development and expansion of modern agricultural system. According to Kuniuki (2001) neglecting pesticides in modern agricultural practices reduces crop yields by almost 10%. However there is a

growing concern about persistent use of atrazine by non-professionals to control weeds because of the significant health hazards associated with its usage. Atrazine causes bone and brain cancers in children and hermaphroditism in frogs (Hayes et al, 2003; Linet et al, 2003). Death cases and pesticide poisoning are common particularly in developing countries due to frequent and improper use of toxic pesticides such as atrazine by farmers (Tariq et al, 2007). For example, seven (7) people died in the Central Gonja District in the Northern Region of Ghana after eating food suspected to be contaminated with atrazine (Der et al, 2013).

It can be stated that many people are unknowingly suffering from atrazine related harmful effects because over 95% of atrazine end up in off-site destinations mainly through air (Miller, 2004). Kumasi and its environs are also recipients of a large volume of atrazine which drifts from adjoining farming communities exposing its inhabitants to the hazards of this chemical.

### **1.3 OBJECTIVE**

The objective of the study was to measure the levels of air particulate-borne atrazine in some communities (Kejetia, Tanoso, Gyinyase, Buokrom Estate and Suame) in the Kumasi metropolis and compare the levels to those from Afari, Mpasatia and NkawieToase farming communities in the Ashanti Region and estimate its potential health impact on the residents of these communities.

### 1.3.1 Specific Objectives

1. To determine the concentration of atrazine in air particulate matter in Kejetia, Tanoso, Gyinyase, Buokrom Estate, Suame Afari, Mpasatia and Nkawie-Toase in the Kumasi metropolis and its surroundings and to compare the mean concentrations.
2. To assess the health impact of atrazine in the urban and farming communities in the Ashanti Region of Ghana.

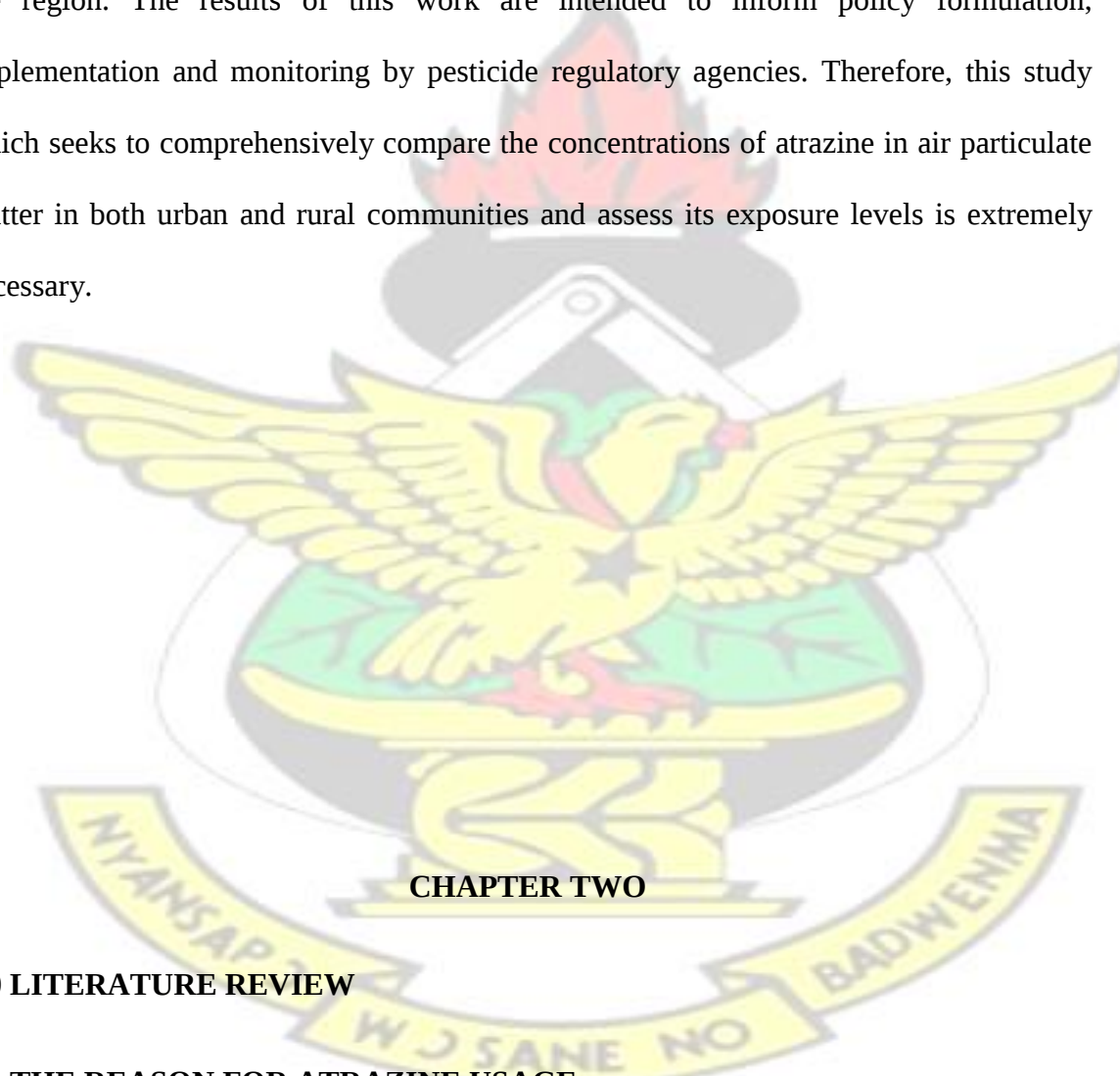
### 1.4 JUSTIFICATION

It has been estimated that 87 % of Ghanaian farmers use chemical pesticides to control pests and diseases on vegetable crops. About 44 % of pesticides in Ghana are herbicides (atrazine), 33 % being insecticides and 23 % are fungicides (Ntow et al, 2006). Unfortunately a lot of farmers are not abreast with the safe use, storage and disposal of pesticides. Although, some famers are aware of the potential health risks of atrazine, they think of immediate economic benefits such as cutting down labour cost and maximizing crop yield (Ntow et al, 2006).

Volatilization and drift of atrazine from treated fields is raising a lot of concerns among the general public, the Ghana Environmental Protection Agency and Commonwealth Health Agencies (enHealth, 2012). Many atrazine users are not adequately informed about its acute and chronic health risks as well as its fate when it is exposed into the environment (Damalas et al, 2011). Atrazine volatilizes rapidly from treated areas resulting in decreased efficiency (Shaner et al, 2010). This means that the more atrazine is applied to a particular field, the higher the rate of volatilization. This causes atrazine to be transported by air to different locations thereby contaminating the environment. Surface run-off introduces residues of atrazine from farmlands into surface water causing contamination which has

negative effect on animals and humans who use the water for domestic purposes (Ntow, 2001). Atrazine can gradually bioaccumulate in food chains and pose great threat to human health and the environment (Lars, 2000).

Determination of atrazine in air particulate matter will set the stage for health risk assessment of atrazine in the Kumasi metropolis and the selected farming communities in the region. The results of this work are intended to inform policy formulation, implementation and monitoring by pesticide regulatory agencies. Therefore, this study which seeks to comprehensively compare the concentrations of atrazine in air particulate matter in both urban and rural communities and assess its exposure levels is extremely necessary.

The logo of Kwame Nkrumah University of Science and Technology (KNUST) is centered in the background. It features a yellow eagle with spread wings perched on a green shield with a red star. Above the eagle is a red torch. Below the eagle is a yellow banner with the text 'NYANSAPET WU SANE NO BADWENMA'.

## **CHAPTER TWO**

### **2.0 LITERATURE REVIEW**

#### **2.1 THE REASON FOR ATRAZINE USAGE**

The World Health Organization (WHO) reported that 20% of pesticide use in the world is found in developing countries posing danger to humans and the environment (Quandt et al,

2004). According to Akobundu (1991), the yields obtained by researchers maintaining weeded plots are 70% more than the yields of most farmers in Africa. The reason being weeding at suboptimal times and labour constraints.

For Vissoh et al (2004), low yields can be attributed to scarcity of skilled labour and the concurrent rise in the cost of hand weeding. Timely removal of weeds by direct labour are therefore difficult and expensive. For example without herbicides, competition of weeds with crops results in losses for the following selected crops: maize (55–90%), common bean (50%), sorghum (40–80%), cowpea (40–60%), rice (50–100%), cotton (80%), wheat (50–80%), groundnut (80%), and cassava (90%) (Ambe et al, 1992, Ishaya et al, 2007; Chikoye et al, 2004).

Atrazine as a selective herbicide has widely become a better alternative to both small and large-scale farmers because it is faster and less tedious. For example, in Nigeria, Ishaya et al (2004) found that 309 hours were required to hand weed one hectare of maize while 324 hours of weeding were needed for one hectare of sorghum. Crop production in Ghana has therefore, evolved from subsistence to commercial or large-scale cultivation with consequent misuse of atrazine and other pesticides (Fiahagbe, 1998). This is to cut down labour cost and increase crop yields in the same season.

## **2.2 BRIEF HISTORY OF ATRAZINE USAGE**

Atrazine was registered in the US in 1958. There has been a general increasing trend in importing and usage of atrazine in major cities like Accra and Kumasi in Ghana (Boahen et al, 2007). Atrazine constituted 50% of pesticides used to control weeds in the Tamale Metropolis in northern Ghana (Sowley et al, 2014). Larbi et al (2013) reported that 4.0 kg

of active ingredient of atrazine (Trazine 500 SC and Callitraz 500 SC) were applied per a hectare of farmland along the coastal belt of Ghana. In 1993, of a total amount of 3,854,126 kg of pesticides used in Ghana, 24 % was reported to be herbicides including atrazine (Fianko et al, 2011).

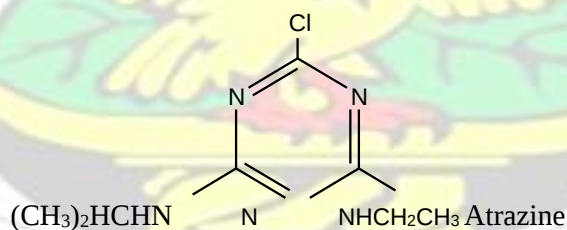
An annual average of 4,338.4 metric tons (mt) of atrazine and other herbicides was imported from the year 2000 - 2009 into Ghana. The lowest import (224 mt) was recorded in the year 2000 whereas the highest import (10,835 mt) occurred in 2008. A total of 43,384 mt of atrazine and related herbicides were imported into Ghana over a period of ten years (MOFA, 2011).

Farmers in the forest, transitional and Guinea savannah zones used a lot of atrazine. For instance, 75 out of 302 herbicides used by farmers were largely atrazine (Ekboir et al, 2002). It was observed that in every year 57 % of agrochemical dealers doubled the amount of atrazine sold to farmers whilst 14 % of the dealers increased their supply by 50 % each year (Ekboir et al, 2002). Ghana is ranked fourth alongside Mali, Tanzania and Sudan in Africa in importation of persistent Toxic Substances like pesticides while South Africa occupies the first position (UNEP, 2002).

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## 2.3 CHEMICAL AND PHYSICAL PROPERTIES OF ATRAZINE

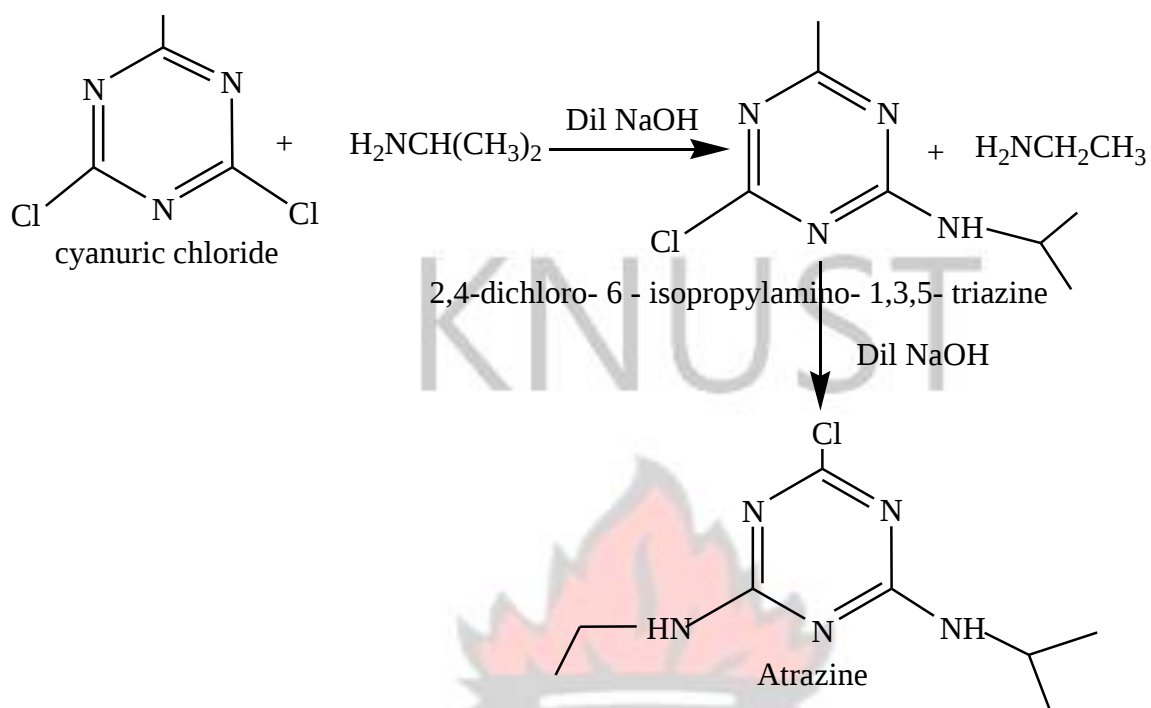
The molecular formula of atrazine is  $C_8H_{14}ClN_5$  and its structural formula is indicated beneath;



Atrazine is produced by reacting cyanuric chloride with isopropylamine under basic condition to give 2,4 -dichloro - 6 - isopropylamine -1, 3, 5 -triazine which in turn reacts with monoethylamine to produce atrazine in presence of dilute caustic soda as presented in scheme 1 below;

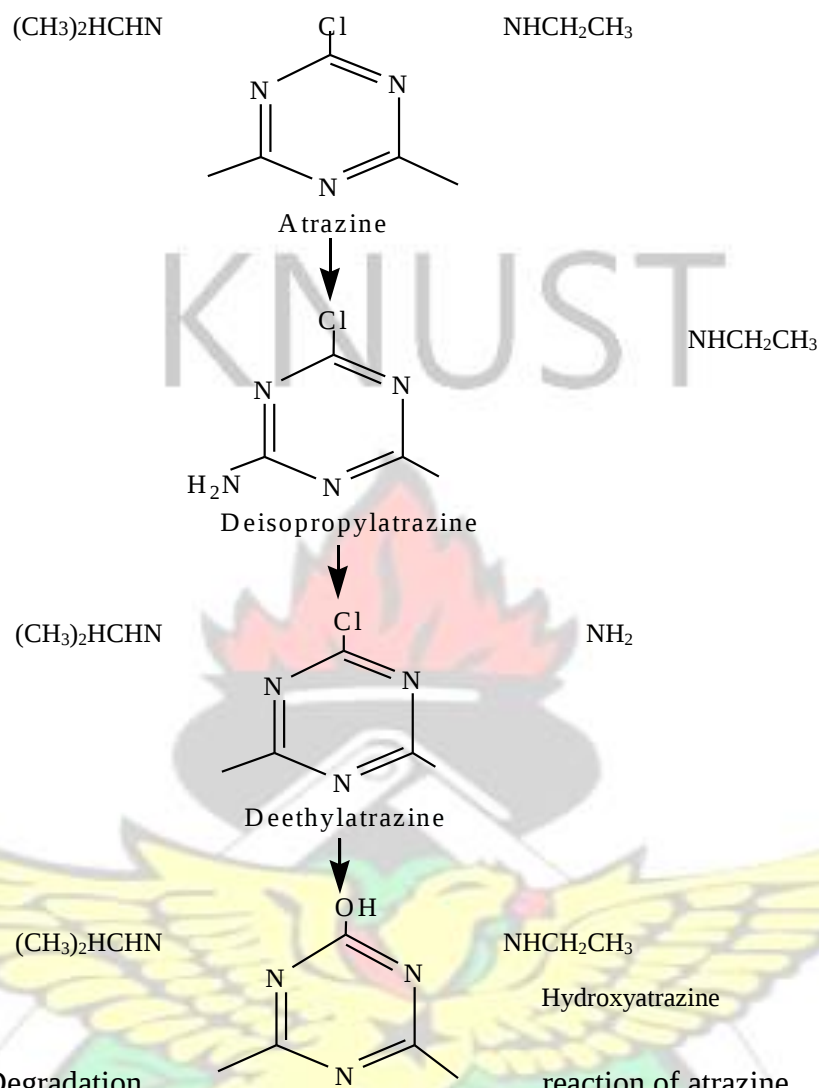
Cl

Cl



**Scheme 1:** Synthetic pathway of atrazine.

Atrazine is an odourless white crystalline powder. The solubility of atrazine in water is 34.7 mg/L. It has vapour pressure of  $2.89 \times 10^{-7}$  mmHg at 25 °C suggesting it exists mainly in the vapour phase in the atmosphere because of the low temperature at which it exists as a gas (US DHHS, 2003). The degradation or metabolites of atrazine are usually found in soil, water or air. The gradual breakdown reaction of atrazine is shown in scheme 2 below;



**Scheme 2:** Degradation

reaction of atrazine

## 2.4 CONCENTRATION OF ATRAZINE IN THE ENVIRONMENT

### 2.4.1 Air

A study conducted in eastern France in 2003 gave higher levels of atmospheric atrazine in rural areas than urban communities. In Geispolsheim, the concentration of atrazine was  $27 \text{ ngm}^{-3}$  in April which dropped slightly to  $25 \text{ ngm}^{-3}$  in May whereas in Gambsheim, it was  $2.5$  and  $1.9 \text{ ngm}^{-3}$  in April and May respectively. The variation in concentrations was as a result of proximity of the sampler to application sites and occurrence of strong wind during sampling which brought adequate pulse of atrazine to the air samplers (Coupe et al, 1998). Atrazine concentrations in Canadian agricultural regions during the application season

were detected to be 1000 and 50  $\text{pg m}^{-3}$  for vapour and particulate phases respectively (Yao et al, 2008).

Atrazine concentrations in air particulate samples from urban communities were found to be usually low. For instance, Sanusi et al (2000) found a range from 690 -51260  $\text{pg/m}^3$  with mean concentration of 20030  $\text{pg/m}^3$  of atrazine in Strasbourg. Sauret (2001) also reported a mean concentration of 130  $\text{pg/m}^3$  within a range of < 15 -794  $\text{pg/m}^3$  for Strasbourg in France. In Mississippi, Coupe et al (2000) reported a concentration range in vapour and particulate matter phases from 0.42 to 2.6  $\text{ngm}^{-3}$ . In Paris, France, atrazine concentration in air was approximately 0.03  $\text{ng/m}^3$  while a maximum concentration in the total atmospheric fallout in rainwater was found to be 350  $\text{ng/L}$ . The atrazine residual concentration range from < 0.03 to 2.00  $\text{ng/m}^3$  was found in the vapour phase in Paris and at a concentration of < 5 to 380  $\text{ng/L}$  in fallout in urban and rural sites in the same vicinity.

The yearly atmospheric deposition of atrazine was estimated to be 77  $\mu\text{g/m}^2$  in Paris community in France (Chevreuil et al, 1996). Atrazine volatilizes more from tilled lands than untilled ones. Cumulative volatilization of atrazine from tilled fields was equal to 14 % of the amount applied but only 9 % of the total amount applied volatilized from no-till fields (Weinhold and Gish 1994). In a study of air-borne dust samples from South Dakota, 50 % of the collected samples contained atrazine. The concentrations of atrazine in these dust samples ranged from 0.29 to 0.76  $\mu\text{g/g}$  (Muller et al, 1997; Asiedu, 2013).

International threshold value of 5.0  $\text{mg/m}^3$  was established by NIOSH, OSHA and ACGIH for atrazine in air (NIOSH, 2001; OSHA, 2001 and ACGIH, 2000). WHO set threshold risk value of 5.0  $\text{ng/m}^3$  for atmospheric atrazine (WHO, 2000).

### 2.4.2 Water

From the records of UNEP (2002), the concentrations of atrazine in Sub-Saharan African states were very high from 1980-1989 period in a Regionally Based Assessment of Persistent Toxic Substances (PTS). Atrazine concentrations between 6900 - 44000 ng/L were detected in waters in South Africa alone. The assessment gave a concentration range of 0.38 - 2500 ng/L in rivers in South Africa whilst in Malawi the concentrations in lakes range from 0.38 - 97705 ng/L.

The level of atrazine in groundwater was 2482 ng/L in Zimbabwe from 1990 to 2015. For water, US EPA has established Maximum Concentration Level (MCL) of atrazine at 3.0 µg/L (US EPA, 1996). US EPA reported substantial amount of atrazine residue in 1,512 wells and 172 of these wells (11%) were found to have concentrations of 1500 µg/L exceeding the MCL of 3 µg/L. In 1993, residues of atrazine had been reported in wells in 21 Californian counties at concentrations ranging from 0.02 to 8.5 mg/L as a result of agricultural applications (Pease et al, 1995).

For example, in an attempt to estimate the amount of alachlor in private and rural domestic wells by National Alachlor Well Water Survey (NAWWS) in Monsanto, atrazine was found to be present in 12 % of the wells in the alachlor use areas. According to NAWWS data, it was estimated that 2.4 million people were exposed to parent atrazine residues of approximately 0.2 mg/L while 184,000 people in this area were exposed to residues greater than or equal to 0.2 mg/L (US EPA, 1994).

Bester and Huhnerfuss (1993) found atrazine concentrations in oceans to range from 1 to 100 ng/L and in estuary concentrations of 200 ng/L were recorded. Concentrations were

generally higher closer to the ocean shores. Elbe River estuary in Germany was one of the estuaries monitored for atrazine residues (Bester and Huhnerfuss, 1993).

#### **2.4.3 Atrazine in Rainfall**

In a study conducted in Italy, atrazine was observed in 10 out of 146 samples of rainwater collected. In the 10 rainwater samples that contained atrazine, its concentrations ranged from 0.15 to 1.99  $\mu\text{g/L}$  with a median concentration of 0.88  $\mu\text{g/L}$  (Trevisan et al, 1993). Atrazine levels had been reported in rainwater in multiple agricultural regions of the US and in National Parks in the mid-west and western US with concentrations ranging from 0.014 - 0.060  $\mu\text{g/L}$  (Mast et al, 2007; Vogel et al, 2008).

Thurman and Cromwell (2000) also reported that atrazine concentrations in rainfall generally ranged from 0.1- 0.5  $\mu\text{g/L}$ . The highest mean concentration for atrazine and DEA were 1.8 and 0.3  $\mu\text{g/L}$  respectively. In another study, Coupe et al (2000) reported maximum and median atrazine concentrations in rainwater of 0.83 and 0.02  $\mu\text{g/L}$  respectively. The concentration of atrazine in rainwater in Switzerland also was detected to be 600  $\text{ng/L}$  (Buser, 1990).

#### **2.4.4 Soil**

Atrazine is persistent in the environment with the half-life of one to twelve months but it can persist in soils for a decade causing environmental hazards (Bouquard et al, 1997). In sub-Saharan African, the concentration of atrazine was reported to be 22  $\text{ng/g}$  in agricultural soil in Mauritius (UNEP, 2002). Investigation into the concentration and leaching of atrazine in drainage water in Gleyic Podzoluvisol, Croatia, it was found that the maximum atrazine concentration in the surface layer of the soil was 0.013  $\text{mg/kg}$  (Simunic et al, 2002).

The initial atrazine concentration in sandy loam soil samples taken from maize farm was 0.670 mg/kg. This concentration reduced drastically to 0.376 mg/kg (56.2%) after 14 days and finally to 0.242 mg/kg (36.1%) after 28 days (Konda and Pasztor, 2001). Again, monitoring atrazine level in surface layer of agricultural soil in Minnesota for 13 months yielded a constant concentration of 0.13 g/kg. In a laboratory study, complete biodegradation of atrazine occurred in clayey soil with concentrations ranging from 5 - 5,000 mg/kg (Gan et al, 1996). In all soils, atrazine concentrations decreased linearly from 5.5 to 1.0 mg/kg over 110 days (US DHHS, 2003).

#### **2.4.5 Food**

The estimated maximum dietary intake of atrazine by Health Canada was 0.0003 mg/kg but residue level of 0.01 mg/kg was detected in all barleys, corn, oats and wheat (Health Canada, 1993). US EPA estimated carcinogenic risk from exposure to atrazine and its 5 chlorometabolites to be  $4.4 \times 10^{-5}$  for all commodities with sugarcane being the largest contributor. Excluding sugarcane the estimated carcinogenic risk is  $2.2 \times 10^{-5}$  with milk, sweet corn, corn, meat and eggs being the major contributors (Fan et al, 1999). The estimated dietary exposure is 0.0001 mg/kg/day for the above food items except sugarcane (Fan et al, 1999).

#### **2.5 VOLATILIZATION AND DRIFT**

Pesticides applied to the soil or crops do not remain static within abiotic or biotic environmental media. They are lost gradually or rapidly through volatilization and drift to the atmosphere. US EPA (1999) defines pesticide spray drift as the physical movement of a pesticide through air at the time of application or soon thereafter, to any site other than that intended for application. This definition does not include the movement of pesticides

to off-target sites caused by erosion, migration, volatility, or contaminated soil particles that are windblown after application.

Volatilization is a process by which a pesticide is transported from a dry or wet surface into the atmosphere. Volatilization can be described by certain parameters like flux which is the amount of pesticide that flows from a unit surface area into the air or half-life which indicates how long it takes for half of the pesticide original present to volatilize.

(Linde and Davis, 1994; Bejarano and Chandler, 2003; Tawiah, 2011).

Volatilization is one of the main transport pathways by which pesticides move from water and soil surfaces into the atmosphere. Air-borne atrazine is transported in the atmosphere by wind. A pesticide that is not volatile can accumulate on the soil and leach to the ground water (Linde and Davis, 1994).

## **2.6 FACTORS INFLUENCING VOLATILIZATION AND DRIFT**

### **2.6.1 Wind**

Lewis et al (1999) showed that pesticide concentrations increases with decreasing dust particle size. This means that as the surface area of the soil particles increases, more atrazine could be adsorbed by these small soil particles which are easily carried by wind to far away destinations. Wind is the most important volatilization rate regulator. The wind carries away atrazine vapour from the treated soils which causes more of the atrazine to volatilize (HDOH, 2013). As the wind speed increases, the volatilization rate of atrazine from soil, seed and plant surfaces equally increases. Wind speed is affected by terrain or fetch (field obstructions) (Linde and Davis, 1994). Volatilization increases with air temperature, soil temperature and wind speed. However, volatilization decreases with high

relative humidity. Wind speed is reduced by high air humidity hence the amount of volatilized herbicide from the treated surfaces is decreased (Fabian and Dyer, 2004).

### **2.6.2 Vapour Pressure**

Vapor pressure is the pressure exerted by the gas particles of herbicides when in equilibrium with the liquid or solid state. The higher the vapour pressure, the greater the rate of volatilization of atrazine from applied fields (Linde and Davis, 1994). If the vapour pressure of atrazine is  $>1.0 \times 10^{-4}$  mmHg at 25 °C, it can be embedded into an appropriate substance like starch to prevent its evaporation into the atmosphere. The rate of volatilization of a herbicide is usually increased by high temperatures and decreased by adsorption to soil particles to which it is applied (US EPA, 1994).

### **2.6.3 Equipment and Application**

The type and size of the nozzles determine the droplet size of atrazine during application. Larger droplets fall more rapidly, evaporate more slowly and are not easily windblown. However, the smaller droplets resulting from high spray pressure and small nozzle tips are easily carried by wind to untreated areas (Lee, 2010). The higher the pressure, the smaller the spray droplets and vice versa. Droplet size is an important factor when considering spray drift (Fishel and Ferrell, 2013). The distance of a nozzle from its target is essential in reducing drift. The further away or higher a nozzle is from its target, the longer the spray droplets remain suspended in air and the greater the possibility of drifting. Topography can also affect the drift of atrazine. Applications made on the windward side of hills are more susceptible to wind gusts and drift than those made on the leeward side (Lee, 2010).

## **2.7 HEALTH EFFECTS OF ATRAZINE**

### **2.7.1 Ways of Exposure to Atrazine**

People who live downstream from contaminated fields and rely on surface or groundwater for drinking may be exposed through contaminated drinking water sources. Factory workers may be exposed to higher amounts of atrazine in the course of production. Farmworkers and herbicide applicators who apply atrazine could be exposed to atrazine during treatment of agricultural lands (Pathak and Dikshit, 2011). Children may be exposed to atrazine by playing in dust that contains atrazine residues. Atrazine exposure through breathing as result of volatilization and drift is the most widespread form of contact (Pathak and Dikshit, 2011). Pregnant women who work on atrazine treated fields expose their unborn babies to atrazine through inhalation and dermal contact causing limb reduction and other birth defects (Rogers and Kavlock, 2008).

### **2.7.2 Some Diseases Caused by Atrazine**

#### **2.7.2.1 Cancer**

The International Agency for Research on Cancer (IARC) through cohort studies found linkage between pesticide exposure and cancers (Baldi and Lebailly, 2007). Based on epidemiological and agricultural health studies on exposure to pesticides, different types of neoplasm (cancerous outgrowths) such as breast cancer, prostate cancer, lung cancer, brain cancer, colorectal cancer, pancreatic cancer, stomach cancer, skin cancer and nonHodgkin lymphoma were reported (Alavanja and Bonner, 2012; Jaga and Dharmani, 2005; Weichenthal et al, 2010).

Van Maele-Fabry et al (2008) pointed out exposure to atrazine as a possible risk factor for prostate cancer and leukemia among pesticide manufacturing workers. In addition,

childhood brain cancer, leukemia, Wilms' tumor, neuroblastoma, and Ewing's sarcoma of bone are associated with parental occupational pesticide exposure (Linnet et al, 2003).

#### **2.7.2.2 Birth Defects and Developmental Toxicity**

Birth defects are defined as structural or functional abnormalities existing at birth or before birth that causes physical or mental disabilities. Atrazine is a teratogen which can induce birth defects such as cryptorchidism, low birth weight, hole-in-heart, orofacial, cleft palate and poliomyelitis (Rogers and Kavlock, 2008). A meta-analysis of literature published from 1966 to 2008 by Rocheleau et al (2009) indicated that higher incidence of hypospadias resulted from parental exposure to atrazine.

#### **2.7.2.3 Diabetes**

There are 347 million people worldwide appraised to be diabetic. The number of reports on the exposure to pesticides and subsequent development of diabetes is rapidly growing (Mostafalou and Abdollahi, 2012b; Rahimi and Abdollahi, 2007). A couple of epidemiological studies included atrazine in potential risk factors for developing diabetes (Everett and Matheson, 2010; Montgomery et al, 2008; Saldana et al, 2007). Exposure to atrazine can be a promoter for other risk factors of diabetes like obesity which distresses neurons regulating feeding behaviour or altering differentiation of adipocytes (Thayer et al, 2012).

#### **2.7.2.4 Cardiovascular diseases**

Apart from hypertension in Oregon pesticide formulating workers, there are also evidences linking exposure of pesticides with atherosclerosis (Antov and Aianova, 1980; Fokina and Bezuglyi, 1978). Atrazine breakdown product, diaminochlorotriazine, damages the heart.

Atrazine tends to influence the enlargement and softening of the heart muscles. It causes thickness and lesion in valves of the heart (Mostafalou and Abdollahi, 2013).

#### **2.7.2.5 Effect of Atrazine on Immune System**

Four studies have shown that atrazine can disrupt the normal functioning of the Immune System (IS) which can lead to the risk of infectious diseases and cancer. Atrazine causes slymphopenia (reduction in the number of WBCs) in rats when fed with atrazine for three weeks at a dose of 100 mg/kg/ day (Pathak and Dikshit, 2011). Atrazine reduces the production of interferon an Immune System protein that fights viral infections and tumor necrosis factor which is another protein responsible for killing tumor cells (Hooghe, 2000).

### **2.8 AIR PARTICULATE MATTER**

Particulate matter is an air pollutant involving a mixture of solid and liquid particles suspended in air (WHO, 2006). The particulates are often described by their size as either coarse or fine. The coarse are labelled as PM<sub>10</sub> or PM<sub>2.5</sub> (aerodynamic diameter < 10 µm or < 2.5 µm) whilst the diameter of ultrafine particulate matter are between 0.1 µm and 1.0 µm in diameter and can remain in the atmosphere for a long time and get transported across regional or international boundaries. The settling down of all these particles is based upon their terminal gravitational velocity as specified in the table below:

**Table 2.1: Terminal Gravitational Settling Velocities and Settling Times for Particles**

| <b>Particle diameter</b> | <b>PM10</b> | <b>PM2.5</b> | <b>PM100nm</b> |
|--------------------------|-------------|--------------|----------------|
| Settling velocity (cm/s) | 0.5         | 0.02         | 0.0001         |
| Time to settle 1 meter   | 3.3 min     | 83 min       | 11.5 days      |

Various anthropogenic and non-anthropogenic sources contribute to the level of particulate matter in Kumasi and its environs. For instance, construction and demolition exercises, combustion of fuel, tyres or organic materials and industrial processes of smelting and steel milling (anthropogenic) release different particulates into the ambient air.

A large volume of particles from volcanoes, wind actions, ocean spray and earthquakes (non-anthropogenic sources) are transported across the atmosphere in the study area. The Total Suspended Particles (TSP) can be estimated by mathematical expression:

$$\text{TSP}(\text{mg}/\text{m}^3) = \frac{W_1 - W_0 \times 100}{V_n}$$

Where:

$W_1$  = weight of membrane with particles in mg.

$W_0$  = weight of clean membrane in mg.

$V_n$  = accumulated sample volume in  $\text{m}^3$  (Yao et al, 2012)

Atmospheric water hydrates particulates making them susceptible to atrazine adsorption. Particulates containing  $0.5 - 6.5 \mu\text{g}/\text{m}^3$  of moisture have atrazine residues dissolving and adsorbing on them. Particle-bound atrazine is then transported in atmosphere over long distances (Tsyoro, 2005). The ultrafine particulates are relatively lighter and have longer transit time in air. They, therefore, carry substantial quantity of adsorbed atrazine to many non-target zones.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Description of the Study Areas

Kumasi is located in the forest belt of Ghana. It is located between latitude  $6.35^{\circ} - 6.40^{\circ}$  N and longitude  $1.30^{\circ} - 1.35^{\circ}$  W with an elevation between 250 – 300 m above sea level.

The land area of the Metropolis is about 254 km<sup>2</sup>. Five percent (5%) of the residents in Kumasi engage in agricultural practices.

The industrial sector which entails small-scale mechanical garages, wood processing companies and food processing factories as well as construction firms absorbs approximately 23% of the population in the city (KMA, 2014). Kumasi has a population of 2.04 million with an annual growth rate of 4.8% (KMA, 2014). Kejetia, Tanoso, Suame, Gyinyase and Buokrom Estate in the Kumasi metropolis were selected for the study because there are a lot of agrochemical stores, vegetable farms, residential lawns and air-borne particulates located in these communities. Nkawie-Toase which is the capital of Atwima Nwabiagya District is located between latitude  $6^{\circ} 32'$  and  $6^{\circ} 75'$  N and longitude  $1^{\circ} 49'$  and  $2^{\circ} 00'$  W with an estimated area of 294.8 km<sup>2</sup>. Afari and Nkawie- Toase communities in the Atwima Nwabiagya District are predominately vegetable and cash crops growing communities.

Atwima Mponua District is found between latitudes  $6^{\circ} 32'$  N and  $6^{\circ} 75'$  N and between longitude  $2^{\circ} 00'$  W and  $2^{\circ} 32'$  W. It has a total land area of 1883.2 km<sup>2</sup> (GSS, 2010).

Mpasatia was chosen in the Atwima Mponua District for the study because a lot of maize farms are located in this community. The sampling sites in urban and farming communities in the Ashanti Region of Ghana have been demarcated in red ink in Fig 3.1.

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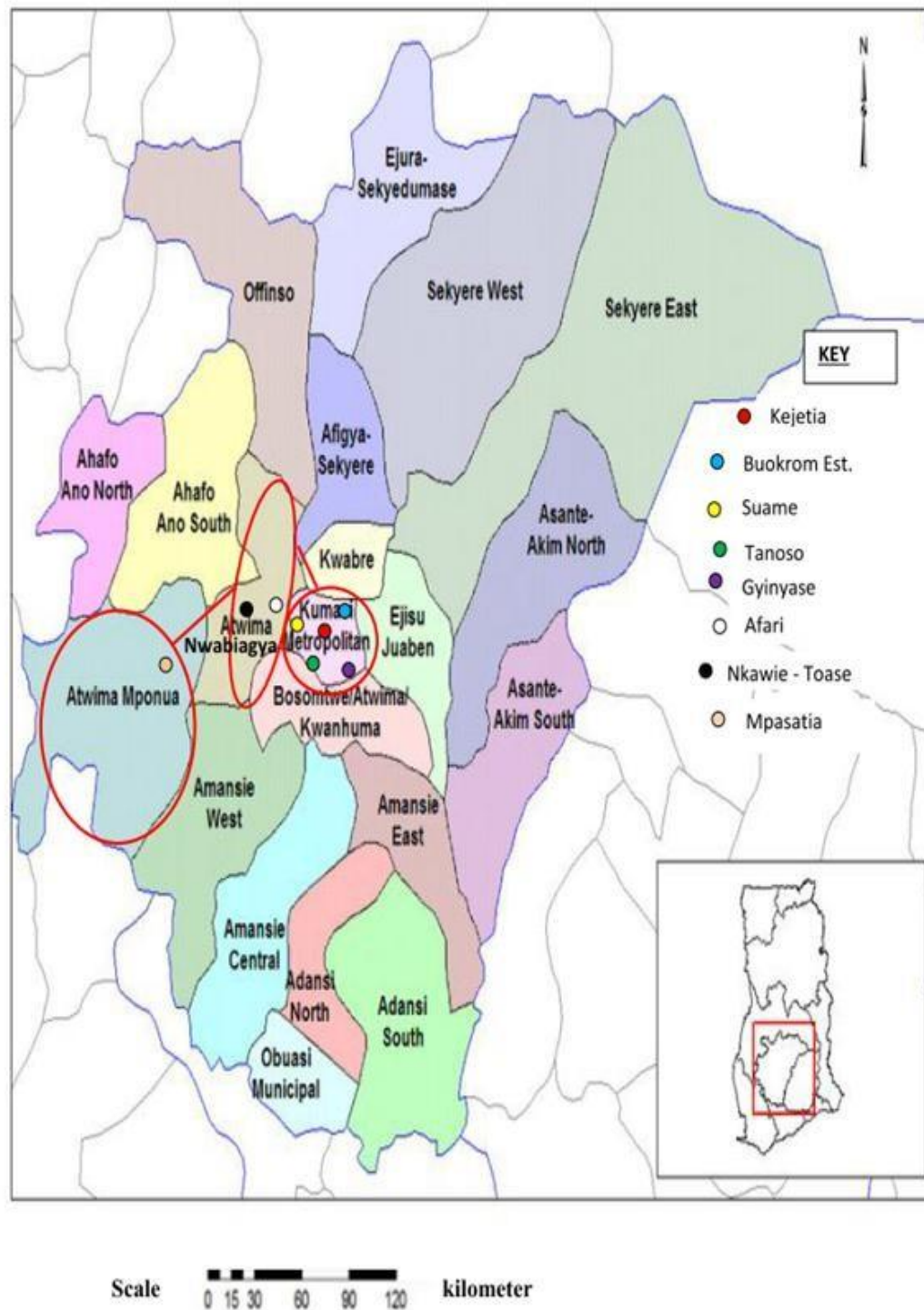


Figure 3.1: Map of Ashanti Region Showing the Sampling sites

### 3.2 MATERIALS AND REAGENTS

#### 3.2.1 Equipment

Sibata low volume air sampler (Model LV- 40 BR) from Digitel Ingenieria de Gestion

(DigiteLig Corporate) (Madrid, Spain)

High Performance Liquid Chromatograph (HPLC) (Varian Incorporated, USA)

Autosampler (model 410 Varian) (Varian Incorporated, USA)

Rotary evaporator with a chiller (model R-210 rotavapor, Buchi, Switzerland)

Separatory funnel (Fisherbrand Glass, USA)

Ultrasonic bath (Grant XUB 18, UK)

Polypropylene cartridge column (Vorex HP, Michigan, USA)

Pasteur pipette (Vorex HP, Michigan, USA)

Pear-shaped flasks (Duran Group GmbH, Wertheim/Main, Germany)

Round bottomed flasks (Duran Group GmbH, Wertheim/Main, Germany)

Mechanical shaker (Ika-Werke HS 501 Digital, Germany)

Stainless steel column: Luna C18 (5  $\mu$ m, 250 x 4.6 mm) (Supelco Inc, Bellefonte, PA, USA)

#### 3.2.2 Reagents

All reagents and solvents were of analytical grade.

Atrazine standard (99.0%) from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Anhydrous sodium sulphate (99.5%), (Sigma-Aldrich, Missouri, USA)

Silica gel (99.99%), Sigma-Aldrich (Missouri, USA,)

Ethyl glycol acetate (99.9%), Merck (Darmstadt, Germany).

Acetonitrile (99.99%), (BDH, England)

Methanol (99.9%), (BDH, England)



### **3.3 SAMPLE COLLECTION**

Eight (8) sampling sites were selected for the study. This included five (5) urban communities comprising of Tanoso, Kejetia, Gyinyase, Buokrom Estate and Suame all in

the Kumasi metropolis and three (3) farming communities comprising of Afari and Nkawie-Toase in the Atwima Nwabiagya district and Mpasatia in Atwima Mponua district of the Ashanti Region.

A total of 5 air particulate samples were collected from each sampling site. A Sibata Low Volume pump (Model LV- 40) air sampler was mounted at a height of 1.5 m during sampling at each of the sites. Air particulate samples were collected by continuously pumping air through a filter paper fixed in the sample inlet for eight (8) hours at a flow rate of 30 L/min (Maria et al, 2009). A total of 14,400 L of air was pumped at the end of the 8 h in each day. The samples collected were carefully placed in zip lock plastic bags and labelled. Each sample was transported in an ice chest (which was thoroughly cleaned and dried) from the field to the laboratory at the end of each sampling period. All the samples were kept in a deep freezer at the Department of Chemistry in KNUST until they were ready for extraction and analysis at Ghana Standard Authority (GSA) in Accra.

### **3.4 SAMPLE EXTRACTION**

The filter papers with their contents were cut into slices. The pieces are then loaded into separatory funnel mounted on a retort stand. Ten (10) mL of acetonitrile was measured and transferred carefully to the contents in the separatory funnel and shaken vigorously. The

sample was then transferred into a flask and ultrasonicated for 5 min. Extra 10 mL acetonitrile was added to the sample in separatory funnel and shaken continuously on mechanical shaker for 60 min at 300 motions /min. The solution was transferred into 50 mL round bottomed flask through filter paper loaded with 5.0 g of anhydrous sodium sulphate for drying. The dried extract was concentrated to 2 mL on a rotary evaporator and stored in 2 mL vial. It was then made ready for clean-up in order to eliminate other possible organic contaminants in the extract.

### **3.5 CLEAN-UP**

The clean-up was done by adopting the procedure of Frimpong et al (2013) in the determination of atrazine. A 1.0 g of activated silica gel was loaded into 10 mL polypropylene cartridge column and conditioned with 6 mL acetonitrile. The extract was introduced onto the column and eluted with 10 mL of acetonitrile into 50 mL pear-shaped flask. The process was accelerated by a suction pump under controlled pressure. The filtrate was concentrated almost to dryness with rotary evaporator (model R-210) at a temperature of 37 °C. The residue was re-dissolved in 1.5 mL of methanol. This was then transferred into 2 mL blue stoppered standard vial for HPLC analysis.

### **3.6 ANALYSIS BY HPLC**

HPLC (Varian Inc, USA) coupled with a UV detector and model 410 Varian autosampler was used to analyze the samples. The chemical analysis was based on modified MultiResidue Method (MRM, GSA- T 24) by Ghana Standards Authority (GSA). Ethyl glycol acetate was added to the extract to enhance the sensitivity of the HPLC. Injection

volume for each sample was 50  $\mu$ L. The mobile phase involves acetonitrile and water (80:20 % v/v) for separation at a flow rate of 1.5 mL/min. Atrazine was detected within 6 min out of the entire run time of 10 min at a wavelength of 254 nm. The Galaxy Workstation Software prepared quantitation reports on the analyte in all the 40 samples with individual chromatograms as per Appendices C and D.

### **3.7 CALIBRATION CURVE OF STANDARD ATRAZINE SOLUTION**

Concentrations of 0.5, 1.0 and 10.0 mg/L of standard atrazine (99.2%) obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) were prepared. A 50  $\mu$ L each of these solutions contained separately in three amber vials were injected into HPLC fitted with a UV detector and an autosampler. The peak areas recorded were 0.751, 1.536 and 15.343 mAU.Min. A graph of peak area was plotted against the concentration to obtain a straight line. The linear regression equation of  $y = 1.5253x - 0.0081$  with correlation coefficient of  $R^2 = 1.0$  was obtained by aid of the Galaxy Workstation Software.

### **3.8 QUALITY CONTROL MEASURES**

A reagent blank was prepared by processing reagents exactly the manner used for each sample. The aim of the blank determination was to establish the magnitude of that component of the analytical signal that might be ascribed to interferences and low level contamination of pesticide residue from reagents, glassware and other components of the extraction process. The reagents were found to be sufficiently free from atrazine contaminations.

The quality of each series of analyses was checked in recovery test by spiking unused filter papers with standard atrazine. Three blank filter papers were each spiked with 2.0 ppm of standard atrazine for each series of analyses. The respective peak areas recorded were used to determine the amount of the surrogate recovered and also the concentration of the analyte. The Percentage Recoveries were used to evaluate the efficiency of MultiResidue Method used for the analysis. The percentage recovery was calculated using the expression below:

$$\% \text{ Recovery} = \frac{\text{Concentration of surrogate recovered}}{\text{Concentration of surrogate spiked}} \times 100\%$$

Cross-contamination of field blank filter papers was prevented by carrying them in different compartments of the ice chest from where the air particulate samples were kept.

The chemicals used were of analytical grade.

### 3.9 ESTIMATION OF ATRAZINE CONCENTRATION

According to Qing et al (2013), concentration of atrazine in air samples is calculated by using the equation below:

$$\text{Air conc. (ngm}^{-3}\text{)} = \frac{\text{Extraction concentration (ng}\mu\text{L}^{-1}\text{)} \times \text{Solution volume (}\mu\text{L)}}{\text{Volume of air sampled (m}^3\text{)}}$$

Where:

Extraction concentration = x mg/kg for various sites (as found in appendix B)

Solution volume = 1.5  $\mu\text{L}$

Volume of air sampled = 14.40  $\text{m}^3$

For example Tanoso site = 0.02  $\text{ng}/\mu\text{L}$

$$\text{Air concentration of atrazine from Tanoso} = \frac{0.02 \text{ ng}\mu\text{L} \times 1.5 \mu\text{L}}{14.4 \text{ m}^3}$$

Air concentration of atrazine from Tanoso =  $2.083 \times 10^{-3} \text{ ng}/\text{m}^3$

Air concentration of atrazine from Tanoso = 0.002083  $\text{ng}/\text{m}^3$

Air concentration of atrazine from Tanoso = 0.0021  $\text{ng}/\text{m}^3$  (Approximately) Air

concentration of atrazine from Tanoso = 2.10  $\text{pg}/\text{m}^3$

### 3.10 HUMAN HEALTH RISK ASSESSMENT

Risk Assessment is the process of evaluating the potential impact of a chemical, physical, microbiological or psychosocial hazard on a specified human population or ecological system under a specific set of conditions for a given time period (enHealth, 2012). The Estimated Average Daily Intake (EADI) was calculated using atrazine mean concentrations from table 4.1 and the standard values set by World Health Organization (WHO) (Mensah et al, 2013) and United State Environmental Protection Agency (US EPA) (US EPA, 2009; US EPA, 2014). The results for adults and children were presented in tables 4.8 and 4.9 respectively.

The Estimated Average Daily Intake (EADI) for atrazine inhalation was determined according to the equation below (enHealth, 2012):

$$I \text{ (mgkg}^{-1}\text{d}^{-1}\text{)} = \frac{C \text{ (mgm}^{-3}\text{)} \times IR \text{ (m}^3 \text{ h}^{-1}\text{)} \times LR \times ET \text{ (hd}^{-1}\text{)} \times EF \text{ (d}^{-1}\text{)} \times 365 \times AT \text{ (d)} \times BW \text{ (kg)}}{BW \text{ (kg)}}$$

Where:

C = mean concentration of atrazine in air in mg/m<sup>3</sup>

I = Inhaled amount of atrazine in a day

IR= Inhalation Rate (20 m<sup>3</sup>/h, US EPA, 2009)

LR= Lung Retention Factor (0.375; NEPC, 1999)

EF= Exposure Frequency (365 d/yr, enHealth, 2012)

ET = Exposure Time (8 hrs, US EPA, 2014)

AT = Averaging Time period (70 years for adults and 6 yrs for children US EPA, 2009)

BW = Body Weight (70 kg for adults and 15 kg for children, US EPA, 2009)

The Estimated Average Daily Intake (*EADI*) is then divided by WHO Threshold Risk Value of 5.0 ng/m<sup>3</sup> to estimate Health Risk Index for the sampling communities.

$$\text{Hazard Index, HI} = \frac{\text{EADI (mgm}^{-3}\text{d}^{-1}\text{)}}{\text{WHO Threshold Risk Value mgm}^{-3}\text{d}^{-1}}$$

If the Health Risk Index (HI) >1, then the community is considered to be at risk from atrazine residues in the atmosphere but if it is less than one (1), it means that the exposure is within the tolerable limits set by Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), American Conference of Governmental Industrial Hygienists (ACGIH) at 5 mg/m<sup>3</sup> (OSHA, 1991; NIOSH, 1992 and ACGIH, 1991b).

### 3.11 STATISTICAL ANALYSIS

Statistical analysis of the data was done using SPSS (version 17.0). Multiple comparisons of the atrazine mean concentrations in air samples were done using LSD Post Hoc test of one-way ANOVA. Significant variations between the mean differentials were marked with asterisks as in table 4.7. Statistical Package for Social Sciences (SPSS) was used to generate mean, standard deviation, and the significant differences in the data

## CHAPTER FOUR

### 4.0 Results and Discussion

**Table 4.1: Mean, Standard Deviation, Range and Recovery of Atrazine Concentration in Air Samples using One-Way ANOVA**

| SAMPLING SITE | RANGE<br>(ng/m <sup>3</sup> ) | MEAN ± STD DEV<br>(pg/m <sup>3</sup> ) | AVERAGE<br>RECOVERY (%) |
|---------------|-------------------------------|----------------------------------------|-------------------------|
| Tanoso        | < 0.01 - 2.10                 | 0.53 ± 1.05                            | 84.0 %                  |
| Kejetia       | < 0.01 - 4.20                 | 1.05 ± 2.10                            | 100.5 %                 |

|                |               |               |         |
|----------------|---------------|---------------|---------|
| Suame          | < 0.01 - 1.10 | 0.28 ± 0.55   | 91.0 %  |
| Buokrom Estate | < 0.01 - 1.20 | 0.29 ± 0.55   | 102.5 % |
| Gyinyase       | < 0.01 - 1.10 | 0.28 ± 0.55   | 91.5 %  |
| Afari          | 4.20 - 25.00  | 13.34 ± 10.70 | 96.0 %  |
| Mpasatia       | 1.10 - 42.70  | 16.48 ± 17.17 | 92.5 %  |
| Nkawie-Toase   | 4.20 - 25.00  | 12.72 ± 7.69  | 95.0 %  |

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Table 4.1 shows a mean concentration of  $0.53 \pm 1.05 \text{ pg/m}^3$  for the 5 air particulate samples collected from Tanoso. Tanoso site recorded the second highest mean concentration of atrazine for the urban samples. The concentration of atrazine in 15 of the samples from urban communities were below the limit of detection of the HPLC (LOD =  $< 0.01 \text{ pg/m}^3$ ). Atrazine level in air particulate samples from Tanoso site ranges from  $< 0.01 - 2.10 \text{ pg/m}^3$ .

The highest mean concentration of atrazine among the samples from the urban sites was  $1.05 \pm 2.10 \text{ pg/m}^3$ . This was recorded at Kejetia. This high concentration of the pesticide at Kejetia may be due to the high number of pesticide dealers within the area. Here pesticides are opened and repacked into smaller containers for easy distribution. Atrazine levels in air particulate matter at Kejetia range from  $< 0.01 - 4.20 \text{ pg/m}^3$ .

Atrazine levels in 15 out of 40 air particulate matter were below detection limit of the HPLC. This makes the results consistent with a study conducted by Baraud et al (2003) in urban and rural settlements in France where only few air particulate samples analyzed by Multi- Residue Method under HPLC conditions for atrazine residues showed positive

results.

Suame and Gyinyase recorded very low urban mean residual concentration of  $0.28 \pm 0.55$   $\text{pg/m}^3$  each in the air particulate samples. Buokrom Estate also had a very low mean concentration of  $0.29 \pm 0.55$   $\text{pg/m}^3$ . The low residual atrazine level in air particulate samples from Suame and Buokrom Estate may be due to volatilization and influx from treated residential lawns, backyard gardens and vegetable farms which are common in these communities. The low mean concentrations of atrazine obtained for this study conformed to the findings of Baraud et al (2003) in communities in Japan, Canada, Germany and France in which very low mean concentrations of atrazine were obtained in the selected communities. Suame and Gyinyase had concentrations ranging from below detection level to  $1.10$   $\text{pg/m}^3$  each while that of Buokrom Estate ranges from  $< 0.01$  –  $1.20$   $\text{pg/m}^3$ .

Relatively higher mean concentrations of atrazine were recorded at farming communities of Afari, Mpasatia and Nkawie-Toase. Mpasatia had the highest mean concentration of  $16.48 \pm 17.17$   $\text{pg/m}^3$ . The concentration range of  $1.10$  -  $42.70$   $\text{pg/m}^3$  was determined at the Mpasatia sampling site. This could be attributed to intense use of atrazine by farmers in the area and subsequent volatilization from these treated farmlands (Yusa et al, 2011). Mean atrazine concentration of  $13.34 \pm 10.70$   $\text{pg/m}^3$  was recorded in air particulate matter collected at Afari. A mean concentration of  $12.72 \pm 7.69$   $\text{pg/m}^3$  was detected in air particulate matter at Nkawie-Toase with a concentration range of  $4.20$  –  $25.00$   $\text{pg/m}^3$ . The recorded mean concentrations in the farming communities for this study were found to be lower than the mean concentration of  $0.05$   $\text{ng/m}^3$  of atrazine in air particulate matter reported for Canadian agricultural region (HDOH, 2013).

The results of this study are in conformity with several other studies which compared atmospheric pesticide concentrations in rural and urban areas. For instance, Foreman et al (2000) compared mean levels of different pesticides including atrazine in atmospheric media in different regions of Mississippi and observed that concentrations of the pesticides from rural settlements were higher than those from urban communities. The same pattern of higher atrazine concentration was reported in rural sites in Alsace region than urban areas in France (Millet et al, 2006). Millet et al (2006) reported that low level pesticide contaminations in urban communities of Gampsheim and Geispolsheim in France was depended on wind direction and amount of atrazine being transported by airborne particles during sampling.

The highest average recovery of 102.5 % was recorded at Buokrom Estate community. Kejetia site had 100.5 % which is the second highest average recovery among the urban communities. The average recoveries for Tanoso, Suame and Gyinyase communities were 84.0 %, 91.0 % and 91.5 % respectively. All the farming communities had average recoveries which were more than 90.0 % as presented in Table 4.1 above. All the average percentage recoveries were within the accepted range of 70 % - 120% (USEPA, 2001).

**4.1 Atrazine Level in Air Particulate Samples from Farming Communities** Atrazine residues were detected in all the 15 samples collected from the farming communities. The data analysis was done using One-Way ANOVA to compare the mean concentrations of atrazine within 95 % confidence interval. If the P – value associated with the One -Way ANOVA is  $< 0.05$ , then there is evidence that the means are significantly different. On the

other hand, if the P-value is  $> 0.05$ , then there is no significant difference among the mean concentrations at the reported P-value (Tawiah, 2011).

**Table 4.2: Variations in Mean Concentrations of Atrazine within Farming Communities Using One-Way ANOVA**

|                | Sum of Squares | Df | Mean Square | F   | Sig. |
|----------------|----------------|----|-------------|-----|------|
| Between Groups | 40.64          | 2  | 20.32       | .13 | .88  |
| Within Groups  | 1873.99        | 12 | 156.17      |     |      |
| Total          | 1914.62        | 14 |             |     |      |

Table 4.2 shows that there is no significant differences between the mean concentrations of atrazine in air particulate samples collected from the farming communities. This is because the p-value of 0.88 is greater than the accepted p-value of 0.05 (Du Preez and Van-Vuren, 1992).

**Table 4.3: Multiple Comparisons of atrazine concentration in Air Samples within Farming Communities Using One-Way ANOVA**

| (I)<br>Rural | (J)<br>Rural  | Mean<br>Difference<br>(I-J) | Sig. | 95% Confidence Interval |             |
|--------------|---------------|-----------------------------|------|-------------------------|-------------|
|              |               |                             |      | Lower Bound             | Upper Bound |
| Afari        | Mpasatia      | -3.14                       | .70  | -20.36                  | 14.08       |
|              | Nkawie-Toase  | .62                         | .94  | -16.60                  | 17.84       |
| Mpasatia     | Nkawie- Toase | 3.76                        | .64  | -13.46                  | 20.98       |

Table 4.3 shows comparisons of atrazine mean concentrations in the farming communities using One-Way Analysis of Variance (ANOVA). From Table 4.3, it was clear that there was no significant variation in the mean concentrations of atrazine in the samples from Afari and Mpasatia sites because the P-value ( $P = 0.70$ ) is greater than 0.05.

The mean difference of  $-3.14 \text{ pg/m}^3$  was computed for Afari – Mpasatia group using Post Hoc test. The negative value meant that atrazine residual level from the atmosphere in Mpasatia exceeded that of Afari by  $3.14 \text{ pg/m}^3$ . However, this value was not significantly different since the P-value of 0.70 was greater than the accepted level of 0.05.

The mean concentration of atrazine in air particulate samples from Afari community was found to be higher by  $0.62 \text{ pg/m}^3$  than the mean concentration of the Nkawie -Toase site. No significant difference exists between the mean concentrations because their significance level was 0.94. Finally, the mean difference of  $3.76 \text{ pg/m}^3$  was recorded for Mpasatia and Nkawie-Toase communities. This mean difference was not found to be significant because the P-value of 0.64 was less than 0.05.

#### **4.2 Atrazine Level in Air Particulate Samples from Urban Communities**

The 25 air particulate samples were collected from the urban communities. The data obtained was analyzed using multiple comparison of One-Way ANOVA to establish mean differences between atrazine residue levels in the samples from the urban communities. If the computed P-values is less than 0.05, then the mean differences are said to be significantly different.

**Table 4.4: Variation in the Mean Concentrations of Atrazine within Urban Areas Using One-way ANOVA**

|                | Sum of<br>Squares | Df | Mean Square | F   | Sig. |
|----------------|-------------------|----|-------------|-----|------|
| Between Groups | 1.81              | 4  | .45         | .35 | .84  |
| Within Groups  | 19.26             | 15 | 1.28        |     |      |
| Total          | 21.07             | 19 |             |     |      |

Table 4.4 shows that there is no significant difference in the mean concentrations of atrazine from the urban communities because the P-value of 0.84 is higher than the accepted P-value of 0.05 (Du Preez and Van-Vuren, 1992). This may be because of evaporation and redistribution of atrazine residues from residential lawns and vegetable farms in the city by wind (HDOH, 2013).

**Table 4.5 Multiple Comparisons of atrazine Concentration in Air Samples within Urban Communities Using One-Way ANOVA**

| (I)               | (J)          | Mean<br>Difference<br>(I-J) | 95% Confiden<br>Interval |             |             |
|-------------------|--------------|-----------------------------|--------------------------|-------------|-------------|
|                   |              |                             | Sig.                     | Lower Bound | Upper Bound |
| Urban<br>Tanoso   | Kejetia      | -.53                        | .52                      | -2.23       | 1.18        |
|                   | Suame        | .25                         | .76                      | -1.46       | 1.96        |
|                   | Buokrom Est. | .26                         | .76                      | -1.46       | 1.96        |
|                   | Gyinyase     | .25                         | .76                      | -1.46       | 1.96        |
| Kejetia           | Suame        | .78                         | .35                      | -.93        | 2.48        |
|                   | Buokrom Est. | .79                         | .35                      | -.93        | 2.48        |
|                   | Gyinyase     | .78                         | .35                      | -.93        | 2.48        |
| Suame             | Buokrom Est. | .01                         | 1.00                     | -1.71       | 1.71        |
|                   | Gyinyase     | .00                         | 1.00                     | -1.71       | 1.71        |
| Buokrom<br>Estate | Gyinyase     | .01                         | 1.00                     | -1.71       | 1.71        |

Table 4.5 shows the variations in concentrations of atrazine from the selected urban communities in the Kumasi metropolis using One-Way ANOVA. The mean difference of -0.53 pg/m<sup>3</sup> of atrazine from Tanoso - Kejetia group was not significant at a  $P > 0.05$ . The negative sign means that Kejetia sampling site contributed more atrazine residues to the atmosphere than the Tanoso community. Also, the mean difference of 0.25 pg/m<sup>3</sup> each was calculated for Tanoso - Suame and Tanoso - Gyinyase group while 0.26 pg/m<sup>3</sup> was calculated for Tanoso - Buokrom Estate as presented in Table 4.5. Their P-values were greater than 0.05 and therefore the mean differences were not significant (Bejarano and Chandler, 2003). The mean differences reported for Kejetia - Suame and Kejetia - Gyinyase were 0.78 pg/m<sup>3</sup> each. Kejetia – Buokrom Estate group had a mean difference of 0.79 pg/m<sup>3</sup>. All the recorded P-values were greater than 0.05. This means that no significant differences exist among the mean atrazine levels within these communities (Table 4.5).

Finally, Table 4.5 shows that the mean difference for Suame – Buokrom Estate was recorded as 0.01 pg/m<sup>3</sup>. No mean difference for Suame – Gyinyase group (0.00 pg/m<sup>3</sup>) because both Suame and Gyinyase communities recorded the same mean concentrations ( $0.28 \pm 0.55$  pg/m<sup>3</sup> each). The recorded mean differences were not statistically significant because  $P > 0.05$ .

The low levels of atrazine residues were reported in air particles in the urban communities. The levels were relatively lower than the results from other studies. For instance, Sanusi et al (2000) found atrazine trace level in Strasbourg in a range of 690 51,260 pg/m<sup>3</sup> with mean concentration of 20,030 pg/m<sup>3</sup>. Sauret (2001) also reported a mean concentration of 130 pg/m<sup>3</sup> within a range below 15 to 794 pg/m<sup>3</sup> for Strasbourg community in France.

#### 4.3 Atrazine Level in Air Particulate Samples from both Urban and Farming Communities

Atrazine volatilizes into the atmosphere from activities such as plowing, burning of grasses, manufacturing and poor storage of pesticides. Atrazine adsorbs on air particulate matter in the atmosphere. Particle-borne atrazine is then transported to other communities. Many people in urban and rural communities are therefore exposed to hazards of atrazine (Linde and Davis, 1994). Therefore, many international organizations have set up permissible emission limits for atrazine. International threshold value of  $5.0 \text{ mg/m}^3$  was set by NIOSH, OSHA and ACGIH for atrazine (NIOSH, 2001; OSHA, 2001 and ACGIH, 2000). WHO threshold risk value was set at  $5.0 \text{ ng/m}^3$  (WHO, 2000).

Atrazine has been detected in all the urban and rural communities in the study area. However, the recorded mean concentrations of atrazine from the eight (8) communities were observed to be below the safe limits set by ACGIH, NIOSH, OSHA and WHO.

**Table 4.6: Variation in the Mean Concentrations of Atrazine in both Urban and Farming Communities**

|                | Sum of<br>Squares | Df | Mean Square | F    | Sig. |
|----------------|-------------------|----|-------------|------|------|
| Between Groups | 1651.22           | 7  | 235.89      | 3.36 | .01  |
| Within Groups  | 1893.25           | 27 | 70.12       |      |      |
| Total          | 3544.47           | 34 |             |      |      |

Table 4.6 shows that there is significant difference in the residual mean concentrations of atrazine in the air particulate samples from the urban and farming communities ( $P < 0.05$ ). The variations in the mean concentrations could be attributed to different levels of atrazine usage in the urban and farming communities as a result of different agricultural activities. Different amount of atrazine residues are therefore released into the atmosphere in the selected communities (Asiedu, 2013).

**Table 4.7: Multiple Comparisons of Atrazine Mean Concentrations from Urban and Farming Communities**

| (I) Site | (J) Site       | Mean             | 95% Confidence Interval |             |             |
|----------|----------------|------------------|-------------------------|-------------|-------------|
|          |                | Difference (I-J) | Sig.                    | Lower Bound | Upper Bound |
| Tanoso   | Kejetia        | -.53             | .93                     | -12.67      | 11.62       |
|          | Suame          | .25              | .97                     | -11.90      | 12.40       |
|          | Buokrom Estate | .26              | .97                     | -11.90      | 12.40       |
|          | Gyinyase       | .25              | .97                     | -11.90      | 12.40       |
|          | Afari          | .25              | .97                     | -11.90      | 12.40       |
|          | Mpasatia       | -12.82*          | .03                     | -24.34      | -1.29       |
|          | Nkawie - Toase | -15.96*          | .01                     | -27.48      | -4.43       |
| Kejetia  | Suame          | -12.20*          | .04                     | -23.72      | -.67        |
|          | Buokrom Estate | .78              | .90                     | -11.37      | 12.92       |
|          | Gyinyase       | .79              | .90                     | -11.37      | 12.92       |
|          | Afari          | .78              | .90                     | -11.37      | 12.92       |
|          | Mpasatia       | -12.29*          | .04                     | -23.82      | -.76        |
|          | Nkawie - Toase | -15.43*          | .01                     | -26.96      | -3.91       |
|          |                | -11.67*          | ~ .05                   | -23.20      | -.14        |

|       |                |         |      |        |       |
|-------|----------------|---------|------|--------|-------|
| Suame | Buokrom Estate | -.01    | 1.00 | -12.15 | 12.15 |
|       | Gyinyase       | .00     | 1.00 | -12.15 | 12.15 |
|       | Afari          |         |      |        |       |
|       | Mpasatia       | -13.07* | .03  | -24.59 | -1.54 |
|       | Nkawie - Toase | -16.21* | .01  | -27.73 | -4.68 |
|       |                | -12.45* | .04  | -23.97 | -.92  |

**Table 4.7: Multiple Comparisons of Atrazine Mean Concentrations from Urban and Farming Communities**

|                |                | Mean Difference (I-J) | 95% Confidence Interval |             |             |
|----------------|----------------|-----------------------|-------------------------|-------------|-------------|
| (I) Site       | (J) Site       |                       | Sig.                    | Lower Bound | Upper Bound |
| Buokrom Estate | Gyinyase       | .01                   | 1.00                    | -12.15      | 12.15       |
|                | Afari          |                       |                         |             |             |
|                |                | -13.05*               | .03                     | -24.59      | -1.54       |
|                | Mpasatia       |                       |                         |             |             |
|                | Nkawie - Toase | -16.19*               | .01                     | -27.73      | -4.68       |
|                |                | -12.43*               | .04                     | -23.97      | -.92        |
| Gyinyase       | Afari          | -13.07*               | .03                     | -24.59      | -1.54       |

|          |                |         |     |        |       |
|----------|----------------|---------|-----|--------|-------|
| Afari    | Mpasatia       | -16.21* | .01 | -27.73 | -4.68 |
|          | Nkawie - Toase | -12.45* | .04 | -23.97 | -.92  |
|          | Mpasatia       | -3.14   | .56 | -14.01 | 7.73  |
|          | Nkawie - Toase | .62     | .91 | -10.25 | 11.49 |
| Mpasatia | Nkawie - Toase | 3.76    | .48 | -7.11  | 14.63 |

**\*The mean difference is significant at 0.05 level.**

Table 4.7 focuses mainly on statistical differences of atrazine mean residual concentrations among the urban and farming communities. The significant mean differences were observed with values with asterisks in Table 4.7. A mean difference of  $-12.82 \text{ pg/m}^3$  was reported for Tanoso – Afari group. This was statistically significant because the P-value was less than 0.05. It can be deduced that Afari study site had high mean concentration of atrazine ( $-12.82 \text{ pg/m}^3$ ) than Tanoso community. The recorded mean difference of  $-15.96 \text{ pg/m}^3$  for Tanoso – Mpasatia group was significantly different because the  $P < 0.05$ . The mean difference for Tanoso - Nkawie-Toase group ( $-12.20 \text{ pg/m}^3$ ) was significant with a P-value of 0.04.

The computed mean differences for Kejetia - Afari, Kejetia - Mpasatia and Kejetia - Nkawie –Toase were  $-12.29$ ,  $-15.43$  and  $-11.67 \text{ pg/m}^3$  respectively. Significant variations exist among these communities because the  $P < 0.05$  for the study groups. The negative

mean differences showed that the farming communities had more atrazine residues in the atmosphere than Kejetia.

The calculated mean differences for the communities are as follows: Suame – Afari (13.07  $\text{pg/m}^3$ ), Suame –Mpasatia (-16.21  $\text{pg/m}^3$ ) and Suame - Nkawie –Toase (-12.45  $\text{pg/m}^3$ ) as presented in Table 4.7. All their P-values were less than 0.05 at 95 % confidence interval. This means that the difference in atrazine levels in the paired communities were significant.

The mean differences of -13.05, -16.19 and -12.43  $\text{pg/m}^3$  were recorded for Buokrom Estate – Afari, Buokrom Estate – Mpasatia and Buokrom Estate – Nkawie-Toase groups respectively. The differences were statistically significant with P-values of 0.03, 0.01 and 0.04 as presented in Table 4.7.

The mean differences in atrazine levels in air particulates from Gyinyase – Afari, Gyinyase – Mpasatia and Gyinyase –Nkawie – Toase were all significant ( $P < 0.05$ ). The negative mean differences (Table 4.7) show that the farming communities had higher mean concentrations of atrazine residue. Other studies in France by Coupe et al (1998) have also reported high levels of atrazine in the rural areas than the cities.

**Table 4.8: Health Risk Assessment of Atrazine for Adults**

| SAMPLING SITE | WHO THRESHOLD RISK VALUE ( $\text{ng/m}^3/\text{d}$ ) | EADI ( $\text{pg/m}^3/\text{d}$ ) | HEALTH INDEX | HEALTH RISK INDICATION |
|---------------|-------------------------------------------------------|-----------------------------------|--------------|------------------------|
| Tanoso        | 5.0                                                   | 6.43                              | 0.0013       | No                     |
| Kejetia       | 5.0                                                   | 12.86                             | 0.003        | No                     |
| Suame         | 5.0                                                   | 3.37                              | 0.001        | No                     |

|                |     |        |       |    |
|----------------|-----|--------|-------|----|
| Buokrom Estate | 5.0 | 3.38   | 0.001 | No |
| Gyinyase       | 5.0 | 3.37   | 0.001 | No |
| Afari          | 5.0 | 163.42 | 0.033 | No |
| Mpasatia       | 5.0 | 201.88 | 0.040 | No |
| Nkawie-Toase   | 5.0 | 155.82 | 0.031 | No |

Hazard Indices as presented in table 4.8 were obtained by dividing the Estimated Average Daily Intake (EADI) of air-borne atrazine by WHO Threshold Risk Value (TRV) of 5.0 ng/m<sup>3</sup> (Mensah et al, 2013). The Hazard Indices obtained for the communities in which sampling were carried out are 0.0013 (Tanoso), 0.003 (Kejetia), 0.001 (Suame), 0.001 (Buokrom Estate), 0.001 (Gyinyase), 0.033 (Afari), 0.040 (Mpasatia) and 0.031 (NkawieToase).

All the Hazard Indices obtained for the communities were less than one (1). This indicates that there are no immediate atrazine health risks for the adult populations in the eight (8) communities where samplings were carried out. However, there is likelihood of health risk among people living in these communities if there is lifetime exposure of atrazine because atrazine is toxic, persistent and it can easily bioaccumulate in biological systems (Fernando et al, 1992).

**Table 4.9: Health Risk Assessment of Atrazine for Children**

| SAMPLING SITE | WHO THRESHOLD RISK VALUE (ng/m <sup>3</sup> ) | EADI (pg/m <sup>3</sup> /d) | HEALTH INDEX | HEALTH RISK INDICATION |
|---------------|-----------------------------------------------|-----------------------------|--------------|------------------------|
|---------------|-----------------------------------------------|-----------------------------|--------------|------------------------|

|                |     |          |      |     |
|----------------|-----|----------|------|-----|
| Tanoso         | 5.0 | 350.02   | 0.07 | No  |
| Kejetia        | 5.0 | 700.04   | 0.14 | No  |
| Suame          | 5.0 | 183.34   | 0.04 | No  |
| Buokrom Estate | 5.0 | 183.34   | 0.04 | No  |
| Gyinyase       | 5.0 | 183.34   | 0.04 | No  |
| Afari          | 5.0 | 8893.80  | 1.78 | Yes |
| Mpasatia       | 5.0 | 10987.00 | 2.20 | Yes |
| Nkawie-Toase   | 5.0 | 8480.40  | 1.70 | Yes |

Hazard index of atrazine in air particulates; calculations for children were 0.04 each for Suame, Buokrom Estate and Gyinyase. The recorded hazard indices for Tanoso, Kejetia, Nkawie-Toase, Afari and Mpasatia were 0.07, 0.14, 1.70, 1.78 and 2.20 respectively. All the Health Indices for urban sites were found to be less than one (1) whereas the farming communities gave hazard indices which were greater than one (1). This means that atmospheric atrazine poses Health hazards to children in Afari, Nkawie – Toase and Mpasatia farming communities. The health effect of atrazine residues on children of Mpasatia is higher than all the other sites because it registered the highest health risk index.

Children also have a greater surface area to volume ratio which facilitates greater intake of atrazine from the polluted atmosphere (Arcury et al, 2007). As found in previous studies, children have high susceptibility to atrazine exposure because their body organs are still developing and their bodies have low abilities of detoxifying atrazine (Eskenazi, Bradman and Castorina 1999; Faustman et al, 2000).

Many diseases and birth defects are associated with exposure of children to atrazine. Atrazine causes childhood brain cancer, leukemia, cryptorchidism, hole-in-heart, orofacial, cleft palate, Attention Deficit hyperactive disorder (ADHD) and limb reduction (Linnet et al, 2003; Rogers and Kavlock, 2008).

Both paternal and maternal exposure to occupational and residential atrazine has been linked to stillbirths (Goulet and Theriault, 1991; Rupa et al, 1991; Taha and Gray 1993; Nurminen et al, 1995; Pastore et al, 1997; Medina-Carrilo et al, 2002). Neonatal death because of congenital abnormalities has also been associated with parental atrazine exposure (Schreinemachers, 2003; de Siqueira et al, 2010). From Table 4.9, children in the farming areas are much more exposed to atrazine than the urban communities.



## CHAPTER FIVE

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

Atrazine was detected in 25 out of 40 air particulate samples collected from 5 urban and 3 farming communities representing 62.5% of the air particulate samples. The mean residual concentrations of atrazine in the air particulate samples from the sampling sites are 0.28  $\text{pg/m}^3$  each for Suame and Gyinyase. Buokrom Estate had a mean atrazine level of 0.29  $\text{pg/m}^3$ . The mean concentrations of 0.53, 1.05, 13.34, 16.48 and 12.72  $\text{pg/m}^3$  were registered for Tanoso, Kejetia, Afari, Mpasatia and Nkawie-Toase sites respectively.

Kejetia site had the highest mean concentration of atrazine among the urban communities whilst Gyinyase and Suame in the Kumasi metropolis registered the lowest mean concentration. The mean residual level in air particulate samples from Mpasatia in the farming communities was found to be the highest. Nkawie- Toase had the lowest mean level among the farming communities. Generally, the mean concentrations from the farming communities were higher than those of the urban communities. Significant differences were observed between mean concentrations of atrazine from the farming communities and that of urban areas.

The Health Risk Indices for inhalation for adults in the selected sampling communities were all below one (1). But that for children in the farming communities were 1.70 (Nkawie-Toase), 1.78 (Afari) and 2.20 (Mpasatia). Children in these communities are at risk from atrazine in air particulates.

## 5.2 RECOMMENDATIONS

Most atrazine users in the farming communities are illiterates. They cannot read and understand the instructions on the labellings of atrazine. The Environmental Protection Agency (EPA) should educate farmers on proper use and disposal methods of atrazine in the farming communities. This can reduce atrazine residues in the atmosphere.

The Environmental Protection Agency should carry out periodic air monitoring of atrazine residues to ascertain its residual level in air. International agreements on reduction of particulate-borne atrazine should be vigorously enforced by Environmental Protection Agency of Ghana.

The health implications of atrazine on children should be communicated to Ghana Health Service for appropriate remedial actions. This would reduce birth defects among children in the farming communities.

Finally, atrazine residual levels should be determined in baby foods, breast milk and blood samples in the communities where the reported mean concentrations of atrazine were relatively higher. The findings should be published to educate nursing mothers and the general public.

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#### APPENDIX A

| SAMPLING |  | DATE OF | TIME | FLOW | TEMPERA | TOTAL |
|----------|--|---------|------|------|---------|-------|
|----------|--|---------|------|------|---------|-------|

| SITE     | AIR<br>SAMPLE | SAMPLIN<br>G | START<br>(AM) | STOP<br>(PM) | RATE<br>(L/min) | TEMPERATURE<br>(°C) | VOLUME<br>OF AIR<br>(L) |
|----------|---------------|--------------|---------------|--------------|-----------------|---------------------|-------------------------|
| TANOSO   | T 01          | 3-10-14      | 10.25         | 7.25         | 30              | 25                  | 14400                   |
|          | T 02          | 5-10-14      | 8.45          | 4.45         | 30              | 25                  | 14400                   |
|          | T 03          | 6-10-14      | 9.20          | 5.20         | 30              | 25                  | 14400                   |
|          | T 04          | 7-10-14      | 10.10         | 6.10         | 30              | 25                  | 14400                   |
|          | T 05          | 8-10-14      | 7.30          | 3.30         | 30              | 25                  | 14400                   |
| KEJETIA  | KJ 01         | 10-10-14     | 8.55          | 5.55         | 30              | 25                  | 14400                   |
|          | KJ 02         | 11-10-14     | 9.05          | 5.05         | 30              | 25                  | 14400                   |
|          | KJ 03         | 12-10-14     | 7.04          | 3.04         | 30              | 25                  | 14400                   |
|          | KJ 04         | 13-10-14     | 11.22         | 5.44         | 30              | 25                  | 11460                   |
|          | KJ 05         | 14-10-14     | 6.25          | 2.25         | 30              | 25                  | 14400                   |
| SUAME    | S 01          | 15-10-14     | 7.36          | 3.36         | 30              | 25                  | 14400                   |
|          | S 02          | 16-10-14     | 7.30          | 3.30         | 30              | 25                  | 14400                   |
|          | S 03          | 17-10-14     | 8.25          | 4.25         | 30              | 25                  | 14400                   |
|          | S 04          | 18-10-14     | 7.40          | 3.40         | 30              | 25                  | 14400                   |
|          | S 05          | 20-10-14     | 7.00          | 3.00         | 30              | 25                  | 14400                   |
| BUOKROM  | B 01          | 21-10-14     | 8.10          | 4.10         | 30              | 25                  | 14400                   |
|          | B 02          | 22-10-14     | 7.42          | 3.42         | 30              | 25                  | 14400                   |
|          | B 03          | 23-10-14     | 7.50          | 3.50         | 30              | 25                  | 14400                   |
|          | B 04          | 24-10-14     | 6.25          | 2.25         | 30              | 25                  | 14400                   |
|          | B 05          | 25-10-14     | 6.45          | 2.45         | 30              | 25                  | 14400                   |
| GYINYASE | G 01          | 26-10-14     | 7.29          | 3.29         | 30              | 25                  | 14400                   |

|              |       |          |       |      |    |    |       |
|--------------|-------|----------|-------|------|----|----|-------|
|              | G 02  | 27-10-14 | 8.35  | 4.35 | 30 | 25 | 14400 |
|              | G 03  | 28-10-14 | 9.25  | 5.25 | 30 | 25 | 14400 |
|              | G 04  | 3-11-14  | 8.40  | 4.40 | 30 | 25 | 14400 |
|              | G 05  | 10-12-14 | 9.00  | 5.00 | 30 | 25 | 14400 |
| AFARI        | A 01  | 15-02-15 | 8.45  | 4.45 | 30 | 25 | 14400 |
|              | A 02  | 17-02-15 | 7.46  | 3.46 | 30 | 25 | 14400 |
|              | A 03  | 20-02-15 | 7.00  | 3.00 | 30 | 25 | 14400 |
|              | A 04  | 25-02-15 | 7.07  | 3.07 | 30 | 25 | 14400 |
|              | A 05  | 26-02-15 | 8.03  | 4.03 | 30 | 25 | 14400 |
| MPASATIA     | M 01  | 28-02-15 | 6.30  | 2.30 | 30 | 25 | 14400 |
|              | M 02  | 3-03-15  | 6.50  | 2.50 | 30 | 25 | 14400 |
|              | M 03  | 5-03-15  | 9.00  | 5.00 | 30 | 25 | 14400 |
|              | M 04  | 7-03-15  | 8.21  | 4.21 | 30 | 25 | 14400 |
|              | M 05  | 10-03-15 | 7.33  | 3.33 | 30 | 25 | 14400 |
| NKAWIE-TOASE | NT 01 | 15-03-15 | 8.09  | 4.09 | 30 | 25 | 14400 |
|              | NT 02 | 16-03-15 | 7.51  | 3.51 | 30 | 25 | 14400 |
|              | NT 03 | 21-03-15 | 10.01 | 6.01 | 30 | 25 | 14400 |
|              | NT 04 | 24-03-15 | 9.38  | 5.38 | 30 | 25 | 14400 |
|              | NT 05 | 26-03-15 | 8.09  | 4.09 | 30 | 25 | 14400 |

# APPENDIX B

| LOCATION     | SAMPLE | WEIGHT OF<br>AIR<br>PARTICULA<br>TE MATTER<br>(g) | EXTRACTION<br>CONCENTRA-<br>TION<br>(mg/kg) | VOLUME<br>OF AIR<br>SAMPLED<br>(m <sup>3</sup> ) | TOTAL<br>CONCENT-<br>RATION<br>(ng/ m <sup>3</sup> ) |
|--------------|--------|---------------------------------------------------|---------------------------------------------|--------------------------------------------------|------------------------------------------------------|
| Tanoso       | T 01   | 0.757                                             | 0.02                                        | 14.40                                            | 0.0021                                               |
|              | T 02   | 0.695                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | T 03   | 0.687                                             | 0.005                                       | 14.40                                            | 0.000525                                             |
|              | T 04   | 0.629                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | T 05   | 0.631                                             | ND                                          | 14.40                                            | 0.0000                                               |
| Kejetia      | KJ 01  | 0.683                                             | 0.04                                        | 14.40                                            | 0.0042                                               |
|              | KJ 02  | 0.728                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | KJ 03  | 0.689                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | KJ 04  | 0.697                                             | ND                                          | 11.40                                            | 0.0000                                               |
|              | KJ 05  | 0.693                                             | 0.01                                        | 11.40                                            | 0.00105                                              |
| Suame        | S 01   | 0.699                                             | 0.01                                        | 14.40                                            | 0.0011                                               |
|              | S 02   | 0.717                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | S 03   | 0.740                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | S 04   | 0.719                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | S 05   | 0.720                                             | 0.00248                                     | 14.40                                            | 0.000273                                             |
| Buokrom Est. | B 01   | 0.721                                             | 0.01                                        | 14.40                                            | 0.0011                                               |
|              | B 02   | 0.732                                             | 0.0025                                      | 14.40                                            | 0.000275                                             |
|              | B 03   | 0.734                                             | ND                                          | 14.40                                            | 0.0000                                               |
|              | B 04   | 0.687                                             | ND                                          | 14.40                                            | 0.0000                                               |

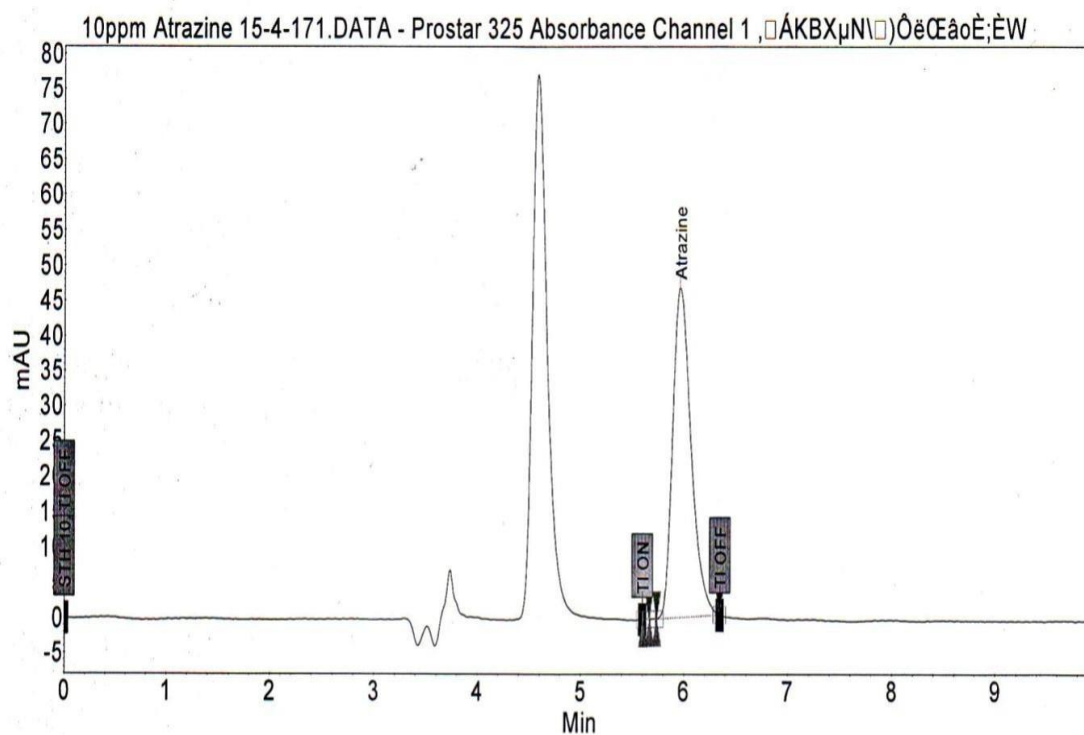
|              |       |       |         |       |          |
|--------------|-------|-------|---------|-------|----------|
|              | B 05  | 0.713 | ND      | 14.40 | 0.0000   |
| Gyinyase     | G 01  | 0.736 | < 0.01  | 14.40 | 0.0011   |
|              | G 02  | 0.726 | ND      | 14.40 | 0.0000   |
|              | G 03  | 0.723 | ND      | 14.40 | 0.0000   |
|              | G 04  | 0.983 | 0.00252 | 14.40 | 0.000277 |
|              | G 05  | 0.991 | ND      | 14.40 | 0.0000   |
| Afari        | A 01  | 0.731 | 0.24    | 14.40 | 0.0250   |
|              | A 02  | 0.719 | 0.04    | 14.40 | 0.0042   |
|              | A 03  | 0.738 | 0.05    | 14.40 | 0.0052   |
|              | A 04  | 0.727 | 0.07    | 14.40 | 0.0073   |
|              | A 05  | 0.735 | 0.24    | 14.40 | 0.0250   |
| Mpasatia     | M 01  | 0.715 | 0.01    | 14.40 | 0.0011   |
|              | M 02  | 0.730 | 0.20    | 14.40 | 0.0208   |
|              | M 03  | 0.743 | 0.41    | 14.40 | 0.0427   |
|              | M 04  | 0.736 | 0.16    | 14.40 | 0.0167   |
|              | M 05  | 0.741 | 0.01    | 14.40 | 0.0011   |
| Nkawie-Toase | NT 01 | 0.726 | 0.11    | 14.40 | 0.0115   |
|              | NT 02 | 0.725 | 0.24    | 14.40 | 0.0250   |
|              | NT 03 | 0.738 | 0.04    | 14.40 | 0.0042   |
|              | NT 04 | 0.713 | 0.13    | 14.40 | 0.0135   |
|              | NT 05 | 0.742 | 0.09    | 14.40 | 0.0094   |

## APPENDIX C

### Chromatogram : 10ppm Atrazine 15-4-171\_channel1

System : HPLC1  
Method : Atrazine-Cal  
User : Administrator

Acquired : 4/17/2015 4:35:41 PM  
Processed : 4/23/2015 12:24:30 PM  
Printed : 5/4/2015 12:43:13 PM



#### Peak results :

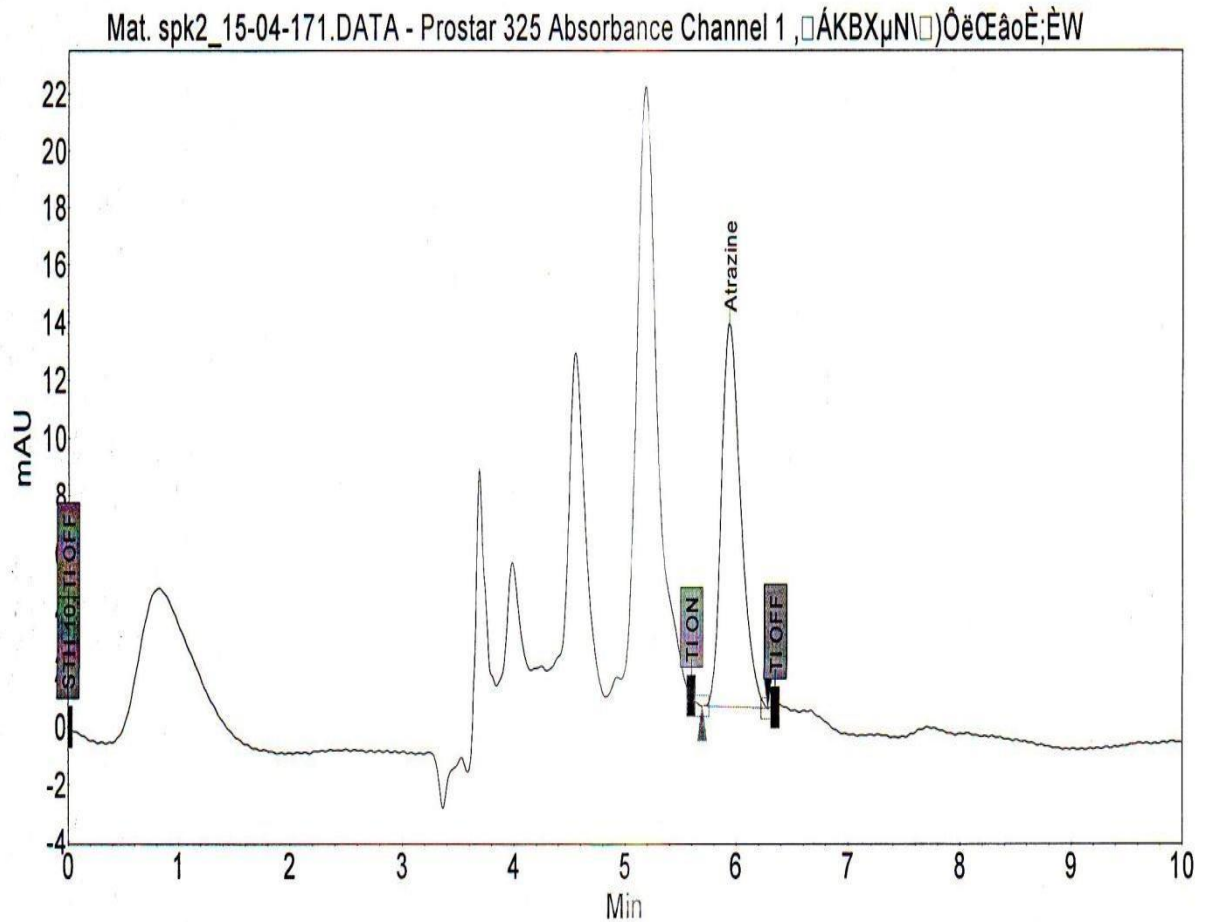
| Index | Name     | Time<br>[Min] | Quantity<br>[% Area] | Height<br>[mAU] | Area<br>[mAU.Min] | Area %<br>[%] |
|-------|----------|---------------|----------------------|-----------------|-------------------|---------------|
| 1     | UNKNOWN  | 5.63          | 0.02                 | 0.1             | 0.002             | 0.019         |
| 2     | UNKNOWN  | 5.71          | 0.02                 | 0.1             | 0.002             | 0.021         |
| 3     | Atrazine | 5.96          | 99.96                | 46.7            | 9.577             | 99.959        |
|       |          |               |                      |                 |                   |               |
| Total |          |               | 100.00               | 46.8            | 9.580             | 100.000       |

# APPENDIX D

## Chromatogram : Mat. spk2\_15-04-171\_channel1

System : HPLC1  
Method : Atrazine  
User : Administrator

Acquired : 4/17/2015 9:02:13 PM  
Processed : 4/23/2015 11:25:13 AM  
Printed : 5/4/2015 12:40:04 PM



### Peak results :

| Index | Name     | Time<br>[Min] | Quantity<br>[% Area] | Height<br>[mAU] | Area<br>[mAU.Min] | Area %<br>[%] |
|-------|----------|---------------|----------------------|-----------------|-------------------|---------------|
| 1     | Atrazine | 5.94          | 100.00               | 13.3            | 2.679             | 100.000       |
| Total |          |               | 100.00               | 13.3            | 2.679             | 100.000       |

## APPENDIX E



**Unprotected Atrazine Applicator Spraying a Field near a School at Buokrom Estate**

