AIR POLLUTANTS IN SCHOOL, URBAN, AND INDUSTRIAL ENVIRONMENTS OF HAWASSA CITY, ETHIOPIA: LEVELS AND POSSIBLE HUMAN HEALTH RISK ASSESSMENT

PHD DISSERTATION

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HAWASSA UNIVERSITY, HAWASSA, ETHIPIA

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A DISSERTATION SUBMITTED TO THE DEPARTMENT OF BIOLOGY, COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES, SCHOOL OF GRADUATE STUDIES, HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA

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ADVISORS' APPROVAL SHEET

This is to certify that the dissertation entitled "**AIR POLLUTANTS IN SCHOOL, URBAN, AND INDUSTRIAL ENVIRONMENTS OF HAWASSA CITY, ETHIOPIA: LEVELS AND POSSIBLE HUMAN HEALTH RISK ASSESSMENT"** submitted in partial fulfillment of the requirements for the degree of **Doctor of Philosophy (PhD)** with specialization in **Environmental Toxicology**, to the Graduate Program of the **Department of Biology**, and has been carried out by **ABEBECH NUGUSE AMARE ID. No. PhDEnTo/0001/11,** under our supervision. Therefore, we recommend that the student has fulfilled the requirements and hence herby can submit the dissertation to the department.

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We, the undersigned, members of the Board of Examiners of the final open defense by **Abebech Nuguse Amare** have read and evaluated his/her thesis/dissertation entitled "**AIR POLLUTANTS IN SCHOOL, URBAN, AND INDUSTRIAL ENVIRONMENTS OF HAWASSA CITY, ETHIOPIA: LEVELS AND POSSIBLE HUMAN HEALTH RISK ASSESSMENT"** and examined the candidate. This is, therefore, to certify that the thesis/dissertation has been accepted in partial fulfillment of the requirements for the Doctor of Philosophy degree (PhD).

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DEDICATION

To my grandfather, Melake Genet Meresa Kidanu, my mother, Mrs. Abadit Meresa, and my father, Priest Nuguse Amare.

DECLARATION

I hereby declare that this PhD dissertation is my original work and has not been presented for a degree in any other University, and all sources of material used for this dissertation have been duly acknowledged.

Name: Abebech Nuguse Amare

Date: June 2024

Signature: _____

BIOGRAPHICAL SKETCH

The author was born on February 23, 1986 G.C., in Mekelle City, Ethiopia. She attended Grades 1 to 8 at Myliham elementary and junior high school. She then went to Mekelle high school, in Grades 9 and 10. She went to Atse Yohannes preparatory school for Grades 11 and 12. She took the Ethiopian University Entrance Examination in 2004 G.C. and joined Hawassa University the same year. She obtained a BSc degree in applied chemistry on July 12, 2007 G.C. After graduation from Hawassa University, she was employed as a graduate assistant (GA-1) at Hawassa University. After serving Hawassa University for four years, she joined Ghent University, Belgium, to study a Master of Science in Environmental Sanitation from September 2011 G.C. to September 2013 G.C. She completed her MSc study on September 13, 2013 G.C., and returned to Hawassa University to serve as a lecturer. She started her PhD study in Environmental Toxicology at Hawassa University on December 12, 2018 G.C., and this Dissertation has been submitted as a partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Toxicology.

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LIST OF ABBREVIATIONS

AQI	Air Quality Index
BTEX	Benzene, Toluene, Ethylbenzene and meta-, para-, and ortho- Xylene
ΣBTEX	Total BTEX
CCl_4	Carbon Tetrachloride
CCR	Cumulative Cancer Risk
CO	Carbon Monoxide
D	Detected
ECD	Electron Capture Detection
ELCR	Excess Lifetime Cancer Risk
EEPA	Ethiopia Environmental Protection Authorities
EPA	Environmental Protection Agency
EU	European Union
FID	Flame Ionization Detection
GC	Gas Chromatography
He	Helium
HQ	Hazard Quotient
IARC	International Agency for Research on Cancer
IS	Internal Standard
I/O	Indoor to Outdoor concentration ratio
LCR	Lifetime Cancer Risk
MIR	Maximum Incremental Reactivity

MS	Mass Spectrometry
m+p-X	m+p-Xylenes
ND	Not Detected
NIST	National Institute of Science and Technology
NO_x	Nitrogen Oxides
NO_2	Nitric Oxide
OFP	Ozone Formation Potential
PM	Particulate Matter
RSRF	Relative Sample Response Factor
SO_x	Sulfur Oxides
SO_2	Sulfur Dioxide
SRF	Sample Response Factor
S/N	Signal to Noise ratio
T/B	Toluene-to-Benzene ratio
TD	Thermal Desorption
THRI	Total Hazard Ratio Indicator
Tol-d_8	[$^2H_8$]Toluene
TVOCS	Total Volatile Organic Compounds
VOCs	Volatile Organic Compounds
UR	Unit Risk
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

ABSTRACT

Air pollution has received enormous attention globally due to its detrimental effects on human health, especially on susceptible populations such as children. However, there is scarce data on concentrations and sources of volatile organic compounds (VOCs), inorganic gaseous pollutants (NO_2, CO, and SO_2), and particulate matter ($PM_{2.5}$ and PM_{10}) in Ethiopia, particularly Hawassa City. The objective of this PhD work was to determine the indoor and outdoor concentrations of VOCs, $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in schools, urban, and industrial environments in Hawassa City, Ethiopia, and evaluate potential health concerns.

VOC samples were taken via the passive sampling method using Tenax TA as a sorbent and analyzed using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). The concentrations of PM_{10} and $PM_{2.5}$ were measured using a portable gas monitor device (HoldPeak Laser PM meter, HP 5800D). Levels of NO_2, CO, and SO_2 were measured using the Aeroqual Series 500 Portable Air Quality Monitor (Aeroqual Ltd., New Zealand). Concentrations of 76 VOCs were determined in air samples from the classrooms and playgrounds of eight primary schools in Hawassa. Concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 were also measured in the outdoor and indoor environments of ten primary schools in Hawassa, Ethiopia. Additionally, indoor and outdoor concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 were measured in urban and industrial areas of Hawassa City, Ethiopia, in the dry and wet seasons.

The highest total VOCs (TVOCs) concentration (83 μg/m^3) was observed in a classroom of School 2, followed by a classroom of School 1 (76 μg/m^3), while the smallest TVOC concentration, 37 μg/m^3, was recorded in the playground of School 8. Among the BTEX, toluene was the most dominant in all samples, ranging from 33% in School 4 to 38% in School 1 of ∑BTEX. The I/O ratios of individual VOC in the schools ranged from 0.44 in School 4 to 9.21 in School 2. The highest cumulative cancer risk (CCR×10^6) and the total hazard ratio indicator (THRI) values were 126 and 1.58E-01, respectively, in a classroom of School 4. The concentrations of $PM_{2.5}$, PM_{10}, and NO_2 in the ten primary schools ranged 11–66.3, 30.8–399.7, and 60.5–152 μg/m^3, respectively, and CO and SO_2 were not detected in any of the schools. The hazard quotient (HQ) for $PM_{2.5}$ and PM_{10} was greater than one in 20% and 50% of the indoor sampling locations, respectively, suggesting moderate risks. The Air Quality Index (AQI) at 40% and 30% of the outdoor sampling sites were unhealthy for sensitive groups due to exposure to $PM_{2.5}$ and PM_{10}, respectively. The concentrations of $PM_{2.5}$ and PM_{10} were found to be above the WHO mean guidelines in 55% and 85% of the sampling sites, respectively, indicating poor quality of the air.

In the urban and industrial areas, $PM_{2.5}$, PM_{10}, and NO_2 were detected during both seasons and at all sampling sites. CO was detected during the wet season but not detected at all during the dry season at any of the sites. SO_2 was detected only at one site, S17 (ambient of industry 1), during both studied seasons. During the dry season, the average concentrations of $PM_{2.5}$, PM_{10}, and NO_2 ranged from 8.8–310.7, 20.1–515.8, and 40.0–123.7 μg/m^3, respectively. In the wet season, the ranges for $PM_{2.5}$, PM_{10}, NO_2, and CO levels were 17.2–117.4, 24.3–167.2, 31.8–111.3, and 77–33312 μg/m^3, respectively.

In both the wet and dry seasons, the hazard quotient for $PM_{2.5}$ and PM_{10} was greater than one, suggesting a non-carcinogenic effect. The $PM_{2.5}$ excess lifetime cancer risk ranged from 0.1 to 0.7, which was greater than the recommended range by the WHO and the US EPA, implying a considerable health risk in urban and industrial areas. The CCR and THRI values indicated that the exposure of children to the measured concentrations of benzene may have potentially harmful effects. Additionally, the AQI, HQ values, and concentrations of $PM_{2.5}$ and PM_{10} indicated poor air quality in the schools and suggested a significant health risk for all populations around the schools.

CHAPTER 1. GENERAL INTRODUCTION

1.1 Background and Justification of the Study

Almost all, or 99%, of the overall population of the world breathes air that exceeds the World Health Organization's (WHO) guidelines and contains high levels of pollutants (WHO, 2023a). Several studies (e.g., Franchini et al., 2015; Newby et al., 2015; WHO, 2023b) have indicated that the effect of indoor and ambient air pollution is correlated with seven million premature deaths worldwide per year. Pollutants of major public health concern include sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), ozone (O_3), particulate matter (PM), and volatile organic compounds (VOCs) (McGranahan & Murray, 2012; US EPA, 2023a; WHO, 2023a).

The major sources of VOCs are emissions from industrial activities, oil refineries, traffic, natural sources such as emissions from vegetation, and household products such as paints, solvents, varnishes, aerosol sprays, cleansers, disinfectants, and air fresheners (Sarigiannis et al., 2011; Mohd Hanif et al., 2021; Yu et al., 2021; Zhang et al., 2022; US EPA, 2023b). VOCs like benzene and formaldehyde are carcinogens, and atmospheric volatile organic compounds play an important role in global warming, stratospheric ozone depletion, and tropospheric ozone formation (Calvert, 1994; Demeestere et al., 2007; Barletta et al., 2008). The major inorganic gaseous air pollutants include nitrogen dioxide (NO_2), carbon monoxide (CO), and sulfur dioxide (SO_2), and their major sources are the combustion of fossil fuels in vehicles, industrial and power generators, and cooking fires (Omidvarborna et al., 2015; Agbo et al., 2021).

Exposure to high concentrations of NO_2 can irritate the airways in the human respiratory system. Likewise, short-term exposures to SO_2 can harm the human respiratory system and make breathing difficult (US EPA, 2021). Low levels of CO exposure make healthy people tired, and heart disease patients experience chest pain. Higher amounts of CO can cause dizziness, headaches, confusion, and fatalities at very high concentrations (Kumie et al., 2009; US EPA, 2021; WHO, 2023c).

The main sources of particulate matter include cooking and combustion activities, the use of kerosene heaters, cigarette smoking, volcanoes, dust storms, forest and grassland fires, transportation, and various industrial processes (Keil et al., 2010; Van Vliet et al., 2013; US EPA, 2023). The effects of inhaling particulate matter ($PM_{2.5}$–PM_{10}) that have been widely studied in humans and animals include asthma, lung cancer, respiratory diseases, cardiovascular disease, premature delivery birth defects, low birth weight, and premature death (Sapkota et al., 2012; WHO, 2023b). However, the air pollutant concentration data in indoor and outdoor school, urban, and industrial areas is very limited in the cities of most African countries, including Ethiopia. This thesis thus attempted to investigate the concentrations of VOCs, particulate matter, and inorganic gaseous pollutants in the indoor and outdoor environments of primary schools, urban areas, and industrial areas of Hawassa city, Ethiopia.

1.2 Statement of the Problem

There is a lack of data on indoor and outdoor air pollutants in developing countries, including Ethiopia. Although there are some studies on VOCs, particulate matter, and inorganic gaseous pollutant concentrations in urban areas of Ethiopia, the data on these air pollutants in primary schools is very limited, as in most African countries. The health risk assessment of school-age children becomes difficult because of such insufficient data. Furthermore, there is still a scarcity of data on the levels and sources of inorganic gaseous pollutants and particulate matter in the cities of most African countries, including Ethiopia. Most of the studies on the concentrations of VOCs, particulate matter, and inorganic gaseous pollutants studied in Ethiopia focused on the capital city, Addis Ababa. However, there is very limited publication on the levels of air pollutants in most Ethiopian cities, including Hawassa. Therefore, the main purpose of this PhD research was to determine the levels of VOCs, $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in primary school environments, urban areas, and industrial areas of Hawassa City, Ethiopia, and evaluate the possible health hazards associated with them.

1.3 Objectives of the Study

1.3.1 General Objective

To determine the concentrations and health risks associated with exposure to VOCs, inorganic gases, and particulate matter in the school, urban, and industrial environments of Hawassa city, Ethiopia

1.3.2 Specific Objectives

1. To assess the concentrations of volatile organic compounds (VOCs) in school environments in Hawassa City, Ethiopia, and assess possible human health risks (Chapter 3)
2. To determine the levels of particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (CO, NO_2, and SO_2) in schools in Hawassa City and assess the possible health risks (Chapter 4)
3. To investigate the concentrations and possible health risks of exposure to particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (CO, NO_2, and SO_2) in urban and industrial areas of Hawassa city, Ethiopia (Chapter 5)

1.4 Scope of the Study

This study focused on the indoor and outdoor concentrations of volatile organic compounds, particulate matter, and inorganic gaseous pollutants in the school, urban, and industrial areas of Hawassa City, Ethiopia, and assessed potential health risks associated with these pollutants. The air pollutants considered in this study were 76 volatile organic compounds, three inorganic gaseous pollutants (NO_2, SO_2, and CO), and two diameter sizes of particulate matter ($PM_{2.5}$ and PM_{10}).

1.5 Significance of the Study

This study is designed to provide information on levels, sources, and risks associated with exposure to VOCs, particulate matter, and inorganic gaseous pollutants in primary schools in Hawassa City, Ethiopia. Additionally, assess the indoor and outdoor concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in the urban and industrial areas of Hawassa City, Ethiopia, during both dry and wet seasons and assess potential health risks associated with these pollutants. The findings of this study are vital in supporting the concerned government bodies in raising awareness and stepping up their initiatives to improve the air quality in schools, urban areas, and industrial areas. The results would also add to the limited data on $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in developing countries and contribute to future global efforts to minimize air pollution.

1.6 Structure of the Dissertation

This dissertation is based on results from the present study on the levels of air pollutants (VOCs, $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2) in the indoor and outdoor environments of primary schools in Hawassa City, Ethiopia, and the potential human health risks.

And on the levels of inorganic gaseous pollutants, particulate matter, and health risk assessment in urban and industrial areas of Hawassa City, Ethiopia. The whole dissertation is presented in six chapters, including the general introduction, as follows:

Chapter 1 General Introduction

This chapter deals with the background of the study, the statement of the problem, the objectives of the study, and the structure of the dissertation.

Chapter 2 Literature review

This chapter presents a literature review introducing the definition of air pollutants, sources of air pollutants, levels of air pollutants, health effects of air pollutants, and measurement methods of air pollutants.

Chapter 3 Volatile organic compounds in school environments of Hawassa city, Ethiopia and assessment of possible human health risks

This chapter focused on the concentrations of volatile organic compounds in primary schools in Hawassa City and assessed potential health risks. 76 VOCs were measured in primary schools in Hawassa, Ethiopia, to evaluate the possible health hazards associated with them. The following published article emanated from the results of this chapter.

Amare, A. N., Sorsa, S., Gebremariam, Z., De Coster, G., Van Langenhove, H., Demeestere, K., & Walgraeve, C. (2023). Volatile organic compounds in school environments of Hawassa city, Ethiopia and assessment of possible human health risks. *Atmospheric Pollution Research*, *14*(12), 1309–1042. https://doi.org/10.1016/j.apr.2023.101943

Chapter 4 Exposure of School Children to Particulate Matter and Inorganic Gaseous Pollutants in Hawassa City, Ethiopia

This chapter presents the concentrations of particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, SO_2, and CO) in primary schools in Hawassa city, Ethiopia.

The concentrations of $PM_{2.5}$, PM_{10}, NO_2, SO_2, and CO were measured in the classrooms and playgrounds of 10 primary schools. The results presented in this chapter constitute the following manuscript:

"Exposure of School Children to Particulate Matter and Inorganic Gaseous Pollutants in Hawassa City, Ethiopia" is under review in the Journal of *Environmental Monitoring and Assessment.*

Chapter 5 Levels and health risk assessments of particulate matter and inorganic gaseous pollutants in urban and industrial areas of Hawassa City, Ethiopia

This chapter presents the concentrations of particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, SO_2, and CO) in urban and industrial areas of Hawassa city, Ethiopia. The concentrations of $PM_{2.5}$, PM_{10}, NO_2, SO_2, and CO were measured outdoors from markets, roadsides, recreational, and ambient areas near industries, and indoors from households near roadsides and industries. The results presented in this chapter constitute the following manuscript:

"Levels and health risk assessments of particulate matter and inorganic gaseous pollutants in urban and industrial areas of Hawassa City, Ethiopia" is under review in the Journal of *Heliyon*.

Chapter 6: GENERAL CONCLUSIONS AND RECOMENDATIONS

This chapter summarized major findings, and conclusions and recommendations were made based on the overall findings.

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CHAPTER 2. LITERATURE REVIEW

2.1 Air Pollution

Air pollution is the term used to refer to any substance, biological, or physical factor that interferes with the natural properties of the atmosphere to pollute the indoor or outdoor environment (WHO, 2023a). Air pollution has received enormous attention worldwide due to its adverse effects on humans, especially on susceptible populations such as children. The majority of people on the globe, about 99% of the total population, breathe air that is polluted to high levels and above WHO guidelines (WHO, 2022). Identification of all possible sources is very important for the design and implementation of effective air emission control strategies. The primary cause of air pollution is the burning of fossil fuels in various industrial activities, cooking, heating, and power generation (Holman, 1999; Sanchez et al., 2008; US EPA, 2023b; WHO, 2023a). Anthropogenic sources contribute to the majority of air pollution emission sources. These include mobile sources like vehicles as well as stationary sources like industries, refineries, and power plants. Natural occurrences like volcanic eruptions and forest fires can also produce certain air pollutants (Van Vliet et al., 2013; US EPA, 2018; WHO, 2023). The use of fossil fuels has increased over the past century, gradually affecting the atmosphere's composition. Air pollution can have both short-term and long-term effects on the various organs and systems in the human body. Airborne pollutants are a risk to human health and have the potential to cause fatalities or serious illness (Kampa & Castanas, 2008; Keil et al., 2010; Van Vliet et al., 2013; WHO, 2023b).

Any chemical or substance present in the air at concentrations high enough to pose a threat to people, other animals, plants, or materials is referred to as an air pollutant (Kampa & Castanas, 2008; Keil et al., 2010; Van Vliet et al., 2013; US EPA, 2017). The air pollutants, which include volatile organic compounds (VOCs), sulfur oxides (SOx), nitrogen oxides (NOx), particulate matter (PM), and carbon monoxide (CO), have the strongest evidence of being detrimental to human health (Holman, 1999; McGranahan & Murray, 2012; US EPA, 2023b; WHO, 2023a).

2.2 Volatile Organic Compounds (VOCs)

2.2.1 Definitions of VOCs

There are more than one definitions of volatile organic compounds (VOCs) based on their effects and their physical-chemical properties. Based on their physical-chemical properties, the definition given by EU Directive 2004/42/EC is "VOC is any organic compound having an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa" (EU, 2004). Because methane exists in the atmosphere in quite different concentration ranges and is relatively non-reactive in the troposphere, it is often considered separately (Demeestere et al., 2007).

Based on their effects, according to the definition given by the US EPA, "VOCs are defined as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions" (US EPA, 2009). In the presence of sunlight, VOCs in ambient air undergo photochemical reactions leading to the formation of secondary pollutants, of which the most prominent is tropospheric ozone (Do et al., 2013; Grant et al., 2008).

In order to assess the extent of VOCs contribution to ground-level ozone formation, quantitative data are needed on both VOCs occurrence and their reactivity towards ozone formation (Do et al., 2013). Between 1994 and 2010, Carter developed and updated ozone reactivity scales for VOCs, making use of maximum incremental reactivity (MIR) values (Carter, 1994, 2010). The MIR is defined as the highest amount of ozone formed per unit amount of VOC added to, or subtracted from, an urban or rural mixture of VOCs (Carter, 1994). Based on MIR (g O_3 per g VOC), the OFP (g O_3/m^3) can be calculated, provided that VOC concentration levels (g VOC/m^3) are known.

2.2.2 Sources of VOCs

The primary outdoor sources of volatile organic compounds (VOCs) include oil refineries, transportation, industrial processes, and natural sources (Mohd Hanif et al., 2021; S. Yu et al., 2021; Zhang et al., 2022). Household items mostly produce indoor VOCs, including paints, varnishes, solvents, air fresheners, disinfectants, cleansers, and aerosol sprays (Sarigiannis et al., 2011; US-EPA, 2022). The levels of several organics average 2 to 5 times higher indoors than outdoors. During and for several hours immediately after certain activities, such as paint stripping, levels may be 1,000 times background outdoor levels (US EPA, 2022b).

2.2.3 Health effects VOCs

The health effects of organic volatile compounds can include cancer, irritability of the senses, respiratory problems, liver, kidney, and central nervous system damage (Rumchev et al., 2007; US-EPA, 2022). Humans are susceptible to cancer from some VOCs, such as benzene.

Common symptoms of VOC exposure include headaches, nausea, exhaustion, dizziness, and allergic skin reactions in addition to conjunctival irritation and sore throat and nose (IARC, 2021; US EPA, 2023g). When humans are exposed to benzene, it can cause harmful short- and long-term health consequences, as well as diseases including cancer and toxic effects on the bone marrow and blood (Lan et al., 2004). As to the International Agency for Research on Cancer (IARC), benzene is categorized as carcinogenic to people under Group 1 and ethylbenzene as possibly carcinogenic to humans under Group 2B (IARC, 2021). Risk assessment in relation with VOCs depends on three main things (i) availability of inhalation unit risks (IUR), (ii) high frequency of occurrence, and (iii) carcinogenicity. Equation (2.1) can be used to compute the cancer risk from inhalation, and Equation (2.2) was used to calculate the cumulative cancer risk (US-EPA, 2009; Zhou et al., 2011; Su et al., 2014).

$$R_{ij} = E_{ij} \times IUR_j \quad (2.1)$$

$$CCR = \sum R_{ij} \quad (2.2)$$

Where: IUR_j represents the inhalation unit risk ($m^3/\mu g$) for chemical j, CCR represents the cumulative cancer risk, and R_{ij} is the estimated inhalation cancer risk from chemical j in each microenvironment i. E_{ij} represents the measured exposure concentration for chemical j in each microenvironment i.

2.2.4 Guidelines for levels of VOCs

Guidelines provide an average exposure that is required to protect the overall population from acute and chronic health effects (WHO, 2010). The Directive 2000/69/EC of the European Parliament and the Council (European Commission, 2000) states, "the ambient benzene concentration should be below 5 $\mu g/m^3$."

Moreover, based on WHO (2010), "benzene exposure is never safe at any level, and the level of aerial benzene associated to an excess lifetime risk of 1/10000, 1/100000, and 1/1000000 are 17, 1.7 and 0.17 μg/m^3, respectively." Whether the exposure occurred indoors or outdoors, there would be a same risk of toxicity from benzene inhalation (WHO, 2010). Table 2.1 summarizes the recommendations for indoor air quality for specific volatile organic compounds.

Table 2.1 Overview of recommended indoor air quality levels for specific volatile organic compounds (WHO, 2010)

Pollutants	Critical outcome(s) for guideline definition	Guidelines
Benzene	- Acute myeloid leukaemia - Genotoxicity	- No safe level of exposure can be recommended - Unit risk of leukaemia per 1 μg/m^3 air concentration is 6×10^{-6}
Formaldehyde	Sensory irritation	0.1 mg/m^3 – 30-minute average
Naphthalene	Respiratory tract lesions leading to inflammation and malignancy in animal studies	0.01 mg/m^3 – annual average
Trichloroethylene	Carcinogenicity (liver, kidney, bile duct and non-Hodgkin's lymphoma), with the assumption of genotoxicity	Unit risk estimate of 4.3×10^{-7} per μg/m^3
Tetrachloroethylene	Effects in the kidney indicative of early renal disease and impaired performance	0.25 mg/m^3 – annual average

2.2.5 Levels of VOCs in Ethiopia

VOCs concentration data is limited in most African countries including Ethiopia. The sum of the concentrations of individual quantified compounds is the total volatile organic compound (TVOC). Some of the studies on VOCs concentrations in urban areas of Ethiopia include (Do et al., 2013, 2015; Kasim et al., 2018a, 2018b; Agbo et al., 2021; Embiale et al., 2019a, 2019b, 2021, 2022). Results from Do et al. (2013) showed that the uppermost TVOCs measured in three cities in three countries were 54, 318, and 507 μg/m^3 in Ghent, Belgium; Addis Ababa, Ethiopia; and Hanoi, Vietnam, respectively. According to Do et al. (2015) the TVOCs concentration in Dhaka, Bangladesh (arithmetic mean: 399 and 343 μg/m^3 for industrial and urban areas, respectively) were more than ten times greater than the levels of TVOCs found in Mekelle, Ethiopia.

In Addis Ababa, Ethiopia, the geometric mean of TVOC using electricity, kerosene, and charcoal fuel varied from 350 to 812 μg/m^3 during the dry and wet seasons (Embiale et al., 2019a). When using clean, improved, and traditional stoves in Addis Ababa, Ethiopia during the wet and dry seasons, the geometric mean of TVOCs was 1,553, 2,234, 4,421, and 845, 1,214, and 2,662 μg/m^3, respectively (Embiale et al., 2021).

2.2.6 Measurement methods of VOCs

The analytical technique used to analyze volatile organic compounds (VOCs) is gas chromatography (GC) coupled with mass spectrometry (MS) (Ras et al., 2009). The GC is used for the separation of a wide range of VOCs and the most common techniques used for quantification of VOCs are flame ionization detection (FID) and MS (Demeestere et al., 2008).

Because of the low levels of pollutants in the atmosphere (from ng/m^3 to $\mu g/m^3$), enrichment is often needed (Demeestere et al., 2008; Ras et al., 2009). Active sampling and passive sampling are the two types of sampling methods.

2.2.6.1 Active sampling

Active or dynamic sampling contains of pumping a defined volume of air through a bed of sorbents in a tube where analytes are retained (Reeve, 2002). Figure 2.1 shows that multi-sorbent tube for active sampling of VOCs.

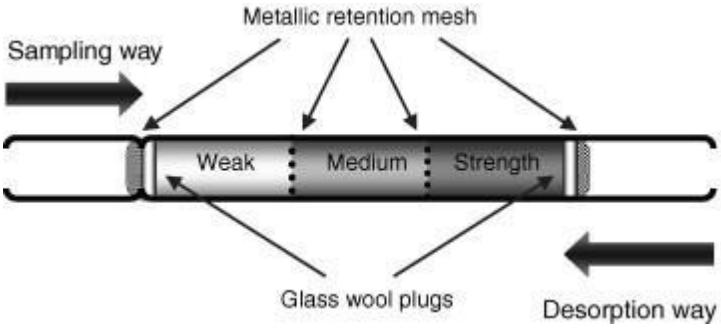

Figure 2.1. Multi-sorbent tube for active sampling of VOCs (Ras et al., 2009).

Many sorbent materials are available, including carbon molecular sieves, graphitized carbon blacks and porous organic polymers like Tenax TA (i.e. a porous 2,6-diphenyl-p-phenylene oxide polymer) (Demeestere et al., 2008; Ras et al., 2009). Target volatile organic compounds (VOCs), sorption equilibrium at sorption and desorption temperatures, reactivity, storage stability, and blank build-up are the most important factors to take into account when choosing an effective sorbent material or materials (Demeestere et al., 2007).

2.2.6.2 Passive sampling

The idea of passive sampling is the analyte molecules' molecular diffusion from the sampled medium to the collecting medium due to the analytes' different chemical potentials in the two media (Górecki & Namienik, 2002). Diffusive or permeative passive samplers are essentially formed like tubes or boxes (badges). The tube-type samplers (shown in Figure 2.2) have low cross-sectional areas and long axial diffusion paths, which resulting in low sampling rates. Generally, badge-type samplers with larger cross-sectional areas and shorter diffusion paths show higher uptake rates (Kot-Wasik et al., 2007).

Figure 2.2. Axial passive VOC sampler (stainless steel sorbent tube)

Passive sampling devices contain of a sorbent, separated from the air to be analyzed by a barrier, which is a static layer of air in diffusion type samplers. The sampling direction is axial and the sampler has a low sensitivity to air perturbations. Mass transport into tube type samplers is also described by Fick’s first law of diffusion which is given in Equation (2.3) (Ras et al., 2009).

$$m = \frac{D \times A}{L} \left(C_a - C_f\right)t \qquad (2.3)$$

Where m is the mass of compound adsorbed (μg), t is the sampling time (minutes), A is the cross-sectional area of the diffusion path (cm^2), D is the diffusion coefficient for the compound in the air (cm^2/min), C_a is the ambient concentration of the substance in the air (μg/cm^3), C_f is the concentration of the substance above the sorbent and L the diffusion path length (cm). Assuming the adsorbent acts as a perfect sink i.e. $C_f = 0$, the Equation (2.3) can be simplified to Equation (2.4) (Ras et al., 2009).

$$C_a = \frac{m}{\left(\frac{D \times A}{L}\right)t} \qquad (2.4)$$

The term $\frac{D \times A}{L}$ is the ideal uptake rate (U_{ideal}) or the sampling rate and is expressed in cm^3/min, which has the same units as the sample flow rate in dynamic devices. Figure 2.3 shows the structure and geometry of the standard thermal desorption tube type passive sample (Jia & Fu, 2017).

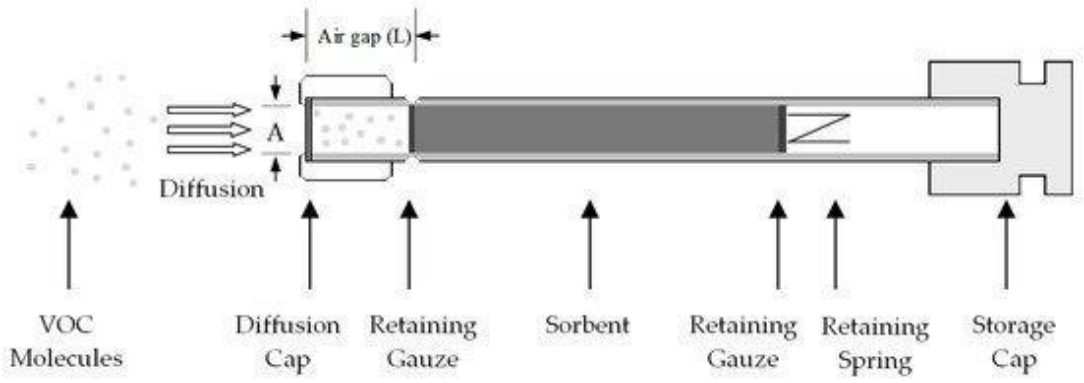

Figure 2.3. Structure and geometry of the standard thermal desorption tube type passive sample (Jia & Fu, 2017).

The magnitude of the diffusive uptake rate is dependent on the diffusion coefficient (temperature and pressure dependent) of a given analyte and on the geometry of the diffusive sampler (A and L) used. The ambient concentration of an analyte C_a can be calculated with the ideal uptake rate, collected mass and the sampling time as shown in Equation (2.4) (Ras et al., 2009).

2.2.6.3 Comparison of passive and active sampling methods

Passive sampling methods have certain advantages over active sampling because no sampling pumps are required and relatively small devices can be used for personal exposure measurement. Passive sampling is ideally suited to determining time-weighted average concentration (TWA) concentrations for periods ranging from hours (8 h) up to several weeks (Górecki & Namienik, 2002). The disadvantage of the passive sampling method is that it requires a sampler and a compound-dependent real uptake rate (UTR_{real}) to calculate TWA concentrations. The advantage of the active sampling method over the passive sampling method is that lower concentrations of target compounds can be measured for a given sampling time (Reeve, 2002).

The active sampling method is preferred for rapid analysis because of the short duration (minutes) in active sampling compared to hours (from 1 to 8 hours in workplace applications) in passive sampling (Demeestere et al., 2007).

2.3 Particulate Matter (PM)

2.3.1 Definitions of particulate matter

Particulate matter, or PM for short, is the word used to describe a mixture of solid and liquid droplets that are present in the air (US EPA, 2021). Certain particles can be seen with the unaided eye due to their size or darkness, such as smoke, soot, dust, or dirt. Others are so tiny that an electron microscope is the only tool needed to identify them (US EPA, 2021). Inhalable particles with diameters of 10 micrometers or less are known as PM_{10}, while fine inhalable particles with diameters of 2.5 micrometers or less are known as $PM_{2.5}$ (US EPA, 2021).

2.3.2 Sources of particulate matter

Volcanoes, forest fires, and dust are some of the natural sources of airborne particles. Solids with diameters ranging from 0.01 to 100 mm and minute sulfuric, sulfurous, and nitric acid droplets are examples of anthropogenic particles. They are byproducts of industrial processes like milling and grinding, or they are byproducts of combustion like fly ash, soot, and numerous metals (Zakrzewski, 2002; Keil et al., 2010). PM detected indoors might originate from indoor sources as well as from outside sources that move indoors. Cooking and combustion activities (such as using fireplaces, kerosene heaters, candles, and cigarettes) can produce particulate matter indoors (Keil et al., 2010; Van Vliet et al., 2013; US EPA, 2022a).

Outdoor PM can be originating from industries, automobiles, volcanoes, dust storms, forest and grassland fires (Omidvarborna et al., 2015; US EPA, 2021).

2.3.3 Health effects of particulate matter

Inhaling particulate matter ($PM_{2.5}$–PM_{10}) can result in a number of health issues for both humans and animals, such as asthma, lung cancer, low birth weight, premature delivery, and birth abnormalities (Sapkota et al., 2012; US EPA, 2023d; WHO, 2023b). For every 10 μg/m^3 increase in short-term exposure to particulate matter with an aerodynamic diameter of less than 10 μm, there is an approximately 0.5% increase in mortality as a result of particulate matter exposure. For every 10 μg/m^3 increase in long-term exposure to particulate matter with an aerodynamic diameter of less than 2.5 μm, there is an approximate 10% increase (S. Bae & Hong, 2018).

2.3.4 Guidelines for levels of particulate matter

Guidelines provide an average exposure, which is necessary to protect the general public from the short- and long-term health impacts of particulate matter exposure. The limits and interim targets for common air pollutants, $PM_{2.5}$ and PM_{10}, are recommended by the WHO air quality recommendations and are shown in Table 2.2.

Table 2.2. Suggested 2021 AQG values compare to 2005 recommendations for air quality, which were derived from (WHO, 2021a)

Pollutant	Averaging time	2005 AQGs	2021 AQGs
$PM_{2.5}$, $\mu g/m^3$	Annual	10	5
	24-hour	25	15
PM_{10}, $\mu g/m^3$	Annual	20	15
	24-hour	50	45

"The government of Ethiopia has mandated the Environmental Protection Authority to set standards. The Ethiopia Environmental Protection Authorities (EEPA) set a guideline standards with respect to the ambient environment" (EEPA, 2003). The guideline standard for particulate matter set by EEPA is presented in Table 2.3.

Table 2.3 Guidelines for priority ambient atmospheric pollutants set by EEPA

Pollutant	Averaging time	Guidelines
$PM_{2.5}$, $\mu g/m^3$	Annual	15
	24-hour	65
PM_{10}, $\mu g/m^3$	Annual	50
	24-hour	150

2.3.5 Levels of particulate matter in Ethiopia

Most of the studies on the concentrations of particulate matter and inorganic gaseous pollutants studied in Ethiopia were focused on the capital city, Addis Ababa (Pennise et al., 2009; Keil et al., 2010; Embiale et al., 2019a, 2019b, 2020, 2021, 2022; Jida et al., 2021; Lemma et al., 2021; Tefera et al., 2021; Asefa & Mergia, 2022; Bizualem et al., 2023). Results from Keil et al. (2010) found that particulate matter in homes during coffee ceremonies reported that the 24-h mean exposure of PM_{10} for coffee preparers the geometric mean (57 $\mu g/m^3$) and median (72 $\mu g/m^3$) in Addis Ababa. And results from Edlund (2019) found that the 24-h mean exposure of $PM_{2.5}$ in Adama ranges from 4.1 $\mu g/m^3$ to 225.6 $\mu g/m^3$. The average exposures in both cities were above World Health Organization (WHO, 2020) guidelines (25 $\mu g/m^3$). Summary of the concentration of particulate matter in Ethiopia are presented in Table 2.4.

Table 2.4. Summary of the concentration of particulate matter in Ethiopia

Study area	Concentration ($\mu g/m^3$)		Site description	References
	$PM_{2.5}$	**PM_{10}**		
Addis Ababa	39.6–85.3	54.2–247.4	Roadsides	(Jida et al., 2021)
Addis Ababa	25.4–57.2	91.8–222	Households	(Embiale et al., 2019a)
Addis Ababa	22.4–207	84.1–594	Households	(Embiale et al., 2021)
Addis Ababa	12.9–27.3	57.7–108	Living rooms	(Embiale et al., 2022)
Addis Ababa	28.3–35.1	54.4–65.8	Roadsides	(Bizualem et al., 2023)
Jimma	60.4–344	143–752.8	Households	(Addisu et al., 2021)
Butajira	330–470	–	Households	(Tamire et al., 2021)

2.3.6 Measurement methods of particulate matter

A filter-based gravimetric sampler and direct reading are the two techniques used to measure particulate matter (PM). Measurements of the concentration in the surrounding air are obtained by direct reading. Continuous measurement is preferable and frequently utilized as filter-based approaches require time and resources to collect PM and weight periodically in the laboratory (Idrees & Zheng, 2020). Currently, PM detection is commonly done with light scattering based devices. These devices may be handheld, desktop, or pole-mounted (Occhipinti & Oluwasanya, 2017). An example of portable gas monitor device is HoldPeak Laser PM meter, HP 5800D. Several previous studies measured particulate matter using HoldPeak Laser PM meter, HP 5800D, for example (Addisu et al., 2021; Lemma et al., 2021; Balogun & Odjugo, 2022; Lavtižar et al., 2023).

2.4 Inorganic Gaseous Pollutants (NO_2, SO_2, and CO)

2.4.1 Definitions of inorganic gaseous pollutants

"Inorganic substances are generally defined as substances that do not contain carbon or have structures that are not carbon-based. Some compounds that contain carbon are considered inorganic and referred to as carbon-containing inorganics because their behavior and characteristics are more similar to those of inorganic compounds for example oxides of carbon such as carbon dioxide and carbon monoxide" (US EPA, 2023c). Carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) are the main inorganic gaseous air pollutants (Katz, 1968; Omidvarborna et al., 2015; Agbo et al., 2021; Villanueva et al., 2022).

2.4.2 Sources of inorganic gaseous pollutants

The main sources of inorganic gaseous pollutants, including sulfur dioxide (SO_2), carbon monoxide (CO), and nitrogen dioxide (NO_2), are fossil fuel combustion in vehicles, industrial and power generators, and cooking fires (Kumie et al., 2009; Omidvarborna et al., 2015; Agbo et al., 2021).

Combustion processes include welding, gas stoves and other unvented appliances, kerosene heaters, tobacco smoke, and defectively installed vented appliances are the main sources of NO_2 indoors (Kumie et al., 2009; US EPA, 2023e). Outside sources of nitrogen dioxide are mostly caused by road traffic (Bae et al., 2004; US EPA, 2023a).

Both natural and man-made factors contribute to atmospheric SO_2. Naturally occurring sulfur compounds are released by volcanic activity, sea salt floating on the ocean surface, and the breakdown of organic matter, which largely releases hydrogen sulfide, or H_2S. About 95% of sulfur (S) emissions into the atmosphere from human activity take the form of SO_2.

The primary human activities that result in SO_2 emissions include nonferrous smelting, petroleum refining, and the burning of coal and petroleum products. Approximately 95% of all emissions in the United States come from fixed and industrial sources (Yu, 2005; US EPA, 2023e). One of the following three processes typically results in the formation of carbon monoxide: incomplete combustion of fuels containing carbon, high-temperature interactions between CO_2 and carbon-containing materials, and dissociation of CO_2 at high temperatures (Yu, 2005; Keil et al., 2010).

2.4.3 Health effects of inorganic gaseous pollutants

Exposure to high NO_2 concentrations can irritate human respiratory tract airways. Such short-term exposures might aggravate respiratory diseases, particularly asthma, which can lead to hospital stays, emergency room visits, and respiratory symptoms (such as breathing difficulties, wheezing, or coughing). Different health issues arise from exposure to various inorganic gaseous pollutants. After a short time of exposure to SO_2, breathing becomes difficult and may even be damaging to the human respiratory system. Individuals with asthma are more vulnerable to these effects of SO_2, especially children. Low levels of carbon monoxide exposure make healthy people tired, and heart disease patients experience chest pain. Higher amounts can cause dizziness, headaches, nausea, confusion, and flu-like symptoms that go away after leaving home, as well as fatalities at very high concentrations (Kume *et al*., 2009; US-EPA, 2020; WHO, 2020; Yu, 2005).

2.4.4 Guidelines for levels of inorganic gaseous pollutants

Table 2.5 lists the recommended limits and interim targets for common air pollutants, namely NO_2, CO, and SO_2, as per the WHO air quality recommendations.

Table 2.5 Suggested Air Quality Guidelines (AQG) levels for 2021 in comparison to the 2005 air quality recommendations derived from (WHO, 2021a)

Pollutant	Averaging time	2005 AQGs	2021 AQGs
NO_2, $\mu g/m^3$	Annual	40	10
	24-hour	-	25
SO_2, $\mu g/m^3$	24-hour	20	40
CO, mg/m^3	24-hour	-	4

Table 2.6 lists the air quality standards for nitrogen dioxide, sulfur dioxide, and carbon monoxide (short averaging times) that were not reevaluated and remain valid.

Table 2.6 Air quality guidelines for nitrogen dioxide, sulfur dioxide, and carbon monoxide (short averaging times) that were not re-evaluated and remain valid (WHO, 2021b)

Pollutant	**Averaging time**	**Air quality guidelines that remains valid**
NO_2, $\mu g/m^3$	1-hour	200
SO_2, $\mu g/m^3$	10-minute	500
CO, mg/m^3	8-hour	10
	1-hour	35
	15-minute	100

"The government of Ethiopia has mandated the Environmental Protection Authority to set standards. The Ethiopia Environmental Protection Authorities (EEPA) set a guideline standards with respect to the ambient environment" (EEPA, 2003). The guideline standard for inorganic gaseous pollutants set by EEPA is presented in Table 2.7.

Table 2.7 Guidelines for priority ambient atmospheric pollutants set by EEPA

Pollutant	**Averaging time**	**Guideline**
NO_2, $\mu g/m^3$	Annual	40
	1-hour	200
	10 minutes	500
SO_2, $\mu g/m^3$	24-hour	125
	Annual	50
CO, $\mu g/m^3$	15 minutes	100000
	30 minutes	60000
	1-hour	30000

2.4.5 Levels of inorganic gaseous pollutants in Ethiopia

Anthropogenic sources of inorganic gaseous pollutants are wood-burning stoves, fireplaces, furnaces, gas stoves and ovens. The major inorganic gaseous air pollutants include sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and carbon monoxide (CO) (Yu, 2005; Omidvarborna et al., 2015). The levels or concentrations of inorganic gaseous pollutants have been studied in the urban areas (Kasim et al., 2018b; Pennise et al., 2009). Results from Pennise et al. (2009) shows that the level of CO in Ghana ranges from 12.3 - 7.4 ppm and in Ethiopia ranges from 38.9 - 9.2 ppm. Results from Kasim et al. (2018) found that the levels in Dire Dawa, Ethiopia the mean concentration of CO: 3.35 ± 2.04 ppm, SO_2: 0.37 ± 0.08 ppm, and NO_2: 0.13 ± 0.17 ppm. Summary of the concentration of inorganic gaseous pollutants in Ethiopia are indicated in Table 2.8.

Table 2.8 Summary of the concentration of inorganic gaseous pollutants in Ethiopia

Study area	Concentration (µg/m^3)		Site description	References
	NO_2	CO		
Addis Ababa, Ethiopia	50–670		Roadside	(Tsegaye et al., 2019)
Dire Dawa, Ethiopia	30–290	3350 –7350	Urban, industrial	(Kasim et al., 2018a)
Hawassa, Ethiopia	-	12–4660	Urban	(Kasim et al., 2018b)
Bahir Dar, Ethiopia	-	10–2590	Urban	(Kasim et al., 2018b)
Addis Ababa, Ethiopia	84.1–101.1	-	Roadside	(Bizualem et al., 2023)

2.4.6 Measurement methods of inorganic gaseous pollutants

Passive samplers can be used to determine the average concentration of a pollutant for a period of 8 hours to several days; however, an active sampling method is more suitable for short-term monitoring, usually up to 1 hour (Villanueva et al., 2022). Fair enough data accuracy and an acceptable detection range can be obtained from the low-cost sensors (Idrees & Zheng, 2020). Currently, the most common portable air quality monitor used to measure the concentrations of NO_2, CO, and SO_2 is the Aeroqual Series 500. Numerous previous studies used the Aeroqual Series 500 to measure inorganic gaseous pollutants (e.g. Kasim et al., 2018a; Tsegaye et al., 2019; Onwuegbuchunam et al., 2021; Dahech et al., 2022; Ogaji et al., 2022).

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CHAPTER 3. VOLATILE ORGANIC COMPOUNDS IN SCHOOL ENVIRONMENTS OF HAWASSA CITY, ETHIOPIA AND ASSESSMENT OF POSSIBLE HUMAN HEALTH RISKS

ABSTRACT

Volatile organic compounds (VOCs) have become a major human wellbeing and environmental concern worldwide. However, evidence on VOC concentrations in primary school environments in Africa, including Ethiopia, is scarce. The goal of this research was to examine VOCs in primary schools in Hawassa, Ethiopia, and to evaluate possible health threats. Concentrations of 76 VOCs were investigated in air samples from classrooms and playgrounds of eight primary schools in Hawassa, Ethiopia. Air samples were taken via passive sampling method using Tenax TA as a sorbent and analyzed by using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). Highest total VOCs (TVOCs) concentration (83 $\mu g/m^3$) was observed in the classroom of School 2 followed by the classroom of School 1 (76 $\mu g/m^3$), while the smallest TVOC concentration, 37 $\mu g/m^3$ in the playground of School 8. Among the BTEX, toluene was the most dominant in all samples, ranging from 33% in School 4 to 38% in School 1 of ∑BTEX. I/O ratios of individual VOC in the schools ranged from 0.44 in School 4 to 9.21 in School 2. The highest cumulative cancer risk ($CCR \times 10^6$) and the total hazard ratio indicator (THRI) values were 126 and 1.58E-01 respectively, in the classroom of School 4. The CCR and THRI values indicated that the exposure of children to the measured concentrations of benzene may have potentially harmful effects.

Keywords: BTEX; volatile organic compounds; passive sampling; primary school; risk assessment; Ethiopia

3.1 Introduction

Almost all, 99%, of the overall population of the world breathes air which contains high levels of contaminants and exceeds the World Health Organization (WHO) guideline limits (WHO, 2022a). Several researches indicated that the effect of indoor and ambient air pollution is correlated with seven million premature deaths worldwide per annum (Franchini et al., 2015; Newby et al., 2015; WHO, 2022b). Volatile organic compounds (VOCs) are involving in the air pollutants with the evidence of harmful health consequences (Li et al., 2021; US-EPA, 2022). Findings of recent studies (Mohd Hanif et al., 2021; Yu et al., 2021; Zhang et al., 2022), indicated that, emissions from industrial activities, oil refineries, traffic, and natural sources are main sources of outdoor VOCs. The major indoor sources of VOCs are household products such as paints, solvents, varnishes, aerosol sprays, cleansers, disinfectants, and air fresheners (Sarigiannis et al., 2011; US-EPA, 2022). Atmospheric VOCs have an important function in tropospheric ozone formation (Calvert, 1994; Demeestere et al., 2007; Barletta et al., 2008).

VOCs can have harmful impacts on health, including cancer, sensory irritation, and respiratory symptoms (Rumchev et al., 2007; US-EPA, 2022). Children spend more time in educational settings, and they might be exposed to unidentified quantities of indoor and ambient pollutants, and they are one of the most vulnerable populations to air pollutants (Faustman et al., 2000; Louis et al., 2006). Besides, compared to adults, children are further exposed to VOCs (Kuang et al., 2021, 2022). Several studies showed that the occurrence and related health hazards of VOCs in primary schools (e.g. Sofuoglu et al., 2011; Widiana et al., 2019; Lu et al., 2021; Szabados et al., 2021).

Although there are some studies on VOCs concentrations in urban areas of Ethiopia (Do et al., 2013, 2015; Kasim et al., 2018a, 2018b; Agbo et al., 2021; Embiale et al., 2019a, 2019b, 2021, 2022), VOCs concentration data in primary schools is very limited as in most African countries. The main objective of this exploratory research was to measure the levels of VOCs in primary schools in Hawassa, Ethiopia, and evaluate the possible health hazards associated with them. To the best of our knowledge, this research is the first investigation on concentrations of a broad range of VOCs in primary schools of Ethiopia. This evidence is very important to raise the awareness of the respective government agencies and to enhance their efforts to improve the air quality of school environments.

3.2 Materials and Methods

3.2.1 Description of the study area

This investigation was conducted in Hawassa, the capital city of the Sidama Regional State, Southern Ethiopia. Hawassa city is situated on the shores of Lake Hawassa in the Great Ethiopian Rift Valley, 275 km South of Addis Ababa, the capital city of Ethiopia. Geographically, the city lies at latitude 7°3'43.4" N and longitude 38°28.581' E. There are two seasons: a lengthy, wet season from March to October and a short dry season from November to February (NMA, 2021; Weatherspark, 2023). Hawassa's population is expected to be 403,288, according to central statistics authority (CSA) of Ethiopia (CSA, 2021).

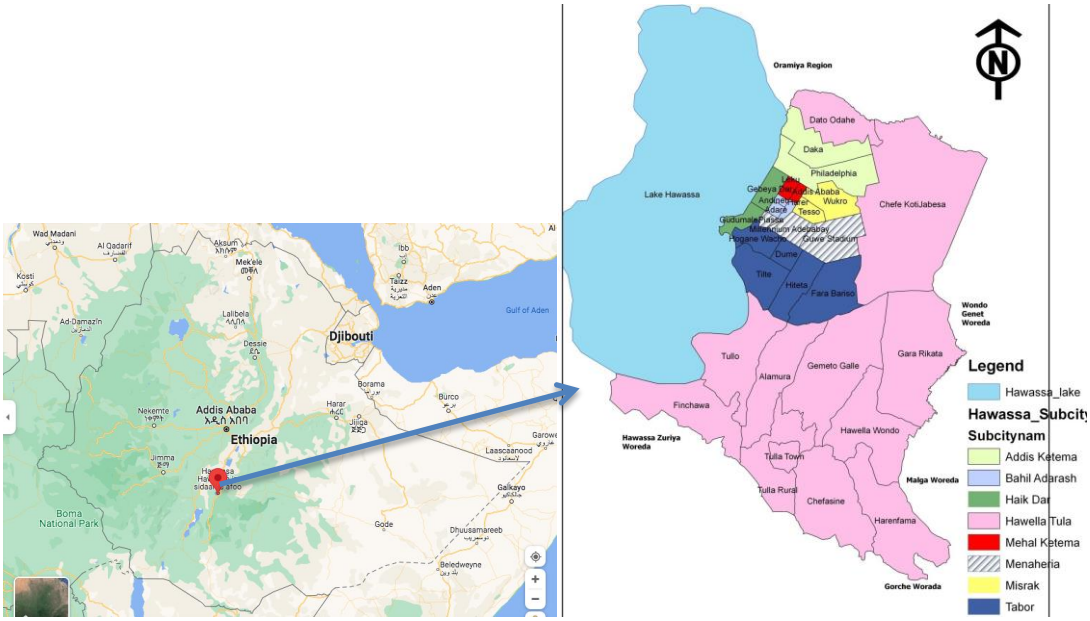

Figure 3.1. Map of the study area i.e. Hawassa city (Assefa et al. 2021; Google map 2022)

3.2.2 Sampling sites

There is a scarcity of data on air quality in Africa, specifically in Ethiopia and we used Hawassa City as a representative urban area of Ethiopia. Additionally, we chose primary schools because young children are more susceptible to pollution. Eight primary schools in Hawassa city, Ethiopia, were purposively selected for this study based on their proximity to high or low traffic or industrial areas, which were taken into consideration to evaluate their impacts on the indoor and outdoor air quality of the schools. The eight schools we selected can represent typical schools in Ethiopia in general and Hawassa City in particular in terms of setting and facilities. Descriptions of the selected primary schools are given in Table 3.1.

Table 3.1 Sampling sites (primary schools) and their descriptions

Sampling sites	Names of primary schools	Descriptions	Roads near the school (based on traffic volume)
School 1	Debub Ethiopia Academy	The school is surrounded by: roads with heavy traffic, residential buildings including a hospital, and a modest garden. The classroom has an area of 70 m^2 and a particleboard ceiling, a door, two windows, painted wall, and cemented floor. Blackboard, chalk, and markers are used in the classroom, and the number of students in the class was 50.	Roads with heavy traffic
School 2	Hayole	Similar to School 1, except that there is no hospital in the surrounding and the classroom has an area of 60 m^2, and the number of students in the class was 40.	Roads with heavy traffic
School 3	Alito	Similar to School 2	Roads with heavy traffic
School 4	Adare	Similar to School 2	Roads with heavy traffic
School 5	Comboni	Similar to School 2, except the roads with low traffic	Roads with low traffic
School 6	St. Gabriel	Similar to School 2	Roads with heavy traffic
School 7	Tabor	Similar to School 2	Roads with heavy traffic,
School 8	Silase	Similar to School 5	Roads with low traffic

3.2.3 Target VOCs

In this study, 76 VOCs were targeted and considered, including alkanes (15), aromatic compounds (11), halogenated, sulfur, and nitrogen compounds (17), oxygenated compounds (30), and terpenes (3) (see Table 3.2), which are commonly found in environmental and occupational settings (Mishra et al., 2015; Jia & Fu, 2017; Lu et al., 2021).

Table 3.2 List of target volatile organic compounds

(Cyclo-) Alkanes, Alkenes (15 VOCs)	Aromatic compounds (11 VOCs)	Oxygenated compounds (30 VOCs)	Halogenated, Sulfur and Nitrogen compounds (17 VOCs)	Terpenes (3 VOCs)
1-Pentene	Benzene	Isopropanol	Acetonitrile	α-pinene
n-Pentane	Toluene	Furan	Dimethyldisulfide	Limonene
2-Methylpentane	Ethylbenzene	Methyl acetate	Dichloromethane	Linalool
1-Hexene	m,p-Xylene	Isobutyraldehyde	1,1,2-Trichlorotrifluoroethane	
n-Hexane	Styrene	Butanal	Carbon disulfide	
Methylcyclopentane	o-Xylene	2-Butanone	Chloroform	
Cyclohexane	Benzaldehyde	2-Methylfuran	1,2-Dichloroethane	
n-Heptane	n-Propylbenzene	Ethyl acetate	Carbon tetrachloride	
n-Octane	1,2,4-Trimethylbenzene	Tetrahydrofuran	1,2-Dichloropropane	
n-Nonane	Methyl benzoate	3-Methylbutyraldehyde	Trichloroethylene	
n-Decane	1,3,5-Trisopropylbenzene	1-Butanol	1,1,2-Trichloroethane	
n-Undecane		Hexamethyldisiloxane	Tetrachloroethylene	
n-Dodecane		n-Propyl acetate	Chlorobenzene	
n-Tridecane		Trimethoxymethylsilane	1,1,1,2-Tetrachloroethane	
n-Tetradecane		3-Methyl-1-butanol	Benzonitrile	
		1-Pentanol	1,2,4-Trichlorobenzne	
		2-Hexanone	1,3-Dichlorobenzene	
		Hexanal		
		n-Butyl acetate		
		2-Heptanone		
		Heptanal		
		5-Methyl-3-heptanone		
		Phenol		
		2-Octanone		
		2-Ethyl-1-hexanol		
		Acetophenone		
		5-Nonanone		
		1-Octanol		
		Nonanal		
		Decamethylcyclopentasiloxane		

3.2.4 Air sampling method

Air samples were taken from eight primary schools from April 19 to April 26, 2022 (an exposure time of 7 days) using a passive sampling method. There were two sampling sites at each school, one indoor and one outdoor. The indoor site was a classroom used by 8–10-year-old students, and the outdoor site was the school's playground, which was assumed to represent the air quality within the school as much as possible. One sampler was exposed at each sampling site for seven days, which includes all days of the week for a total of about 168 hours. The air samples were taken by using Markes stainless steel sorbent tubes (outer diameter: 1/4 inch; length: 3.5 inches) filled with 200 mg of Tenax TA (35/60 mesh) (Markes, Llantrisant, UK). On the sampling side, the sampling tubes were outfitted with aluminum diffusion caps (Markes, Llantrisant, UK) to reduce the influence of air movement. One classroom was selected from each school (see Table 3.1), and the selected classrooms had more or less similar characteristics, such as the floor type and space, number and dimensions of doors and windows, the floor areas, the wall, and ceiling, and the number of students. Outdoor samples were collected from each school's playground in parallel with the indoor measurements. In the classrooms, sampling tubes were situated at a height of about 1.5 m above the ground and 1 m far from windows and doors. For the playground of each school, the sampling tubes were situated at a height of about 2 m above the ground. Blank samples were sealed at both ends using 0.25-inch brass, long-term storage caps and served as a control. Blank samples are Tenax tubes that have not been sampled and were conditioned and loaded with internal standard (Tol-d_8) in the same way as the sampled tubes. The blanks were also carried with the sampled tubes, were kept closed until analysis, and were analyzed in the same way as the sampled tubes.

Immediately after sampling, the Tenax TA tubes were tightly closed with brass closure caps containing white Teflon ferrules, which create a better airtight seal, and wrapped in aluminum foil, and then transported to Ghent University, Belgium, for analysis.

3.2.5 Air sample analysis

The analyses of air samples were done using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). For VOC quantification Internal standard calibration was done on the tubes by applying the method described in Demeestere et al. (2008). Before the analysis of the air samples, calibration of the TD-GC-MS was performed. All the standards used in this experiment were purchased from Acros Organics (Geel, Belgium) or Sigma–Aldrich (Bornem, Belgium) with a purity of 99.8%. The solvent used for all standard compounds was methanol (LC–MS grade, 99.95%, Biosolve, Valkenswaard, The Netherlands). Standard compounds with a known mass of internal standard (Tol-d8) consisting of the target VOCs were divided into two stock solutions (to avoid the co-elution of compounds during the chromatographic separation). The lists of compounds in stock solution A and stock solution B are indicated in Supplementary Table S1 and Supplementary Table S2, respectively. The sorbent tubes were conditioned in an oven (Carlo Erba Instruments, MFC 500) by heating them for 1 hour at 300°C and flushing them with a helium flow of 31 ml/min to remove any residual contaminants present on the adsorbent. 1μL volume of the stock solution loaded into conditioned tubes by using Nano Volume Syringe (SGE Analytical Syringe) under a 100 mL/min Helium flows at 150°C. The Helium stream was kept on for 3 minutes before the tubes were closed again with 1⁄4'' brass caps after injection.

Immediately after loading the sorbent tubes with 1μL of standard stock solution A or B, the tubes were analyzed by TD-GC-MS. The relative sample response factors (RSRF) were calculated for each VOC by dividing the response factor of the compound (peak area/ng loaded on the tube) by the response factor of the internal standard (Tol-d8). Compounds were identified based on retention time and comparison of the spectra with the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) V2.0 database and chromatograms and mass spectra were processed using XCalibur software (Thermo Finnigan, version 2.07). When the signal-to-noise ratio (S/N) was higher than three a VOC was detected and when the S/N was higher than 10 the VOC was quantified. Only when the VOC could be quantified in the blank, blank correction of the samples was done. The concentrations in $\mu g/m^3$ of the VOCs in the sampled air were computed using Equation (3.1) (Ras et al., 2009).

$$C_a = \frac{m_a}{UR \times t} \qquad (3.1)$$

Where C_a is the concentration ($\mu g/m^3$), m_a is the analyte mass (ng), UR is the uptake rate (ml/min) and t is the sampling time (minutes). The values of the used uptake rates (URs) and their sources are given in Supplementary Table S3.

3.2.6 Assessment of possible human health risks

The risk of cancer from inhalation was calculated by using Equation (3.2) as described in (US-EPA, 2009; Zhou et al., 2011; Su et al., 2014) and the cumulative cancer risk was calculated using Equation (3.3).

$$R_{ij} = E_{ij} \times IUR_j \quad (3.2)$$

$$CCR = \Sigma R_{ij} \quad (3.3)$$

Where: R_{ij} is the estimated lifetime cancer risk from chemical j in each microenvironment i, E_{ij} is the measured exposure concentration for chemical j in each microenvironment i, IURj is the inhalation unit risk (probability of cancer for a 70-year exposure to 1 μg/m^3) (m^3/μg) for chemical j and CCR is the cumulative cancer risk.

The hazard ratio was used to determine the non-carcinogenic effects of VOCs. Hazard ratio (HR) of each compound (i) was computed by dividing its concentration by its corresponding reference concentration (RfC), both expressed in μg/m^3 based on Equation (3.4). Total hazard ratio (THR) was computed as the sum of the single HRi based on Equation (3.5) as described in (Ramírez et al., 2012; De Gennaro et al., 2013; Datta et al., 2017).

$$HR_i = C_i/RfC_i \quad (3.4)$$

$$THRI = \sum HR_i \quad (3.5)$$

Where: HR_i is the hazard ratio of each compound i, C_i is concentration of compound i, RfC_i is reference concentration of compound i, and THRI is the total hazard ratio indicator.

The cancer inhalation unit risk and non-cancer reference concentration of VOCs are indicated in Table 3.3.

Table 3.3 Cancer inhalation unit risk (IUR) and non-cancer reference concentrations of VOCs

VOC	IUR ($m^3/\mu g$)	Source	USEPA class	IARC class	Reference Concentration ($\mu g/m^3$)	Source
Benzene	2.9×10^{-5}	CalEPA	A	1	30	IRIS
Ethylbenzene	2.5×10^{-6}	CalEPA	D	2B	1000	IRIS
Styrene	5.0×10^{-7}	(Zhou et al., 2011)	C	2A	1000	IRIS
Carbon tetrachloride	4.2×10^{-5}	CalEPA	B2	2B	100	IRIS
Toluene	-		-	-	5000	IRIS
m -xylene	-		-	-	100	IRIS

IRIS (Integrated Risk Information System)(IRIS, 2018),CalEPA (California Environmental Protection Agency)(OEHHA, 2023), IARC (International Agency for Research on Cancer) (IARC, 2021)

3.2.7 Ozone formation potential (OFP) of VOCs

Ozone formation potential was computed by multiplying the Maximum Incremental Reactivity (MIR, 2010) with concentration ($\mu g/m^3$) of the measured VOCs (Carter, 2010). Some previous studies was also computed the OFP using the maximal incremental reactivity scale (Na et al., 2005; Luo et al., 2020; Zhan et al., 2021; Wang et al., 2022).

3.2.8 Statistical analysis

Excel and statistical software packages were used in this study. IBM SPSS (Version 25) was used to perform the correlation analysis and Excel was used to perform, data entry, data presentation and description, and to compare the measured concentration levels at eight primary schools using tables and graphs.

3.3 Results and Discussion

3.3.1 Concentrations of VOCs

Out of the analyzed 76 target volatile organic compounds, 17 VOCs were not detected in all of the samples (i.e. S/N < 3). From the undetected VOCs, the eight VOCs were halogenated compounds, which included: chloroform, 1,3-dichlorobenzene, 1,1,2-trichloroethane, 1,2-dichloroethane, 1,2-dichloropropane, 1,1,1,2-tetrachloroethane, trichloroethylene, and 1,2,4-trichlorobenzene. The total concentrations of VOCs (TVOCs), described as the sum of the concentrations of quantified individual VOCs, were found to be higher (39-83 μg/m^3) in indoor samples than those from outdoor (37-59 μg/m^3) in all sampling locations except in Schools 4 and 5 as indicated in Figure 3.2.

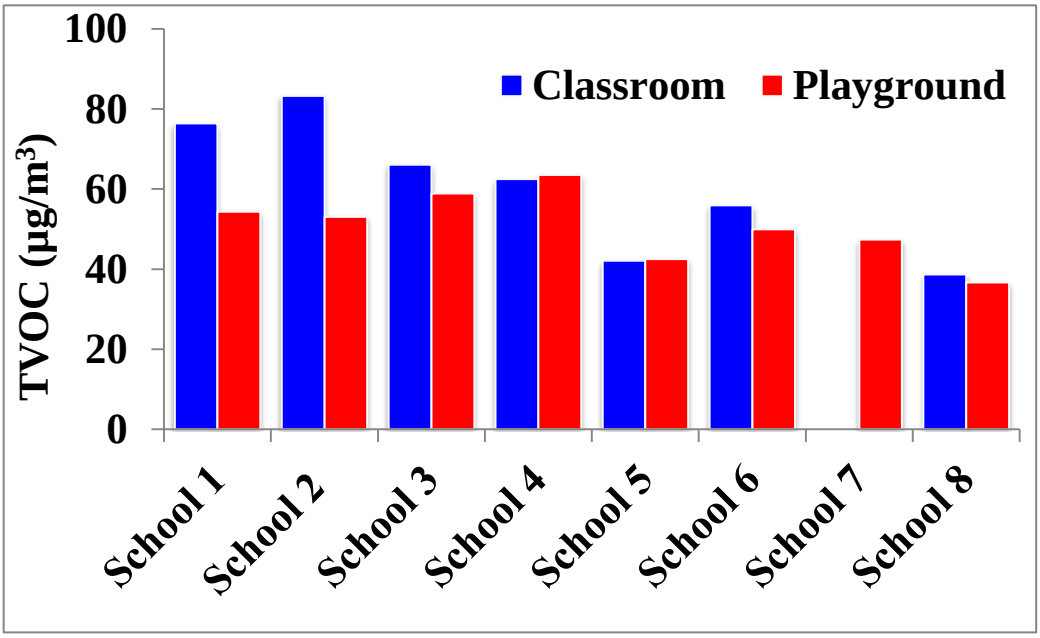

Figure 3.2. Total volatile organic compounds (TVOCs) in 15 sampling locations of the eight primary schools (for School 7, there was only a playground result due to accidental loss of the sample)

The highest TVOCs (83 μg/m^3) was determined in the classroom of School 2 followed by the classroom of School 1 (76 μg/m^3), whereas the lowest was TVOCs (37 μg/m^3) was found in the playground of School 8. In this study, the schools near roads with heavy traffic showed 1.1 to 1.73 times higher outdoor and 1.3 to 2.15 times higher indoor TVOCs than the schools near roads with low traffic (Figure 3.2). The indoor and ambient TVOCs concentrations found in this study are in agreement with the average TVOCs in previously reported studies, where the geometric mean for outdoor concentrations was 71 μg/m^3 in schools in Australia (Mishra et al., 2015). In two primary schools in Taiwan (Wang et al., 2016), outdoor average TVOC values of 69.8 μg/m^3, and 20.2 μg/m^3, respectively.

However, the indoor and outdoor TVOCs concentrations in our current study were lower than the concentrations of average TVOCs in similar studies, where the geometric mean for indoor TVOCs concentration was 125 μg/m^3 in schools in Australia (Mishra et al., 2015). Similarly, concentrations of average TVOCs in the playgrounds of four primary schools in Taiwan (Wang et al., 2016), were 114 μg/m^3, 162 μg/m^3, 207 μg/m^3, and 175 μg/m^3, respectively, and the median TVOCs concentration was 140.3 μg/m^3 in primary schools in Porto, Portugal (Madureira et al., 2015).

The ranges of concentrations of individual volatile organic compound in groups of volatile organic compounds are indicated in Table 3.4. Concentration levels of most of the VOCs detected in this study are lower or equivalent to the concentrations range of individual VOCs in primary schools in Vietnam (Lu et al., 2021).

Table 3.4 The range of concentrations of individual VOC in the groups of VOCs

Groups of VOCs	Range of concentration of individual VOC (μg/m^3)
(Cyclo-) Alkanes	0.21–6.79
Alkenes	0.21–0.45
Aromatic hydrocarbons	0.0005–6.29
Aldehydes	0.17–17.52
Alcohols	0.05–3.44
Ketones	0.02–10.33
Esters	0.10–2.06
Other oxygenated compounds	0.25–0.60
Halogenated compounds	0.01–3.11
Nitrogen containing compounds	0.35–0.91
Silicone containing compounds	1.40–1.99
Terpenes	0.0 –0.48

The overview of the determined concentrations of VOCs in 15 sampling locations (for School 7, there was only a playground result due to accidental loss of the sample) is given in the Supplementary Table S4. The stacked column (100%) contribution of each group to the TVOCs measured in eight primary schools is indicated in Figure 3.3. Aromatic compounds, (cyclo-) alkanes, and aldehydes were the major contributor to TVOCs in fifteen sampling locations and the main reason might be the location of the schools (i.e. the nearness to traffic roads). The contributions of aromatic compounds to TVOCs range from 19% in the classroom of School 8 to 29% in the playground of School 7. The contribution of (cyclo-) alkanes ranges from 19% in the classroom of School 8 to 38% in the classroom of School 4, and 2-methylpentane was the abundant compound in all sampling locations, ranging from 2.7 μg/m^3 to 6.8 μg/m^3.

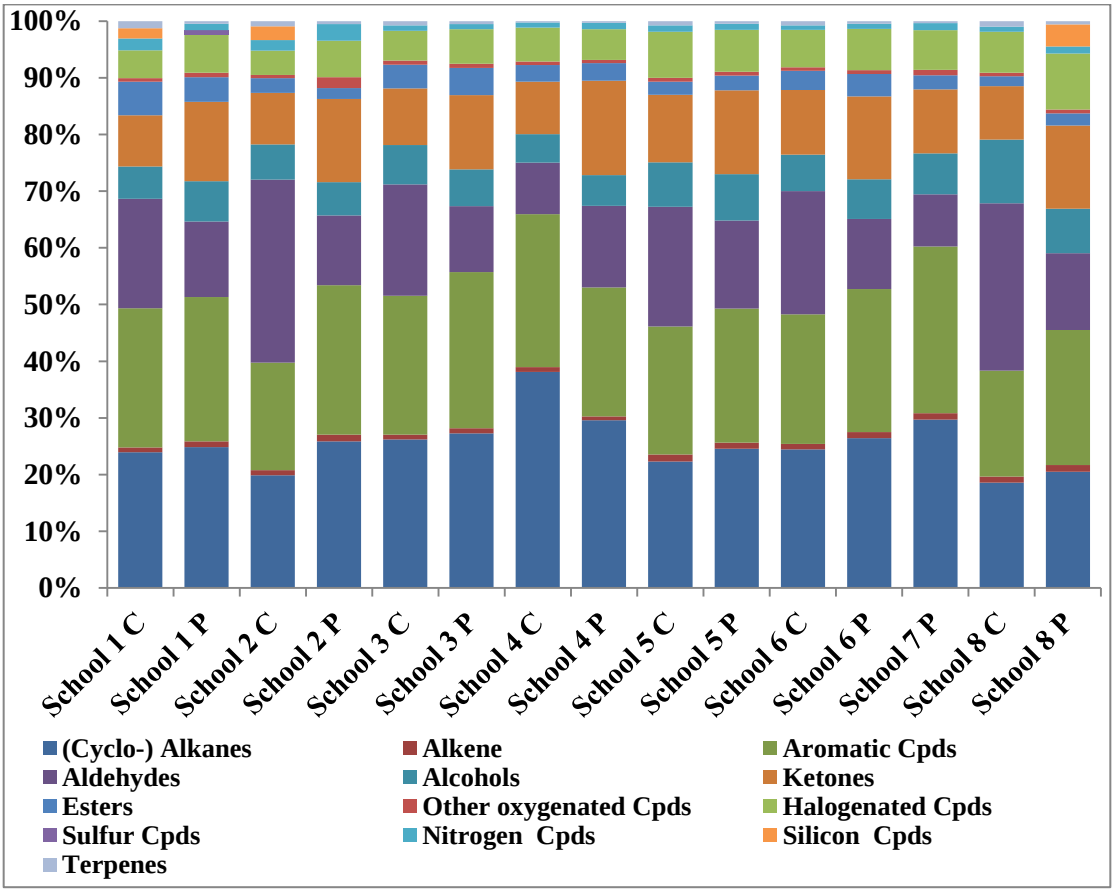

Figure 3.3. The stacked column (100%) contribution of each group to TVOCs in 15 sampling locations of primary schools (C, represents classroom and P, Playground)

The contributions of aldehydes range from 9.0% in the classroom of School 4 to 32% in the classroom of School 2, and nonanal, 1.3–18 μg/m^3, and benzaldehyde, 2.6–6.8 μg/m^3 are the most abundant compounds in all sampling locations. Similarly, a previous study reported that the concentration of nonanal was in the range from 8.80 to 27.66 μg/m^3 in primary schools in Vietnam (Lu et al., 2021). In this study, benzene, toluene, ethylbenzene, and xylenes (BTEX), were the most abundant VOCs among the aromatic hydrocarbons. The main factor to the presence of BTEX may be the proximity of schools to traffic roads.

As depicted in Figure 3.4, the highest ∑BTEX levels were observed in classrooms of School 1 (16 µg/m^3), followed by School 4 (15 µg/m^3), the playground of School 3 (15 µg/m^3), and the classroom of School 3 (14 µg/m^3), while the smallest ∑BTEX levels were observed in the classroom of School 8 (6.4 µg/m^3).

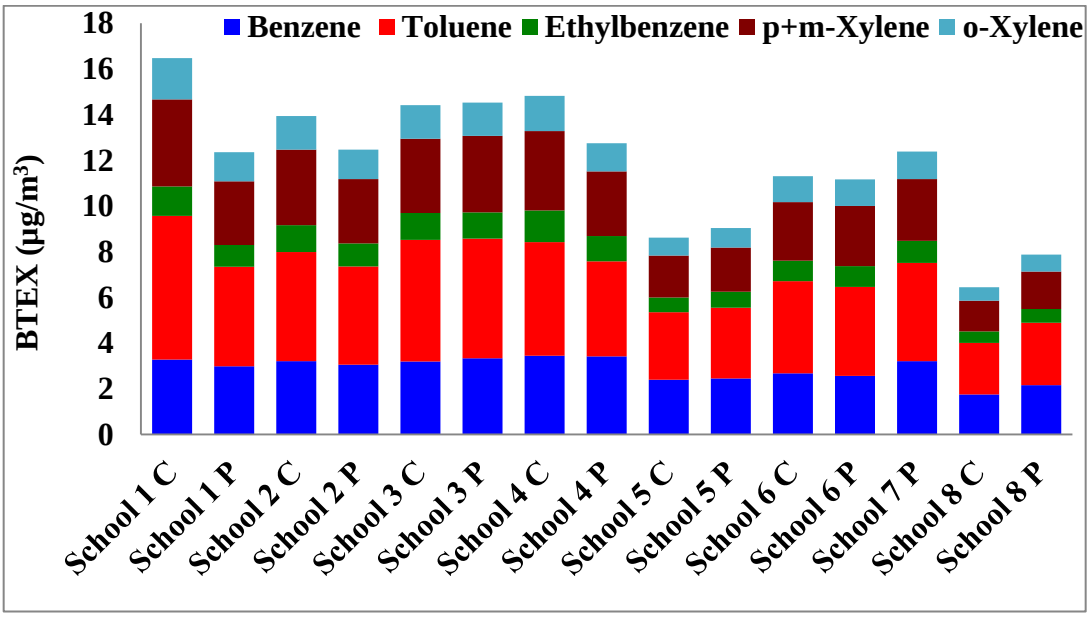

Figure 3.4. Comparison of BTEX (µg/m^3) within the 15 sampling locations of primary schools (C represents Classroom and P, Playground)

Among the BTEX, toluene is the most dominant in all sampling locations. Which varied from 33% in School 4 (playground) to 38% of the ∑BTEX in School 1 (classroom), followed by benzene, which varied from 12% in School 1 (classroom) to 28% in School 5 (classroom). The most abundant compound in all sampling locations was toluene with concentrations ranging from 2.3 µg/m^3 to 6.3 µg/m^3. Similar results were reported in earlier studies on the concentration of toluene, for example, the mean concentration of toluene, 4.1 µg/m^3 in outdoors, 6.4 µg/m^3 in indoors of primary schools in Portugal (Madureira et al., 2015, 2016).

Similarly, (Lu et al., 2021) reported that the concentration of toluene in primary schools in Vietnam were 1.21 to 24.37 μg/m^3. Yet the concentration of toluene in this study was lower than concentrations of mean toluene concentration, 68.2 μg/m^3 in playgrounds of primary schools in Taiwan (Wang et al., 2016), and overall mean concentrations of toluene 18.7 μg/m^3 in schools in Turkey (Sofuoglu et al., 2011).

Some studies (Lan et al., 2004; WHO, 2010; IARC, 2021), indicated that benzene can have long-term and acute hostile health effects, such as cancer, because of its harmful effects on the blood and marrow. According to Directive 2000/69/EC of the European Parliament and the Council (European Commission, 2000), the ambient benzene concentration should be below 5 μg/m^3. Furthermore, according to WHO (2010), benzene exposure is never safe at any level, and the level of aerial benzene associated to an excess lifetime risk of 1/10000, 1/100000, and 1/1000000 are 17, 1.7 and 0.17 μg/m^3, respectively. According to WHO, (2010), the toxicity risk from inhaled benzene would be equivalent, whether the exposure was indoor or ambient. Our current study showed that concentrations of benzene from indoors ranging, 1.8–3.5 μg/m^3 in Schools 8 and 4, and outdoors concentrations varied from 2.2 to 3.4 μg/m^3 in Schools 8 and 4, respectively. The levels of benzene obtained in the current study are similar with the levels of benzene ≤ 4.39 μg/m^3 in schools in Vietnam (Lu et al., 2021). However, lower than the overall mean concentrations of benzene, 10.4 μg/m^3 in schools in Turkey (Sofuoglu et al., 2011). Results from our study indicated the levels of benzene in the investigated schools might pose potential health risks to the students and staffs because benzene exposure is never safe at any level.

3.3.2 Indoor to outdoor (I/O) ratios of VOC concentrations

In this study I/O ratios of 35 individual compounds from the seven primary schools (presented in Table 3.5) were computed to assess the sources of the VOCs.

Table 3.5 Indoor to outdoor (I/O) ratios of VOC concentrations in seven primary schools (for School 7, there was only a playground result due to accidental loss of the sample)

	I/O Ratios						
VOC Name	**School 1**	**School 2**	**School 3**	**School 4**	**School 5**	**School 6**	**School 8**
n-Pentane	**1.44**	**1.06**	**1.07**	**1.31**	**0.97**	**1.06**	**0.87**
n-Heptane	**1.31**	**1.12**	**1.09**	**1.29**	**0.92**	**0.92**	**0.88**
n-Octane	**1.58**	**2.05**	**1.43**	**1.60**	**1.53**	**1.33**	**1.44**
n-Nonane	**1.55**	**1.15**	**1.28**	**1.37**	**1.01**	**0.86**	**1.35**
n-Decane	**0.86**	**0.98**	**0.83**	**1.41**	**0.97**	**0.96**	**1.00**
Undecane	**1.42**	**1.25**	**1.03**	**1.37**	**1.12**	**0.94**	**0.97**
Dodecane	**1.36**	**1.27**	**1.05**	**1.06**	**1.17**	**0.95**	**1.25**
Methylcyclopentane	**1.28**	**1.16**	**1.13**	**1.31**	**0.88**	**0.99**	**0.81**
2-Methylpentane	**1.26**	**1.23**	**1.09**	**1.28**	**1.00**	**1.06**	**0.86**
1-Pentene	**1.12**	**1.34**	**0.92**	**0.94**	**1.08**	**1.09**	**0.90**
1-Hexene	**1.23**	**1.14**	**1.05**	**1.48**	**1.20**	**0.92**	**1.03**
Benzene	**1.10**	**1.05**	**0.96**	**1.01**	**0.97**	**1.05**	**0.82**
Toluene	**1.44**	**1.11**	**1.02**	**1.19**	**0.95**	**1.03**	**0.83**
Ethylbenzene	**1.36**	**1.16**	**1.03**	**1.27**	**0.94**	**0.99**	**0.83**
P,m-Xylene	**1.37**	**1.17**	**0.97**	**1.23**	**0.95**	**0.97**	**0.81**
o-Xylene	**1.41**	**1.15**	**1.01**	**1.25**	**0.90**	**0.98**	**0.79**
Styrene	**2.30**	**1.58**	**1.20**	**0.89**	**1.04**	**1.07**	**1.17**
Propylbenzene	**1.36**	**1.15**	**1.03**	**1.27**	**0.88**	**1.03**	**0.84**
1,2,4-Ttrimethylbenzene	**1.38**	**1.14**	**1.05**	**1.29**	**0.87**	**0.99**	**0.84**
Nonanal	**2.89**	**9.21**	**2.83**	**1.90**	**2.19**	**3.49**	**5.84**
Benzaldehyde	**1.16**	**1.07**	**1.03**	**0.47**	**0.85**	**0.93**	**0.70**
2-Ethyl-1-hexanol	**2.38**	**4.45**	**3.08**	**1.85**	**1.23**	**1.50**	**4.05**
1-Octanol	**2.45**	**2.95**	**1.59**	**1.72**	**1.59**	**1.58**	**1.92**
Phenol	**1.00**	**1.25**	**0.96**	**0.70**	**0.80**	**0.92**	**0.82**
2-Heptanone	**1.49**	**1.41**	**1.07**	**1.26**	**0.99**	**1.27**	**1.46**
Acetophenone	**0.87**	**0.94**	**0.82**	**0.44**	**0.79**	**0.85**	**0.66**
Ethyl acetate	**1.87**	**1.51**	**1.09**	**0.97**	**0.87**	**1.04**	**0.87**
n-Butylacetate	**2.65**	**0.79**	**0.90**	**0.90**	**0.97**	**0.97**	**0.84**
2-Methylfuran	**1.12**	**1.16**	**1.11**	**1.18**	**0.99**	**1.04**	**1.00**
Carbon tetrachloride	**1.02**	**1.09**	**0.97**	**1.05**	**0.95**	**1.00**	**0.84**
Chlorobenzene	**1.33**	**0.93**	**1.12**	**0.99**	**1.19**	**0.91**	**0.78**
1,1,2-Trichlorotrifluoroethane	**1.01**	**1.03**	**0.96**	**1.06**	**1.05**	**1.01**	**0.75**
Benzonitrile	**1.17**	**0.89**	**1.23**	**0.80**	**1.03**	**1.04**	**0.76**
α-Pinene	**1.30**	**1.68**	**1.19**	**0.84**	**1.14**	**1.13**	**0.96**
Linalool	**3.76**	**4.34**	**2.21**	**ND**	**1.95**	**2.48**	**2.98**

The I/O ratio of the individual VOCs in all schools ranging from 0.44 (acetophenone) in School 4 to 9.21 (nonanal) in School 2. The I/O values were >1 for about 94% of 35 individual compounds in School 1, 86% in School 2, 74% in School 3, 69% in School 4, 46% in School 5, 54% in School 6, and 34% in School 8. If the I/O ratio is less than one, the VOCs may have originated from outdoor sources; if it is greater than one, it indicates the presence of an indoor source. If the I/O ratio is between one and four, it is reasonable to believe that both indoor and outdoor sources are present; if it is greater than five, it is reasonable to infer that indoor sources predominate (De Gennaro et al., 2013; Marzocca et al., 2017; WHO, 2022c). This implies that there were indoor sources in addition to outdoor sources in the schools.

Indoor activities using paint, glue, art products, markers, correction fluids, and building materials like, particleboards and painted equipment may emit various VOCs (Missia et al., 2010; WHO, 2022c). The indoor sources in this study may be due to students' activities, for example, using different markers during drawing class, and the building materials of the classrooms, for example, particle board ceilings, and interior wall paints, in addition to outdoor sources. The I/O values of n-octane, nonanal, 2-ethyl-1-hexanol, and 1-octanol were >1 in all schools; this indicates that there were indoor emission sources for these compounds in all examined schools. Similarly, the I/O values of n-pentane and 2-methyl pentane were >1 for all schools except School 8. Individual compounds with an I/O values that are >2 were n-octane in School 2, styrene and n-butyl acetate in School 1, nonanal in all schools except School 4, 2-ethyl-1-hexanol in Schools 1, 2, 3, and 8, 1-octanol in Schools 1and 2, and linalool in all schools except Schools 4 and 5.

Therefore, the I/O values that are >2 suggest that indoor sources (markers used by the students, particle board ceilings, and interior wall paints) were probably the primary contributors for these individual compounds in addition to outdoor sources. The I/O values for ethylbenzene (1.03–1.36) were > 1 in Schools 1, 2, 3, and 4 and <1 (0.83–0.99) in Schools 5, 6, and 8. This indicates that the measured concentrations of ethylbenzene were likely influenced by both indoor and ambient sources. The I/O values for benzene (1.01–1.10) were >1 in Schools 1, 2, 4, and 6 and <1 (0.82-0.97) in Schools 3, 5, and 8 which suggests that the measured concentrations were presumably influenced by both ambient and indoor sources. Similarly, the I/O values for toluene (1.02–1.44) were >1 in Schools 1, 2, 3, 4, and 6 and <1 (0.83–0.95) in Schools 5 and 8 which indicates that the sources of toluene were probably from both outdoor and indoor.

Next to the I/O also a toluene to benzene (T/B) were calculated. The effect of vehicle emissions are significant on aromatic VOCs emissions, if the T/B value is less than two (Singh et al., 2023). The T/B ratios of all schools were less than two and range from 1.22 (School 4 playground) to 1.92 (School 1 classroom). Therefore, vehicular sources may have an important effect on aromatic VOCs concentrations in all sampling locations.

3.3.3 Correlation analysis

The coefficients of the correlation of alkanes, alkenes, aromatic hydrocarbons, terpenes, oxygenated, and nitrogen compounds in 15 sampling locations were calculated using Pearson correlation. The Pearson correlation coefficients of some of the alkanes and alkenes were found to be high and statistically significant ($r > 0.7$, p-value =0.01, Supplementary Table S5).

The correlation between n-nonane, n-decane, and n-dodecane was found to be very high and statistically significant ($r > 0.95$, p-value = 0.01). Therefore, they likely have a common emission sources. The Pearson correlation coefficients of numerous aromatic compounds were found to be very high and statically significant ($r > 0.9$, p-value =0.01, Supplementary Table S6). The linear correlation coefficients among the concentrations of aromatic VOCs indicated that the sources of aromatic volatile compounds were from similar sources.

Pearson correlation coefficients of terpenes, oxygenated compounds, and nitrogen compounds were moderately positive and statistically significant ($r > 0.7$, p-value = 0.01, Supplementary Table S7). 2-ethyl-1-hexanol, 1-octanol, and nonanal showed high positive correlations to each other ($r = 8$, p-value = 0.01), therefore most probably they are from the same emission source.

3.3.4 Assessment of possible human health risks

Inhalation cancer risks for four VOCs were determined based on the availability of inhalation unit risk values (see Table 3.3) using Equation (3.2), and the cumulative cancer risks (CCR) were calculated using Equation (3.3). According to (OEHHA, 2019; Zhou et al., 2011), the inhalation unit risks of benzene, ethylbenzene, styrene, and carbon tetrachloride are 2.9×10^{-5} $m^3/\mu g$, 2.5×10^{-6} $m^3/\mu g$, 5.0×10^{-7} $m^3/\mu g$ and 4.2×10^{-5} $m^3/\mu g$. As shown in Table 3.6, the $CCR\times10^6$ values ranged from 69.7 in School 8 classroom to 126.4 in School 4 classroom. The cumulative cancer risks in the indoors of schools near heavy-traffic roads were 1.02–1.09 times higher than the cumulative cancer risks in the outdoors, except for school 3.

However, the CCR in the indoors for the schools near low-traffic roads was slightly less than the CCR in the outdoor (Table 3.6). This indicates that outdoor concentrations may affect indoor concentrations in schools near roads with heavy-traffic in addition to indoor sources.

Table 3.6 Inhalation cancer risk (R), hazard ratio (HR), cumulative cancer risks (CCR), and total hazard ratio indicator (THRI) values in the eight primary schools

Primary school	Benzene		Ethylbenzene		Styrene		CCl_4		Toluene	m, p-xylene	CCR ($\times 10^6$)	THRI
	R ($\times 10^6$)	HR	R ($\times 10^6$)	HR	R ($\times 10^6$)	HR	R ($\times 10^6$)	HR	HR	HR		
School 1 Classroom	95.2	1.E-01	3.2	1. E-03	0.3	6. E-04	22.4	5. E-03	1.E-03	4.E-02	121.1	2.E-01
Playground	86.5	1.E-01	2.4	1. E-03	0.1	3. E-04	22.1	5. E-03	9.E-04	3.E-02	111.1	1.E-01
School 2 Classroom	93.0	1.E-01	2.9	1. E-03	0.2	3. E-04	25.3	6. E-03	1.E-03	3.E-02	121.4	1.E-01
Playground	88.7	1.E-01	2.5	1. E-03	0.1	2. E-04	23.2	6. E-03	9.E-04	3.E-02	114.6	1.E-01
School 3 Classroom	92.9	1.E-01	2.9	1. E-03	0.1	3. E-04	23.5	6. E-03	1.E-03	3.E-02	119.5	1.E-01
Playground	96.9	1.E-01	2.9	1. E-03	0.1	2. E-04	24.2	6. E-03	1.E-03	3.E-02	124.1	2.E-01
School 4 Classroom	100.2	1.E-01	3.5	1. E-03	0.1	3. E-04	22.6	5. E-03	1.E-03	3.E-02	126.4	2.E-01
Playground	99.3	1.E-01	2.7	1. E-03	0.2	3. E-04	21.6	5. E-03	8.E-04	3.E-02	123.8	1.E-01
School 5 Classroom	69.5	8.E-02	1.6	7. E-04	0.1	2. E-04	20.0	5. E-03	6.E-04	2.E-02	91.2	1.E-01
Playground	71.3	8.E-02	1.7	7. E-04	0.1	2. E-04	21.1	5. E-03	6.E-04	2.E-02	94.2	1.E-01
School 6 Classroom	77.8	9.E-02	2.3	9. E-04	0.1	2. E-04	23.3	6. E-03	8.E-04	3.E-02	103.5	1.E-01
Playground	74.3	9.E-02	2.3	9. E-04	0.1	2. E-04	23.2	6. E-03	8.E-04	3.E-02	99.9	1.E-01
School 7 Playground	93.2	1.E-01	2.4	1. E-03	0.2	4. E-04	23.0	5. E-03	9.E-04	3.E-02	118.8	1.E-01
School 8 Classroom	51.0	6.E-02	1.3	5. E-04	0.1	2. E-04	17.4	4. E-03	5.E-04	1.E-02	69.7	8.E-02
Playground	62.5	7.E-02	1.5	6. E-04	0.1	1. E-04	20.8	5. E-03	5.E-04	2.E-02	84.9	9.E-02

In this study, the lifetime cancer risks for benzene ranged from 5.10×10^{-5} (school 8, classroom) to 1.00×10^{-4} (school 4, classroom), and the mean lifetime cancer risks of benzene, ethylbenzene, styrene, and carbon tetrachloride ranged from 1.7×10^{-5} (school 8, classroom) to 3.2×10^{-5} (school 4, classroom). Similar ranges of mean cancer risks from 0.88×10^{-5} to 1.7×10^{-5} were reported for primary school children in Turkey (Demirel et al., 2014).

According to WHO, lifetime cancer risk between 1×10^{-5} and 1×10^{-6} is considered acceptable, while USEPA recommends acceptable risk levels below 1×10^{-6} as described in (Demirel et al., 2014; Shi et al., 2022). Therefore, action is required for the schools with cancer risk values higher than 1×10^{-5}.

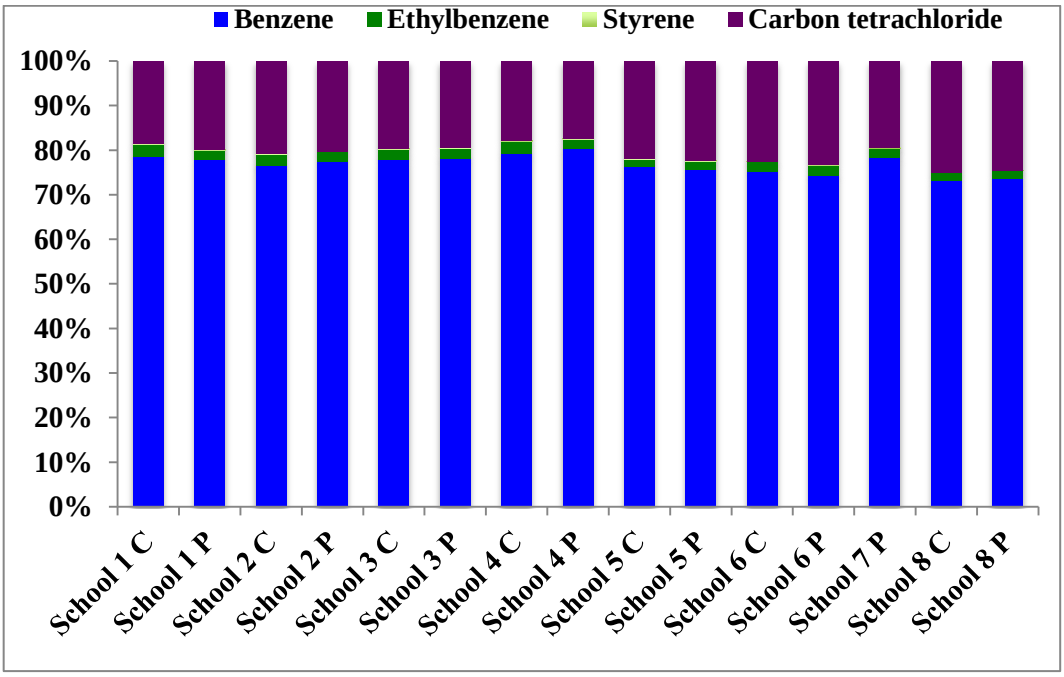

Figure 3.5. The stacked column (100%) contribution of each VOC to CCR $\times 10^{6}$ in 15 sampling locations of primary schools (C, represents classroom and P, Playground)

As indicated in Figure 3.5, the main contributions of benzene (73-80%) to the estimated cumulative cancer risk were found in all sampling locations, and in most schools near heavy-traffic roads, the indoor contributions of benzene were slightly higher than outdoor. This finding is in agreement with a former study in schools in Italy that revealed the highest contribution of benzene to cancer risk indicator (CRI) (De Gennaro et al., 2013). Similarly, previous study in urban and industrial locations in four developing countries revealed that benzene accounted for 84 ± 10% of the CCR values in all cases (Do et al., 2015).

Results from this study revealed that the exposure of students to the measured concentrations of benzene might have harmful effects. Therefore, schools, respective government agencies, and all the relevant bodies should take both indoor and outdoor remedial environmental measures to decrease the concentration of benzene. Non-cancer Risks of exposure to VOCs was determined by using hazard ratio. Hazard ratio indicators for six VOCs were determined based on the availability of reference concentration values for non-cancer effects (see Table 3.3). Indoor total hazard ratio indicator (THRI) values were larger than outdoor values in Schools 1, 4, and 6, and lower in Schools 3, 5, and 8, as shown in Table 3.6. The highest values of THRI were found in classrooms of Schools 4 and 1. As depicted in Table 3.6, the indoor THRI in schools near heavy-traffic roads was 1.03–1.16 times higher than the outdoor THRI, except for school 3. However, the indoor THRI in the schools near low-traffic roads was less than the outdoor THRI. This shows that the indoor concentrations in the schools near heavy-traffic roads may be affected by their outdoor concentrations in addition to the indoor sources. In this study, the hazard ratio levels for individual VOCs were less than one, ranging from 0.0001 for styrene in the playground of School 8 to 0.12 for benzene in the classroom of School 4 (Table 3.6), which means that their concentrations were below the level of concern.

Similar levels of hazard ratio for BTEX for non-cancer health effects were found as 0.0057 (benzene), 0.043 (toluene), 0.015 (ethyl benzene), 0.0088 (m, p-xylene), and 0.0016 (o-xylene) in primary schools in Turkey (Demirel et al., 2014).

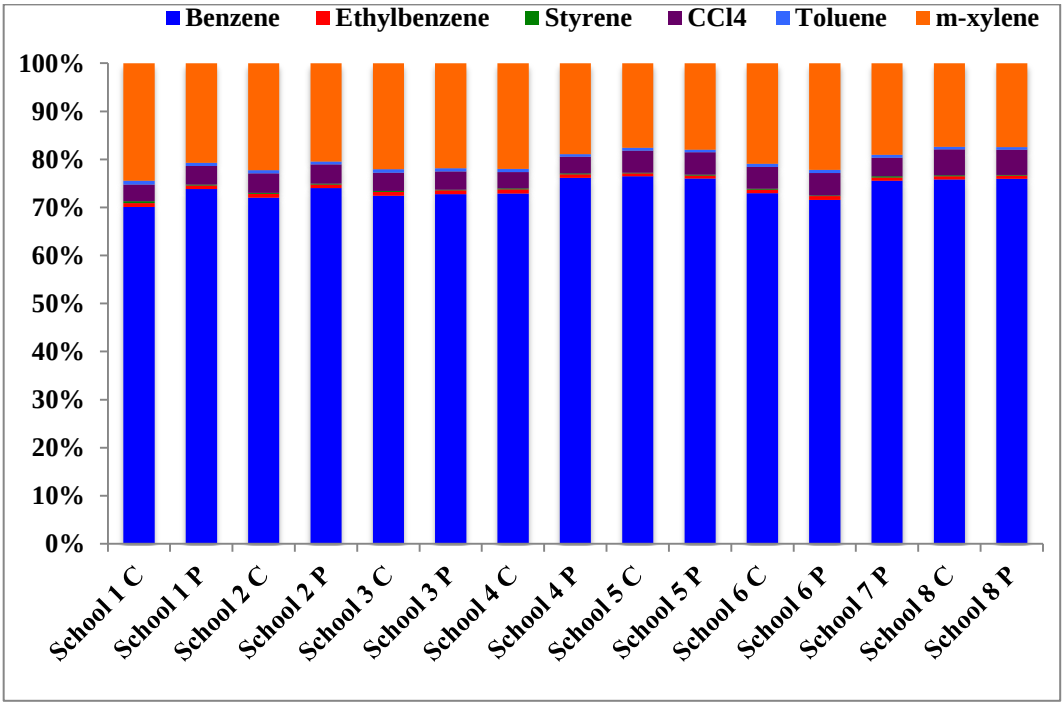

Figure 3.6. The stacked column (100%) contribution of each VOC to THRI in 15 sampling locations of primary schools (C, represents classroom and P, Playground)

Figure 3.6 reveals that higher contributions of benzene (70–77%) to THRI were observed in all sampling locations. Similar results were described in a study in schools in Italy (De Gennaro et al., 2013). The higher contributions of benzene to both CCR and THRI indicate that corrective environmental actions are required in both indoor and outdoor environments.

3.3.5 Ozone formation potential (OFP) of VOCs

The ozone formation potential of volatile organic compounds in outdoor sampling locations (playgrounds of eight primary schools) is presented in Table 3.7.

Table 3.7 Ozone formation potential of volatile organic compounds in playgrounds of eight primary schools

VOC Name	MIR (2010)	Ozone Formation Potential (µg/m3)							
		School 1	School 2	School 3	School 4	School 5	School 6	School 7	School 8
n-pentane	1.31	3.92	4.64	4.91	3.77	3.39	3.91	4.50	2.72
n-hexane	1.24	1.34	1.21	1.57	1.12	1.38	1.16	1.48	-
n-heptane	1.07	0.73	0.72	0.87	0.96	0.61	0.75	0.72	0.50
n-octane	0.90	0.43	0.44	0.48	0.49	0.34	0.44	0.37	0.31
n-nonane	0.78	0.25	0.26	0.32	0.67	0.20	0.31	0.30	0.17
n-decane	0.68	0.51	0.36	0.55	1.04	0.22	0.32	0.39	0.17
undecane	0.61	0.25	0.27	0.33	0.85	0.18	0.33	0.27	0.15
dodecane	0.55	0.20	0.20	0.26	1.10	0.14	0.27	0.24	0.12
methylcyclopentane	2.19	1.80	1.87	2.21	2.09	1.49	1.78	1.95	1.15
2-methylpentane	1.50	8.08	7.49	8.83	7.45	6.00	6.93	7.76	4.78
tridcane	0.53	-	0.17	0.17	0.74	-	0.24	0.16	-
tetradecane	0.51	0.12	0.12	0.12	0.23	-	0.16	0.12	-
Total (Cyclo-) Alkanes		**17.63**	**17.75**	**20.63**	**20.52**	**13.95**	**16.61**	**18.26**	**10.06**
1-pentene	7.21	2.13	2.40	1.91	1.70	1.79	1.96	1.63	1.85
1-Hexene	5.49	1.47	1.61	1.53	1.17	1.13	1.46	1.70	1.00
Total Alkene		**3.60**	**4.01**	**3.44**	**2.87**	**2.92**	**3.42**	**3.33**	**2.85**
benzene	0.72	2.15	2.20	2.41	2.46	1.77	1.85	2.32	1.55
toluene	4.00	17.44	17.19	20.97	16.65	12.37	15.57	17.20	10.94
ethylbenzene	3.04	2.89	3.09	3.48	3.34	2.11	2.78	2.93	1.83
p+m-xylene	7.80	21.72	21.90	26.05	22.07	15.09	20.62	21.06	12.83
o-xylene	7.64	9.80	9.85	11.19	9.46	6.59	8.78	9.18	5.65
styrene	1.73	0.45	0.38	0.41	0.54	0.28	0.39	0.65	0.26
propylbenzene	2.03	0.34	0.34	0.39	0.36	0.23	0.31	0.33	0.20
1,2,4-trimethylbenzene	8.87	9.33	10.06	11.01	10.49	6.63	9.40	9.71	5.44
Total Aromatic compounds		**64.12**	**65.00**	**75.90**	**65.37**	**45.07**	**59.70**	**63.37**	**38.69**
Isopropanol	0.61	0.11	-	0.03	0.08	0.03	0.07	0.07	0.06
2-ethyl-1-hexanol	2.00	0.44	0.33	0.39	0.24	0.53	0.52	0.57	0.41
1-Octanol	1.43	0.27	0.25	0.28	0.32	0.23	0.29	0.31	0.21
phenol	2.76	9.05	7.60	9.43	8.21	8.31	7.42	7.32	6.32
Total Alcohols		**9.87**	**8.18**	**10.12**	**8.85**	**9.10**	**8.30**	**8.27**	**7.00**
2-butanone	1.48	1.26	1.23	1.23	-	-	1.19	-	-
2-heptanone	2.36	0.27	0.31	0.30	0.37	0.23	0.25	0.31	0.19
Total Ketones		**1.53**	**1.54**	**1.53**	**0.37**	**0.23**	**1.44**	**0.31**	**0.19**
methylacetate	0.07	0.05	-	0.05	-	-	0.04	-	-
ethyl acetate	0.63	0.69	0.41	0.75	0.75	0.50	0.56	0.52	0.37
n-butylacetate	0.83	0.49	0.31	0.67	0.55	0.26	0.28	0.21	0.16
Total Esters		**1.23**	**0.72**	**1.47**	**1.30**	**0.76**	**0.88**	**0.74**	**0.54**
Furan	9.15	-	5.50	-	-	-	-	-	-
2-methylfuran	8.30	3.57	3.46	3.62	2.79	2.42	2.73	3.83	2.05
Total Other oxygenated compounds		**3.57**	**8.96**	**3.62**	**2.79**	**2.42**	**2.73**	**3.83**	**2.05**
chlorobenzene	0.32	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
dichloromethane	0.04	0.00	-	0.00	0.00	-	-	-	-
Total Halogenated compounds		**0.01**	**0.01**	**0.01**	**0.02**	**0.01**	**0.01**	**0.01**	**0.01**
α-pinene	4.51	0.87	0.73	0.90	0.86	0.53	0.61	0.79	0.60
linalool	5.43	0.31	0.65	0.62	-	0.51	0.57	-	0.46
Total Terpenes		1.18	1.37	1.52	0.86	1.05	1.18	0.79	1.06
Total VOCs		**102.75**	**107.56**	**118.24**	**102.94**	**75.50**	**94.28**	**98.90**	**62.45**

The values of OFPs (μg/m^3) in the playgrounds of School 7 (99 μg/m^3), School 6 (94 μg/m^3), School 5 (76 μg/m^3), and School 8 (63 μg/m^3) were lower than 100 μg/m^3 which is the guideline limit value given by WHO (2020). The OFPs (μg/m^3) in the playgrounds of School 3 (118 μg/m^3), School 2 (108 μg/m^3), School 4 (103 μg/m^3), and School 1 (103 μg/m^3) were larger than the guideline value (100 μg/m^3). However, the OFP results from our study were lower than the results of OFP reported in previous studies in urban China, 315.9 μg/m^3 (Luo et al., 2020), Benin City, Nigeria, 281.1 μg/m^3 (Olumayede, 2014), and Jinghong, China, 588.07 μg/m^3 and 535.38 μg/m^3 in the dry season and rainy season, respectively (Shi et al., 2022).

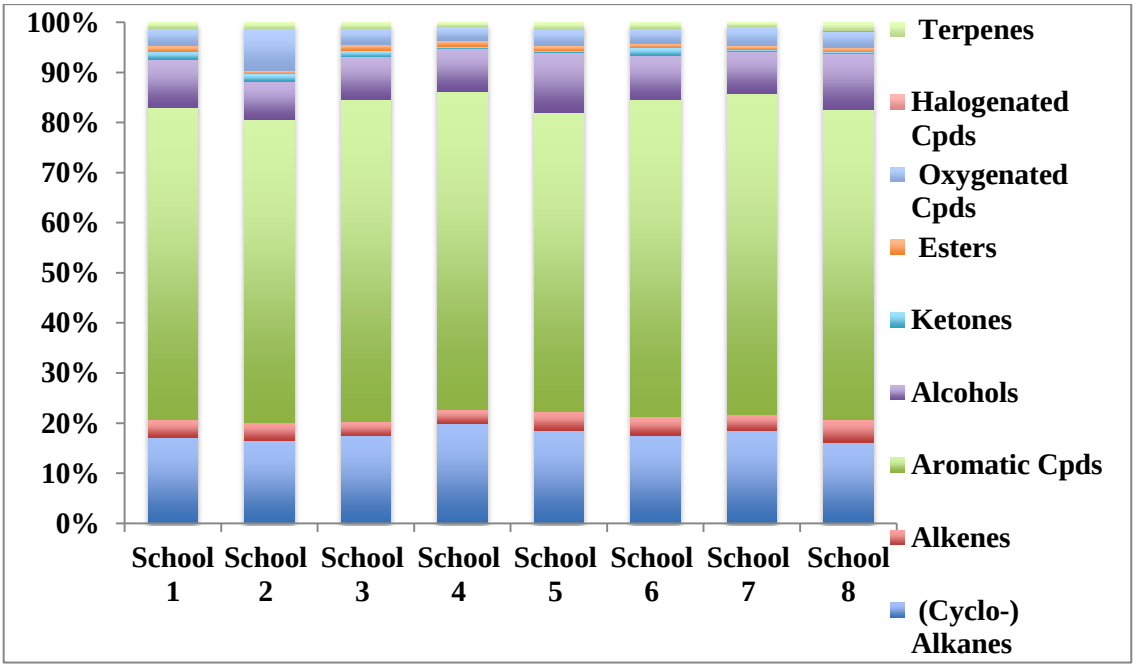

Figure 3.7. The stacked column (100%) contribution of each group to OFP in the playground of eight primary schools

In this study, the most significant contributors to the computed values of the OFP were aromatic compounds, ranging from 59.7 to 64.2%, followed by alkanes, ranging from 16.1 to 19.9% (Figure 3.7).

Similarly, the contributions of olefins (57.73%) and aromatic hydrocarbons (30.78%) were higher than those of alkanes (11.49%) to the calculated OFP in Jinghong, China (Shi et al., 2022). A previous study in a flame retardant industrial park in China also showed that aromatic hydrocarbons were the largest contributor (94%) to OFPs in the factory, ranging from 54.8 to 291 μg/m^3 (Lin et al., 2023).

Conclusions and Recommendations

The current study is the first research to examine 76 VOCs in eight primary schools in Ethiopia. In most of the primary schools the concentrations of TVOCs in the classrooms were higher than the concentrations in the playgrounds suggesting that there were possible sources of the measured VOCs from the classrooms. The I/O ratios of individual compounds also suggested that the occurrence of possible indoor sources. The T/B ratios in all schools were less than two, suggesting that vehicular sources may have an important effect on aromatic VOCs concentrations. The cumulative cancer risk and total hazard ratio indicators showed that the exposure of children to the measured concentrations of benzene might have harmful effects. Therefore, schools, respective government agencies, and all the relevant bodies should take remedial environmental measures to decrease the concentration of benzene in educational settings. This study offers a crucial data set that governments and academic experts may use to step up efforts to enhance the air quality in school settings. In addition, the findings here would complement the limited information on VOCs in developing countries and help inform future international endeavors to reduce air pollution**.**

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CHAPTER 4. EXPOSURE OF SCHOOL CHILDREN TO PARTICULATE MATTER AND INORGANIC GASEOUS POLLUTANTS IN HAWASSA CITY, ETHIOPIA

ABSTRACT

The detrimental consequences of air pollution on humans, particularly vulnerable groups like children, have drawn a lot of attention globally. Studies on the levels and sources of particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, CO, and SO_2) in primary schools in Africa, including Ethiopia, are inadequate. Therefore, the objective of this study was to determine the levels of particulate matter and inorganic gaseous pollutants in primary schools in Hawassa, Ethiopia, and assess potential health risks. The $PM_{2.5}$ and PM_{10} levels were determined using a portable gas monitor device (HoldPeak Laser PM meter, HP 5800D). NO_2, CO, and SO_2 levels were determined using the Aeroqual Series 500 Portable Air Quality Monitor (Aeroqual Ltd., New Zealand). The levels of $PM_{2.5}$, PM_{10}, and NO_2 in all sampling sites ranged from 11–66.3, 30.8–399.7, and 60.5–152 µg/m^3, respectively. The hazard quotient (HQ) values for PM_{10} and $PM_{2.5}$ ranged from 0.3 to 3.2 and 0.2 to 1.1, respectively. The AQI (Air Quality Index) at 40% and 30% of the outdoor sampling sites were unhealthy for sensitive groups due to exposure to $PM_{2.5}$ and PM_{10}, respectively. The levels of $PM_{2.5}$ in 55% of the sampling sites and PM_{10} in 85% of the sampling sites were found to be above the WHO recommendations. The levels of $PM_{2.5}$ and PM_{10}, as well as the AQI and HQ values, indicate poor condition of the air in the schools and suggest a significant health risk for all populations around the schools.

Keywords: Air quality; particulate matter; inorganic gaseous pollutants; primary schools; Ethiopia

4.1 Introduction

Indoor and outdoor air pollution has drawn a lot of attention worldwide due to its adverse effects on humans, especially on susceptible populations such as children. School-aged children spend the majority of the day in schools, making them more vulnerable to air pollution due to their greater rate of inhalation and lower ability to cope with harmful pollutants (Louis et al., 2006; Stranger et al., 2008; Li et al., 2015).

Asthma, respiratory conditions, lung cancer, and early mortality have all been linked to particulate matter ($PM_{2.5}$–PM_{10}) inhalation, and these effects have been well studied in both humans and animals (Sapkota et al., 2012; US EPA, 2023; WHO, 2023).

Sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and carbon monoxide (CO) are three examples of inorganic gaseous air pollutants that may irritate and inflame the respiratory system (Stranger et al., 2008; Yoda et al., 2014; Zhang et al., 2019). The burning of fossil fuels in automobiles, factories, and power plants is one of their main sources (Omidvarborna et al., 2015; Agbo et al., 2021). The main causes of particulate matter in school classrooms are inadequate ventilation, deterioration of the building materials, using chalk on the whiteboard, re-suspension from student physical activity, and outdoor sources (Almeida et al., 2011; Canha et al., 2014). The sources and quantities of particulate matter and inorganic gaseous pollutants in school environments have been evaluated by a number of researches (Stranger et al., 2008; Almeida et al., 2011; Canha et al., 2014; Jan et al., 2017; Zhang et al., 2019; NAYAN et al., 2022). However, such studies have been mostly done in well-developed countries, leaving underdeveloped countries like Ethiopia with little information.

Although there are some studies on particulate matter and inorganic gaseous pollutants in the urban areas of Ethiopia (Keil et al., 2010; Tefera et al., 2016, 2021; Agbo et al., 2021; Embiale et al., 2021; Jida et al., 2021; Asefa & Mergia, 2022), there is little data on the amounts of these pollutants in school settings across Ethiopia and other parts of Africa. The health risk assessment of school-age children becomes difficult because of such insufficient data.

Therefore, the aim of this study was to determine the concentrations of particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, SO_2, and CO) in primary schools in Hawassa city, Ethiopia, and assess potential health risks. To the best of our knowledge, this is the first study to determine particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, SO_2, and CO) in primary schools in Ethiopia. The findings of the study will help policymakers, public health professionals, and school administrators become more aware of the state of the air quality in school environments. Furthermore, as one of the biggest problems in developing nations is a lack of data on air pollutants, the study's results will contribute to the efforts being made to reduce air pollution by providing a further source of data.

4.2 Material and Methods

4.2.1 Description of the study area

This study was carried out in Hawassa City, Ethiopia, which is the capital of the Sidama Regional State. Hawassa is located 275 kilometers south of Ethiopia's capital, Addis Ababa. The city's coordinates are 7°3'43.4" N latitude and 38°28.581' E longitude. According to projections of the Ethiopian Statistical Service (ESS), Hawassa's population is estimated to be 441536 (ESS, 2023).

4.2.2 Sampling site

Samples for this study were collected from ten primary schools in Hawassa city between January 21, 2022, and February 26, 2022. Particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, SO_2, and CO) were studied in the indoor (classrooms) and outdoor (playgrounds) of ten primary schools in the city. The ten schools were purposefully selected based on some attributes of the specific locations. The attributes included proximity to traffic roads, industrial areas, and types of buildings in the surroundings, taken into account to assess their effects on the schools' air condition, as we described in our previous study (Amare et al., 2023). Table 4.1 presents comprehensive information of the chosen schools.

Table 4.1 Descriptions of sampling sites (PS = Primary School)

Sampling sites	Names of primary schools	Descriptions	Coordinates
PS1	Debub Ethiopia Academy	Very close to busy traffic road Surrounded by residential buildings and a hospital Use of chalk and blackboard	7°02'01.2"N 38°29'42.7"E
PS2	Hayole	Very close to a busy traffic road Surrounded by residential and commercial buildings Use of chalk and blackboard	7°02'05.3"N 38°29'21.4"E
PS3	Alito	Close to a busy traffic road Surrounded by residential buildings Use of chalk and blackboard	7°02'16.7"N 38°28'48.6"E
PS4	Adare	Close to a busy traffic road Surrounded by residential buildings Use of chalk and blackboard	7°02'31.7"N 38°28'22.0"E
PS5	Comboni	Close to a low traffic road Surrounded by residential buildings Use of chalk and blackboard	7°02'46.0"N 38°28'10.0"E
PS6	St. Gabriel	Very close to a busy traffic road Surrounded by residential buildings Use of chalk and blackboard	7°02'45.2"N 38°28'44.7"E
PS7	Tabor	Close to a busy traffic road Surrounded by residential buildings Use of chalk and blackboard	7°3'11.15"N, 38°28'44.45"E
PS8	Hykdar	Close to a moderate traffic road Surrounded by residential buildings Use of chalk and blackboard	7°04'00.5"N 38°28'59.0"E
PS9	Silase	Close to a low traffic road Surrounded by residential buildings Use of chalk and blackboard	7°04'06.9"N 38°29'19.7"E
PS10	SOS	Close to a low traffic road Surrounded by residential and commercial buildings Use of chalk and blackboard	7°04'43.4"N 38°29'00.2"E

4.2.3 Sampling design and measurement methods

The target pollutants for this study were inorganic gaseous pollutants (NO_2, CO, and SO_2) and particulate matter (PM_{10} and $PM_{2.5}$). The measurement of the levels of PM_{10} and $PM_{2.5}$ was done using a portable gas monitor device (HoldPeak Laser PM meter HP 5800D, Zhuhai Jida Huapu Instrument Company Limited, China). The range of $PM_{2.5}$ and PM_{10} detection is 0–999.9 $\mu g/m^3$ and 0–1999.9 $\mu g/m^3$, respectively, with a resolution of 0.1 $\mu g/m^3$. Levels of NO_2, CO, and SO_2 were determined using the Aeroqual Series 500 Portable Air Quality Monitor (Aeroqual Ltd., New Zealand), a real-time sampler with a replaceable electrochemical gas sensor head. An automated hand-held Garmin GPS 72H Global Positioning System (GPS) navigator (Taiwan) was used to determine the sampling location coordinates.

From each indoor and outdoor site, levels of $PM_{2.5}$, PM_{10}, SO_2, NO_2, CO, and meteorological data (relative humidity and temperature) were measured on three separate days (two weekdays and a weekend day) at two moments during the day: From 7:00 to 12:00 in the mornings and 13:30 to 18:30 in the afternoons. During these moments, measurements of $PM_{2.5}$, PM_{10}, SO_2, NO_2, and CO were performed continuously for 1 hour at each sampling site, and the concentrations displayed on the detector screen were recorded every 3 minutes. Once the measurements were finished, the levels of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 for each sampling location were determined by averaging the results of 20 notes. The indoor measurements were done in the classroom of each school, and the devices were placed one meter away from windows and doors and at a height of approximately 1.5 meters above the ground. The outdoor measurements were taken in each school's playground, and the devices were positioned at a height of about 2 meters from the ground.

4.2.4 Risk assessment of gaseous and particulate pollutants

4.2.4.1 The non-carcinogenic risk assessment of indoor air pollutants

The hazard quotient (HQ) was used in health risk assessments to estimate the exposure risk associated with inhaling pollutants. The hazard quotient is a frequently used method for assessing the possible effects of non-carcinogenic contact to a known pollutant (US EPA, 2009). The average daily dose (ADD) was used to explain human exposure. ADD was calculated based on United States Environmental Protection Agency (US EPA) methodology using Equation (4.1) (US EPA, 1989; Bixapathi et al., 2021).

$$ADD = \frac{C \times IR \times EF \times ET \times ED}{BW \times AT} \quad (4.1)$$

Where, ADD is expressed in μg kg^{-1} day^{-1}; IR is the inhalation rate in m^3/day; C is the concentration of pollutants in μg/m^3; ET is the exposure time in h/day; ED is the exposure duration in days; EF is the exposure frequency in days/year; AT is the average time in days, and BW is the body weight of the exposed group in Kg. Table 4.2 presents the values of these variables.

Table 4.2 Parameters used for calculating HQ for $PM_{2.5}$, PM_{10}, and NO_2 (Matooane & Diab, 2003; WHO, 2021; Embiale et al., 2022)

Parameters	**Children (6-14 years)**
Exposure time (ET)	8h/day
Exposure frequency (EF)	180 days/year
Exposure duration (ED)	8 years
Averaging time (AT)	2920 days
Body weight (BW)	45.3 Kg
Inhalation rate (IR)	13.5 m^3/Day
Inhalation reference concentration (RfC)	10 µg/m^3 for $PM_{2.5}$ 20 µg/m^3 for PM_{10}

RfD = RfC (inhalation reference concentration µg/m^3) × Assumed inhalation rate (m^3/day) × 1 / BW (kg); AT = ED ×365 days

Equation (4.2) was used to calculate the HQ (hazard quotient), which was obtained by dividing the average daily dose (ADD) by the reference dose (RfD) of each pollutant.

$$HQ = \frac{ADD}{RfD} \qquad (4.2)$$

Where, RfD is expressed in µg kg^{-1} day^{-1}, and RfD = RfC (inhalation reference concentration µg/m^3) × Assumed inhalation rate (m^3/day) × 1/BW (kg). The standard adult inhalation rate of 20 m^3/day and weight of 70 kg were used to calculate the RfD values because these values are used in the conversion factor for calculating RfD (US EPA, 2004). RfD for NO_2 was taken 10.1 µg kg^{-1} day^{-1} (Phantu & Bootdee, 2022).

There is either no risk or very little risk when the HQ is less than 0.1. Low hazards are present when the HQ values fall between 0.1 and 1.0. Modest concerns exist when the HQ values fall between 1.1 and 10. There are significant hazards if the HQ values are higher than 10 (Lina Thabethe et al., 2014; US EPA, 1989).

4.2.4.2 Air quality index (AQI) of outdoor air pollutants

The AQI for the outdoor samples was determined using the mean values of the pollutants. The AQI for each pollutant was derived using Equation (4.3) as described in (Kasim et al., 2018; Mopa Wambebe & Duan, 2020; ACT Government, 2022). The World Health Organization guidelines (WHO, 2021) used for this calculation were the 1-hour mean for NO_2 (200 µg/m^3) and CO (35000 µg/m^3) and the 24-hour mean for $PM_{2.5}$ (25 µg/m^3) and PM_{10} (50 µg/m^3).

$$AQI_{Pollutant} = \frac{Pollutant\ Concentration}{WHO\ Standard} \times 100 \qquad (4.3)$$

Table 4.3 presents the six levels of AQI and respective health concerns taken from the US EPA (2020) and described as follows:

Table 4.3 The six levels of AQI, health concern, and break point concentrations of $PM_{2.5}$, PM_{10}, NO_2, and CO (US EPA, 2020)

AQI Values	Levels of Health Concern	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)	NO_2 (µg/m^3)	CO (ppm)	Colors	Air pollution level
0 to 50	Good	0–12	0–54	0–53	0–4.4	Green	Level 1
51 to 100	Moderate	12.1–35.4	55–154	54–100	4.5–9.4	Yellow	Level 2
101 to 150	Unhealthy for Sensitive Groups	35.5–55.4	155–254	101–360	9.5–12.4	Orange	Level 3
151 to 200	Unhealthy	55.5–150.4	255–354	361–649	12.5–15.4	Red	Level 4
201 to 300	Very Unhealthy	150.5–250.4	355–424	650–1249	15.5–30.4	Purple	Level 5
301 and Higher	Hazardous	250.5–Higher	425–Higher	1250–2049	30.5–50.4	Maroon	Level 6

Level 1 air pollution is considered to have satisfactory air quality as it poses minimal risk to human health. Level 2 pollution is deemed acceptable, but small number of individuals may perceive it as a moderate health concern. Level 3 is labeled as unhealthy for sensitive groups, with the general population less likely to be affected, but individuals from sensitive groups may experience health issues. Level 4 is classified as unhealthy, with potential health consequences for anyone and more severe effects on vulnerable groups. Level 5 is extremely harmful, triggering a health alert and leading to more severe health impacts for everyone. Level 6 poses a public health risk, resulting in emergency situations and health alerts, with a higher likelihood of serious health repercussions for the entire population.

4.2.5 Statistical analysis

Microsoft Excel and IBM SPSS (Version 25) were used for the statistical data analysis. The Shapiro-Wilks test was used to test the normality of the data, and the data were not normally distributed for all pollutants. Consequentially, the independent sample Kruskal-Wallis test was used to examine statistical differences in the measured concentration levels, followed by a post-hoc test. The correlation coefficients between temperature, relative humidity, NO_2, CO, $PM_{2.5}$, PM_{10}, and NO_2 were determined using Spearman's rho correlation.

4.3 Results and Discussion

4.3.1 Concentrations of particulate matter and inorganic gaseous pollutants

The concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, SO_2, and meteorological data (temperature and relative humidity) were measured in the outdoor (playgrounds) and indoor (classrooms) of ten primary schools in Hawassa city, Ethiopia. $PM_{2.5}$, PM_{10}, and NO_2 were detected at all sampling sites; however, CO and SO_2 were not detected in any of the sampling sites. The levels of $PM_{2.5}$, PM_{10}, and NO_2 in all sampling sites ranged from 11–66.3, 30.8–399.7, and 60.5–152 µg/m^3, respectively (Table 4.4).

The overall indoor mean concentrations of $PM_{2.5}$, PM_{10}, and NO_2 were 33, 138.8, and 84.8 µg/m^3, which were slightly higher than the outdoor concentrations of 32.3, 119.8, and 83.7 µg/m^3, respectively (Figure 4.1). The concentrations of $PM_{2.5}$ and PM_{10} in the present study were lower than those reported in primary schools in Pune (India), with indoor and outdoor levels of 135.8 and 263.9 µg/m^3 and 88.9 and 166.6 µg/m^3, respectively (Jan et al., 2017). Similarly, the findings of the current study were lower than the indoor and outdoor concentrations of $PM_{2.5}$ and PM_{10} (82.65 and 236.13 µg/m^3 and 56.25 and 162.89 µg/m^3, respectively), reported from primary schools in Athens, Greece (Diapouli et al., 2007). On the other hand, the mean concentration of $PM_{2.5}$ in this study was comparable with the mean indoor $PM_{2.5}$ concentration (46.9 ± 33 µg/m^3) and outdoor concentration (36.8 ± 33µg/m^3) in schools in Sari, Iran (Mohammadyan et al., 2017), and in classrooms (35 µg/m^3) in schools in Lisbon, Portugal (Faria et al., 2020).

The average concentration of NO_2 in the current study was higher than 46.7 μg/m^3, which was reported at primary schools in Pune, India (Jan et al., 2017). The levels of $PM_{2.5}$ ranged from 11.5–66.3 μg/m^3 outdoor and 11–64.2 μg/m^3 indoors (Table 4.4). The findings of this study showed higher minimum but lower maximum values of $PM_{2.5}$ than those reported in primary schools in Barcelona, with outdoor and indoor values of 1–192 μg/m^3 and 7–105 μg/m^3, respectively (Amato et al., 2014). On the other hand, the ranges of indoor $PM_{2.5}$ levels in this study were comparable with those reported in primary schools in Athi River Township, Kenya, with indoor median values of 17.7–52.4 μg/m^3 and 28.5–75.5 μg/m^3 during the dry and wet seasons, respectively (Were et al., 2020). The findings of this study have indicated that the concentrations of $PM_{2.5}$ in 55% of the sampling sites were above the WHO guidelines for $PM_{2.5}$ (25 μg/m^3), which showed the low air quality in the schools, particularly those close to crowded roads.

The outdoor and indoor concentration of PM_{10} ranged from 38.9–399.7 and 30.8–374.9 μg/m^3, respectively. The results of this study were comparable to the indoor median PM_{10} levels that ranged from 60.8–269.1 μg/m^3 and 52.8–232.3 μg/m^3 during the dry and wet seasons, respectively, in Athi River Township, Kenya (Were et al., 2020). However, the levels of PM_{10} in this study were higher than those reported in primary schools in Lisbon (Portugal), with indoor and outdoor concentrations of 30–146 μg/m^3 and 8–47 μg/m^3, respectively (Almeida et al., 2011).

Table 4.4 Arithmetic mean concentration values (μg/m^3) of $PM_{2.5}$, PM_{10}, NO_2, CO, SO_2, Temperature (T), and Relative Humidity (RH) in all sampling locations (PS = Primary School; C = Classroom; P = Playground)

School	$PM_{2.5}$	PM_{10}	NO_2	CO	SO_2	T (°C)	RH (%)
PS1 C	59.0	361.0	152.0	ND	ND	27.5	32.8
PS1 P	66.3	399.7	61.2	ND	ND	27.7	32.0
PS2 C	41.9	103.6	80.0	ND	ND	27.1	34.2
PS2 P	35.7	68.9	108.0	ND	ND	27.0	32.0
PS3 C	42.9	121.4	77.7	ND	ND	27.0	36.4
PS3 P	26.7	105.3	88.0	ND	ND	27.4	35.6
PS4 C	25.3	107.8	73.7	ND	ND	27.5	33.7
PS4 P	60.7	93.5	106.0	ND	ND	28.0	32.3
PS5 C	22.3	86.6	71.7	ND	ND	27.0	33.0
PS5 P	29.9	212.1	78.2	ND	ND	26.5	34.8
PS6 C	64.2	374.9	81.3	ND	ND	26.6	35.2
PS6 P	36.8	62.1	64.8	ND	ND	27.3	31.8
PS7 C	20.8	58.6	85.5	ND	ND	27.3	33.5
PS7 P	20.2	93.3	84.3	ND	ND	27.8	32.0
PS8 C	22.1	90.4	60.5	ND	ND	28.2	31.8
PS8 P	17.4	49.3	82.2	ND	ND	28.5	31.7
PS9 C	20.3	53.2	72.3	ND	ND	28.3	34.3
PS9 P	17.4	75.0	83.7	ND	ND	28.1	33.8
PS10 C	11.0	30.8	93.3	ND	ND	27.7	34.1
PS10 P	11.5	38.9	81.0	ND	ND	28.0	33.0

In 85% of sampling sites, the concentrations of PM_{10} were above the WHO guidelines for values (50 μg/m^3), which indicate poor air quality in the schools, especially in the schools near busy roads. The concentrations of NO_2 in this study ranged from 61.2–108 μg/m^3 and 60.5–152 μg/m^3 in the outdoor and indoor, respectively, which were higher than those reported from primary schools in Rayong City (Thailand), with outdoor and indoor levels of 13.0–43.7 μg/m^3 and 12.8–32.9 μg/m^3, respectively (Bootdee et al., 2019). The concentrations of NO_2 in all sampling sites were below WHO guideline value (200 μg/m^3).

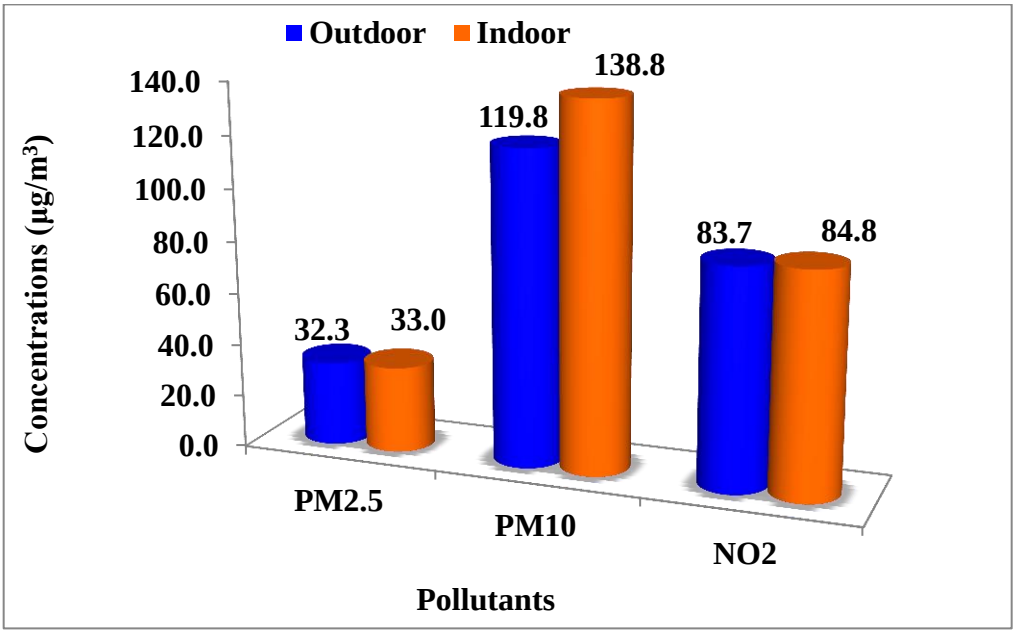

Figure 4.1. The overall mean concentrations of $PM_{2.5}$, PM_{10}, and NO_2 in the classrooms and playgrounds of the ten primary schools

The Shapiro-Wilks test was used to test the normality of the concentration data for $PM_{2.5}$, PM_{10}, and NO_2, and the data were not normally distributed for all pollutants. Consequently, the Kruskal-Wallis sample test was applied to the $PM_{2.5}$, PM_{10}, and NO_2 data in all the sampling sites, and the results showed that there were no significant differences in the concentration of NO_2 across all sampling sites (p = 0.05). However, there were significant differences in the concentrations of $PM_{2.5}$ and PM_{10} across all sampling sites (p = 0.05). However, it does not indicate where this difference has occurred. Thus, a detailed pair comparison between the sampling sites was done using a post hoc test, and significance values have been adjusted by the Bonferroni correction for multiple tests. The results for $PM_{2.5}$ data from the post hoc test showed that there were significant differences ($P \leq 0.001$) in three pairwise comparisons (i.e., PS10 vs. PS6; PS10 vs. PS3; PS10 vs. PS1). Likewise, the results for PM_{10} data from the post hoc test showed that there was a significant difference ($P \leq 0.035$) in one pairwise comparison, i.e., PS10 vs. PS1.

The indoor-to-outdoor (I/O) ratio of the concentrations of $PM_{2.5}$, PM_{10}, and NO_2, in ten primary schools is indicated in Table 4.5. The I/O concentration ratios were calculated by dividing the levels of $PM_{2.5}$, PM_{10}, and NO_2 in each classroom by the levels in each school's playground. The I/O concentration ratio of $PM_{2.5}$, PM_{10}, and NO_2 was higher than one in 50%, 50%, and 30%, respectively, of the primary schools. This indicated that $PM_{2.5}$, PM_{10}, and NO_2 could have indoor origins alongside outdoor ones. The higher I/O concentration ratios of $PM_{2.5}$ and PM_{10} were 1.7 and 6.0, respectively, in PS6 and 2.5 for NO_2 in PS1. Similar studies reported higher I/O ratios in schools (Mohamad & Latif, 2013; Jan et al., 2017).

Table 4.5 Indoor to outdoor (I/O) ratio of concentrations of $PM_{2.5}$, PM_{10}, and NO_2 in ten primary schools

School	$PM_{2.5}$	PM_{10}	NO_2
PS1	0.9	0.9	2.5
PS2	1.2	1.5	0.7
PS3	1.6	1.2	0.9
PS4	0.4	1.2	0.7
PS5	0.7	0.4	0.9
PS6	1.7	6.0	1.3
PS7	1.0	0.6	1.0
PS8	1.3	1.8	0.7
PS9	1.2	0.7	0.9
PS10	1.0	0.8	1.2

4.3.2 Correlation of air pollutants with meteorological data

Table 4.6 indicates the correlation between $PM_{2.5}$, PM_{10}, and NO_2 concentration, temperature, and relative humidity. The correlation between the concentrations of $PM_{2.5}$ and PM_{10} was shown to be positively statistically significant based on the results of Spearman's rho correlation (r = 0.897, p-value = 0.01). Furthermore, $PM_{2.5}$ was positively correlated with relative humidity (r = 0.314, p-value = 0.01) but negatively correlated with NO_2 (r = –0.243, p-value = 0.01) and temperature (r = –0.392, p-value = 0.01). Similarly, PM_{10} was positively correlated with relative humidity (r = 0.281, p-value =0.01) but negatively correlated with NO_2 (r = –0.197, p-value = 0.05) and temperature (r = –0.282, p-value = 0.01). Temperature was negatively correlated with relative humidity (r = –0.781, p-value = 0.01).

Table 4.6 Spearman's rho correlation coefficients of $PM_{2.5}$, PM_{10}, NO_2, temperature, and relative humidity (RH) (n= 120)

	$PM_{2.5}$ (µg/m^3)	**PM_{10} (µg/m^3)**	**NO_2 (µg/m^3)**	**T (°C)**	**RH (%)**
$PM_{2.5}$ (µg/m^3)	1.000				
PM_{10} (µg/m^3)	.897**	1.000			
NO_2 (µg/m^3)	-.243**	-.197*	1.000		
T (°C)	-.392**	-.282**	.095	1.000	
RH (%)	.314**	.281**	-.118	-.781**	1.000

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

4.3.3 Health risk assessment

4.3.3.1 The non-carcinogenic risk assessment of indoor air pollutants

In the present study, the non-carcinogenic health risk assessment was estimated by using the hazard quotient (HQ) for the classrooms of the primary schools. The average daily dose (ADD) was computed using Equation (4.1) and the HQ using Equation (4.2). The values of HQ and ADD are depicted in Table 4.7. The HQ value for PM_{10} ranged from 0.3 to 3.2, which implies that there were low to moderate non-carcinogenic effect due to exposure to the measured PM_{10}. The HQ values for $PM_{2.5}$ ranged from 0.2 to 1.1 (Table 4.7), indicating low to moderate non-carcinogenic risks due to exposure of the children to $PM_{2.5}$. Similarly, HQ for NO_2 ranged from 0.3 to 0.7 (Table 4.7), suggesting low to moderate non-carcinogenic health risks to children due to exposure to NO_2 in the classrooms, as describe in (Lina Thabethe et al., 2014; US EPA, 1989) .

Table 4.7 Mean of $PM_{2.5}$, PM_{10}, NO_2, ADD (μg kg^{-1} day^{-1}) and HQ of $PM_{2.5,}$ PM_{10}, and NO_2

	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	NO_2 ($\mu g/m^3$)	ADD $PM_{2.5}$	ADD PM_{10}	ADD NO_2	HQ $PM_{2.5}$	HQ PM_{10}	HQ NO_2
PS1 C	59.0	361.0	152.0	2.9	17.7	7.4	1.0	3.1	0.7
PS2 C	41.9	103.6	80.0	2.1	5.1	3.9	0.7	0.9	0.4
PS3 C	42.9	121.4	77.7	2.1	5.9	3.8	0.7	1.0	0.4
PS4 C	25.3	107.8	73.7	1.2	5.3	3.6	0.4	0.9	0.4
PS5 C	22.3	86.6	71.7	1.1	4.2	3.5	0.4	0.7	0.3
PS6 C	64.2	374.9	81.3	3.1	18.4	4.0	1.1	3.2	0.4
PS7 C	20.8	58.6	85.5	1.0	2.9	4.2	0.4	0.5	0.4
PS8 C	22.1	90.4	60.5	1.1	4.4	3.0	0.4	0.8	0.3
PS9 C	20.3	53.2	72.3	1.0	2.6	3.5	0.3	0.5	0.4
PS10 C	11.0	30.8	93.3	0.5	1.5	4.6	0.2	0.3	0.5

4.3.3.2 Air quality index (AQI) of outdoor air pollutants

The AQI of $PM_{2.5}$, PM_{10}, NO_2, and CO was computed using Equation (4.3). The AQI was computed using the mean concentrations in Table 4.4 and the WHO guideline of 25 $\mu g/m^3$ for $PM_{2.5}$, 50 $\mu g/m^3$ for PM_{10}, 200 $\mu g/m^3$ for NO_2, and 35000 $\mu g/m^3$ for CO. Based on the levels of AQI and respective health concerns given by the US EPA (2020), the air quality of the primary schools is discussed as follows: Figure 4.2 shows the AQI of $PM_{2.5}$ in the playgrounds of the primary schools. The results of this study revealed that 10% of the playgrounds of the studied schools (1 out of 10 sites with a green color code) had a good level of air pollution and satisfactory air quality, and there was little or no health risk due to exposure to $PM_{2.5}$. In another way, the air quality at 30% of the playgrounds of the schools (3 out of 10 sites have a yellow color code) was acceptable; however, for a very small percentage of children, it might constitute a moderate health issue due to exposure to $PM_{2.5}$.

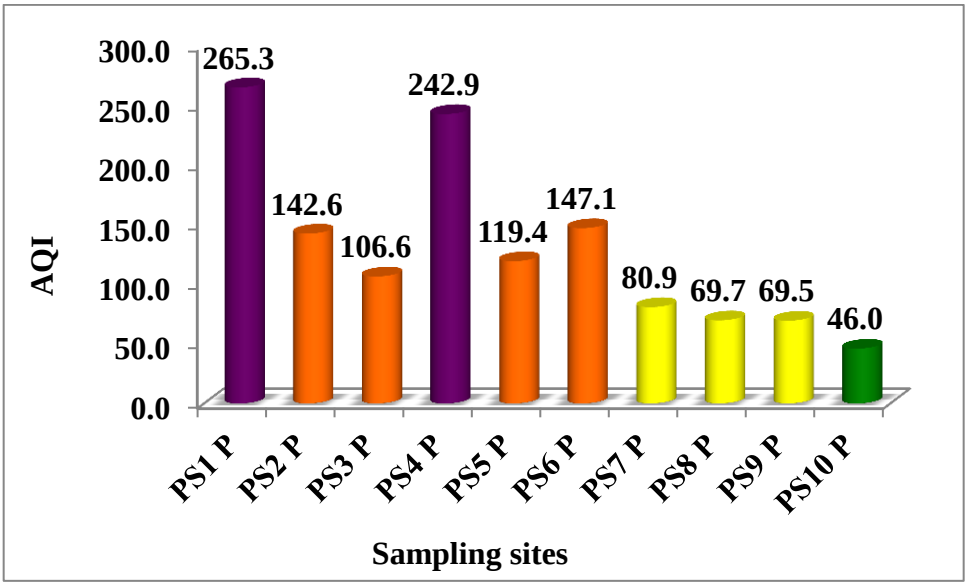

Figure 4.2 Air Quality Index (AQI) of $PM_{2.5}$ in the playgrounds of the primary schools and corresponding AQI color code.

Forty percent of the outdoor sampling sites (4 out of 10 sites with an orange color code) were unsuitable for children in vulnerable groups and would have adverse health effects, but it's unlikely that the general population would be impacted due to exposure to $PM_{2.5}$. The AQI in 20% of the outdoor sampling sites (2 out of 10 sites are with purple color code) were very unhealthy and will cause a health alarm, indicating that there could be further detrimental consequences on everyone's health.

The AQI of PM_{10} in the outdoors of the primary schools is shown in Figure 4.3. Findings of the current study showed that the air quality at 20% of the playgrounds of the schools (2 out of 10 sites with a yellow color code) was acceptable; however, for a very small percentage of people, it might constitute a moderate health issue.

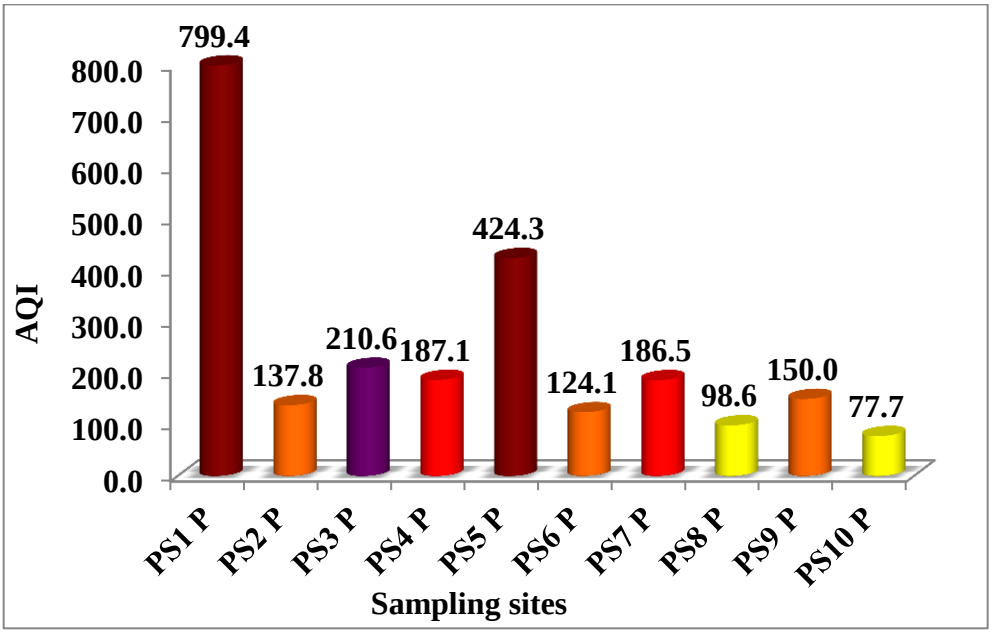

Figure 4.3. Air Quality Index (AQI) of PM_{10} in the playgrounds of the primary schools and corresponding AQI color code.

Thirty percent of the outdoor sampling sites (3 out of 10 sites with an orange color code) were harmful for sensitive groups; the majority of the population is unlikely to be impacted, while members of vulnerable groups might suffer health impacts due to exposure to PM_{10}. The condition of the air in 20% of the playgrounds of the schools (2 out of 10 sites with a red color code) was considered unhealthy; everyone may start to feel the consequences on their health, and people in vulnerable groups might feel the effects more severely. The AQI in 10% of the outdoor sampling sites (1 out of 10 sites with a purple color code) was very unhealthy and will cause a health alert, which means that more serious health problems could happen to everyone. The AQI in 20% of the outdoor sampling sites (2 out of 10 have a maroon color code) was hazardous and will result in emergency health alerts, and there is an even greater chance that major health consequences may impact the entire community due to exposure to PM_{10}.

Figure 4.4 shows the air quality index of NO_2 in the outdoor sampling locations. The results of this study shown that 80% of the outdoor sampling locations (8 out of 10 sites with a green color code) had a good level of air pollution and satisfactory air quality, and there was little or no health risk due to exposure to NO_2. The results of the present study showed that the air quality at 20% of the playgrounds of the schools (2 out of 10 sites with a yellow color code) were acceptable; however, a very small percentage of individuals may find it to be a moderate health risk.

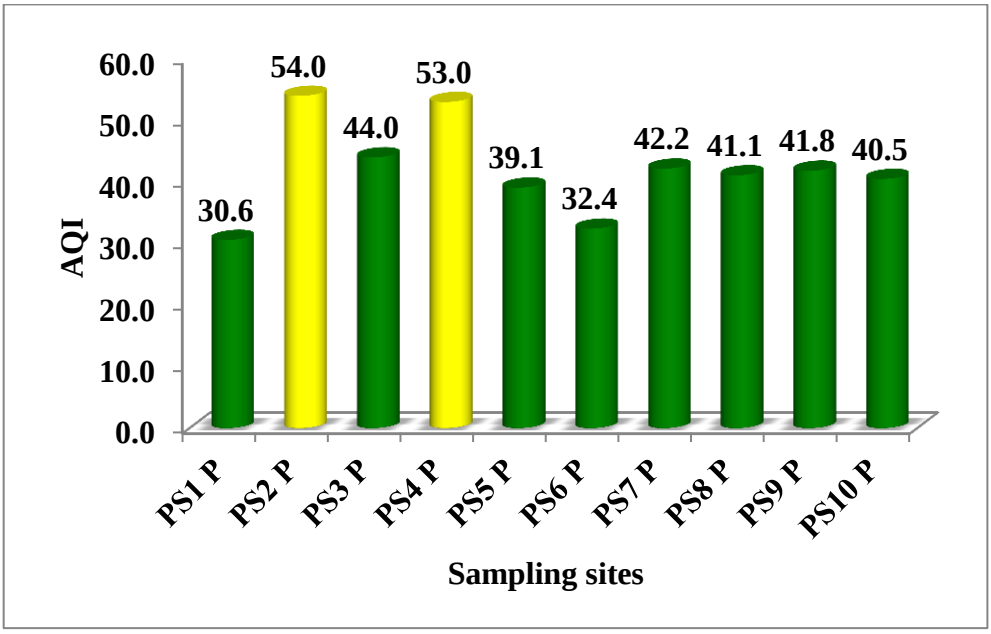

Figure 4.4. Air Quality Index (AQI) of NO_2 in the playgrounds of the primary schools and corresponding AQI color code.

Conclusions and Recommendations

The levels of inorganic gaseous pollutants and particulate matter in both indoor and outdoor environments in primary schools in Hawassa, Ethiopia, were examined in this study. The levels of $PM_{2.5}$ and PM_{10} were found to be above the WHO recommendations in 55% and 85% of sampling sites, respectively. The I/O concentration ratios of $PM_{2.5}$, PM_{10}, and NO_2 were greater than one in 50%, 50%, and 30% of the primary schools, respectively, which revealed that there were possible indoor sources. The Air Quality Index (AQI) at 40% and 30% of the outdoor sampling sites were unhealthy for sensitive groups due to exposure to $PM_{2.5}$ and PM_{10}, respectively. The AQI at 20% of the outdoor sampling sites was very unhealthy and will cause a health alert due to exposure to $PM_{2.5}$. The AQI in 20% of the outdoor sampling sites was hazardous and will result in emergency health alerts, and major health consequences are far more likely to affect the entire community due to exposure to PM_{10}.

Thus, the AQI value and the levels of $PM_{2.5}$ and PM_{10} indicated poor air quality in the schools and suggested a significant health risk for the students and all populations around the schools. Therefore, schools, respective government agencies, and all the relevant bodies should take remedial environmental measures to decrease the levels of $PM_{2.5}$ and PM_{10} in educational settings. The findings of this study will help government bodies and experts increase their efforts to improve the condition of the air in educational settings. The results would also add to the scant data on $PM_{2.5}$ and PM_{10} in developing countries and contribute to future global efforts to minimize air pollution. Based on our study, a policy recommendation to improve air pollution quality could be to implement more stringent regulations on emissions from vehicles and industries. Additionally, investing in green infrastructure and promoting public awareness about the importance of reducing air pollution could also be effective measures to improve the air quality of the schools environments.

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CHAPTER 5. LEVELS AND HEALTH RISK ASSESSMENTS OF PARTICULATE MATTER AND INORGANIC GASEOUS POLLUTANTS IN URBAN AND INDUSTRIAL AREAS OF HAWASSA CITY, ETHIOPIA

ABSTRACT

Air pollution is a main public health concern globally owing to its harmful health effects. However, there is scarce data on concentrations and sources of inorganic gaseous pollutants (NO_2, CO, and SO_2) and particulate matter ($PM_{2.5}$ and PM_{10}) in Ethiopia, particularly Hawassa City. Thus, the goal of this research is to evaluate potential health concerns and determine the indoor and outdoor concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in Hawassa City, Ethiopia's urban and industrial areas. A portable gas monitor device (HoldPeak Laser PM meter, HP 5800D) was used to measure the levels of PM_{10} and $PM_{2.5}$. The Aeroqual Series 500 Portable Air Quality Monitor (Aeroqual Ltd., New Zealand) was used to measure the concentrations of NO_2, CO, and SO_2. The average concentrations of $PM_{2.5}$, PM_{10}, and NO_2 ranged from 8.8–310.7, 20.1–515.8, and 40.0–123.7 μg/m^3, respectively, in the dry season. In the wet season, the ranges for $PM_{2.5}$, PM_{10}, NO_2, and CO levels were 17.2-117.4, 24.3-167.2, 31.8-111.3, and 77-33312 μg/m^3, respectively. For $PM_{2.5}$ and PM_{10}, the hazard quotient (HQ) was greater than one in both the wet and dry seasons, suggesting a non-carcinogenic effect. The $PM_{2.5}$ excess lifetime cancer risk (ELCR) ranged from 0.1 to 0.7, which is greater than the recommended values by the WHO (that ranges from 1×10^{-5} to 1×10^{-6}) and the US EPA (less than 1×10^{-6}). The HQ and ELCR values imply a considerable health risk for the general population.

Keywords: Air quality; particulate matter; inorganic gaseous pollutants; health risks assessment; Ethiopia

5.1 Introduction

The harmful consequences of air pollution on health make it a serious global public health concern. Nitrogen dioxide, sulfur dioxide, carbon monoxide, and particulate matter are among the pollutants that pose a severe risk to public health (Kampa & Castanas, 2008; Keil et al., 2010; WHO, 2023a). Particulate matter ($PM_{2.5}$–PM_{10}) inhalation can trigger a variety of health difficulties in both humans and animals, including birth defects, low birth weight, premature delivery, lung cancer, respiratory diseases, and asthma (Sapkota et al., 2012; WHO, 2023b). Indoor particulate matter can be produced during cooking and combustion activities, including the uses of fireplaces, and kerosene heaters, as well as cigarette smoking (Keil et al., 2010; Van Vliet et al., 2013; US EPA, 2023). Outdoor PM can originate from transportation, various industrial processes, volcanoes, dust storms, and forest fires (US EPA, 2023c).

Cooking fires, combustion of fossil fuel in industries, power generators, and vehicles are the primary producers of inorganic gaseous air pollutants, which include sulfur dioxide (SO_2), carbon monoxide (CO), and nitrogen dioxide (NO_2) (Omidvarborna et al., 2015; Agbo et al., 2021). The respiratory system of humans might experience irritation of the airways due to significant NO_2 exposure. Short-term exposures to SO_2 may damage the human respiratory system. Exposure to CO at low levels causes tiredness in healthy people and chest achy in people with heart disease, and it is lethal at very high levels (Kumie et al., 2009; US EPA, 2021; WHO, 2023c). Air pollution data is limited in most African countries, including Ethiopia. The existing studies in Ethiopia indicate high concentrations of air pollution that exceeded the WHO guidelines (Tefera et al., 2016; Asefa & Mergia, 2022). There is still a scarcity of data on the levels and sources of inorganic gaseous pollutants and particulate matter in most of the African countries, including Ethiopian.

Therefore, the purpose of this study is to investigate the indoor and outdoor concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in the urban and industrial areas of Hawassa City, Ethiopia, in both dry and wet seasons and assess potential health risks. To the best of our knowledge, this study is the first to investigate $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 with broad sampling sites, i.e., the indoor and outdoor of industrial and urban areas, including roadsides, recreational areas, marketplaces, and households in Ethiopia in the dry and wet seasons. The outcomes of this study are vital in supporting the concerned government bodies in raising awareness and stepping up their initiatives to improve the air quality in urban and industrial areas. The results would also add to the scant data on $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2 in developing countries and contribute to future global efforts to minimize air pollution.

5.2 Material and Methods

5.2.1 Description of the study area

The research was conducted at Hawassa, Ethiopia, the capital of the Sidama Regional State, which is located 275 kilometers south of Addis Ababa, the capital of Ethiopia.

Hawassa City's coordinates are 7°3'43.4" N latitude and 38°28.581' E longitude in terms of geology. The two seasons are from November to February for the dry season and from March to October for the wet season (NMA, 2023; Weatherspark, 2023). According to projections from the Ethiopian Statistical Service (ESS), the projected population of Hawassa city is 441536 (ESS, 2023).

5.2.2 Sampling site

Samples were collected from the urban and industrial environments of the city during the dry season between December 10, 2021, and January 19, 2022, and in the wet season between August 1, 2023, and September 10, 2023.

Table 5.1 Description of sampling sites (S = Sampling site)

	Sampling site	Description of the Sampling Locations	Coordinates
Urban areas (Outdoor)	**S1**	Roadside of Main highway road (There were coffee venders making coffee on charcoal stoves at the roadside during sampling in the wet season.)	7°2'57.12"N, 38°29'43.21"E
	S2	Roadside of near a bus station	7°2'52.30"N, 38°29'18.36"E
	S3	Roadside of Turufat road	7°2'30.26"N, 38°28'46.22"E
	S4	Roadside of Piasa Road	7°3'04.76"N, 38°28'23.14"E
	S5	Roadside of Areb sefer Road	7°3'23.85"N, 38°28'36.22"E
	S6	The old market	7°3'26.47"N, 38°28'30.02"E
	S7	Fikir Haike (Lakeside recreational area)	7°3'11.17"N, 38°27'58.56"E
	S8	Amoragedel (Lakeside fish market and recreational area)	7°2'41.01"N, 38°27'23.69"E
Urban areas (Indoor)	**S9**	Household near S1	7°2'58.69"N, 38°29’35.68"E
	S10	Household near S2 (Injera was being baked using biomass wood at all sampling times.)	7°2'56.10"N, 38°29'34.61"E
	S11	Household near S3	7°2'30.27"N, 38°28'43.98"E
	S12	Household near S4	7°3'00.89"N, 38°28'20.40"E
	S13	Household near S5	7°3'22.55"N, 38°28'29.53"E
	S14	Household (Residential with a separate kitchen)	7°2'07.90"N, 38°29'14.72"E
	S15	Household (Residential with a kitchen inside, there was a coffee ceremony using stove during sampling in the wet season)	7°1'49.58"N, 38°29'50.80"E
	S16	Household near S15	7°1'53.96"N, 38°29'48.79"E
Industrial areas (Outdoor)	**S17**	Ambient of Industry 1 (BGI)	7°1'54.11"N, 38°30'32.41"E
	S18	Ambient of Industry 2 (Industrial park)	7°4'22.02"N, 38°29'48.15"E
	S19	Ambient of Industry 3 (Ceramics)	7°4'52.5"N, 38°29'29.16"E
Industrial areas (Indoor)	**S20**	Household near S17	7°1'53.96"N, 38°30'33.90"E
	S21	Household S18	7°4'21.01"N, 38°29'47.46"E
	S22	Household S19	7°4'54.05"N, 38°29'31.29"E

Representative sampling sites were selected purposively from an urban and industrial area, taking into consideration high-traffic roadsides, industries, recreational areas, marketplaces, and households near the selected roadsides and industries. Samples were collected in the wet and dry seasons; the indoor samples were taken from the living rooms of the selected households near roadsides and industries. The outdoor samples were collected from the ambient air near selected industries, roadsides, recreation areas, and a market. The exact sampling site coordinates were obtained using the Global Positioning System (GPS), and the detailed information of sampling locations is described in Table 5.1.

5.2.3 Sampling design and measurement methods

The target pollutants for this study were particulate matter ($PM_{2.5}$ and PM_{10}) and inorganic gaseous pollutants (NO_2, CO, and SO_2). The measurement of the concentrations of $PM_{2.5}$ and PM_{10} was done using a portable gas monitor device called a laser particulate meter (HoldPeak Laser PM meter-HP 5800D, Zhuhai Jida Huapu Instrument Company Limited, China). The range of $PM_{2.5}$ and PM_{10} detection is 0-999.9 $\mu g/m^3$ and 0-1999.9 $\mu g/m^3$, respectively, with a resolution of 0.1 $\mu g/m^3$. The Aeroqual Series 500 Portable Air Quality Monitor (Aeroqual Ltd., New Zealand) was used to measure the concentrations of NO_2, CO, and SO_2. It is a real-time sampler with an electrochemical gas sensor head that is interchangeable. The sampling location coordinates were obtained with a hand-held automated Garmin GPS 72H Global Positioning System (GPS) navigator (Taiwan).

The following parameters were measured from each sampling site: temperature, relative humidity, and the concentrations of NO_2, CO, SO_2, $PM_{2.5}$, and PM_{10} on three separate days (two weekdays and a weekend day) at two moments during the day: in the morning from 7:00 to 12:00 and in the afternoon from 13:30 to 18:30.

Every sampling site underwent a continuous measurement for an hour during these moments, and the concentration shown on the device screen was recorded every three minutes. At the end of each measurement, the mean of the 20 notes was given as the particulate matter and inorganic gaseous pollutant concentrations for each sample site. The indoor measurements were performed in the living room of each household, and the devices were positioned at a height of about 1.5 meters above the ground and 1 meter away from doors and windows. The instruments were placed approximately two meters above the ground for the outdoor measurements.

5.2.4 Risk assessment

5.2.4.1 The cancer risk and non-carcinogenic risk of $PM_{2.5}$ and PM_{10}

The excess lifetime cancer risk and non-carcinogenic risk were estimated according to the risk assessment methodology used by the United States Environmental Protection Agency (US EPA, 2009; Heydari et al., 2019; Sun & Zhou, 2017; Yunesian et al., 2019). ELCR was computed using Equation (5.1) (US EPA, 1989; Yunesian et al., 2019; Cipoli et al., 2023).

$$\mathrm{ELCR} = \mathrm{LADD} \times \mathrm{SF} \qquad (5.1)$$

In this case, SF is the slope factor (kg day μg^{-1}), LADD is the lifetime average daily dose (μg kg^{-1} day^{-1}), and ELCR is the excess lifetime cancer risk.

LADD was computed by using Equation (5.2) (Heydari et al., 2019; Yunesian et al., 2019).

$$\mathrm{LADD} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{AT} \times \mathrm{BW}} \qquad (5.2)$$

In this case, BW is body weight (kg), AT is average exposure time (days), ED is exposure duration (years), EF is exposure frequency (days/year), IR is inhalation rate (m^3/day), and C is the pollutant concentration ($\mu g/m^3$).

The SF value of every contaminant is available through the USEPA's IRIS (Integrated Risk Information System). However, if the exact value of SF is not present, Equation (5.3) is used as described in (Greene & Morris, 2006).

$$SF = \frac{UR \times BW}{IR} \qquad (5.3)$$

Where, UR stands for unit risk $(\mu g/m^3)^{-1}$, IR is for inhalation rate (m^3/day), and SF (kg day μg^{-1}) is the slope factor.

Equation (5.4) was used to estimate the risk assessment for the non-carcinogenic risk using the hazard quotient (HQ), which is the ratio of LADD to the reference dose (RfD) (Heydari et al., 2019; Yunesian et al., 2019; Cipoli et al., 2023).

$$HQ = \frac{LADD}{RfD} \qquad (5.4)$$

Where RfD is the reference dose (μg kg^{-1} day^{-1}) and RfD = RfC (inhalation reference concentration μg /m^3) × Assumed inhalation rate (m^3/day) × 1 / BW (kg). The HQ stands for hazard quotient. LADD is the lifetime average daily dose (μg kg^{-1} day^{-1}) (Equation (5.2)).

A 1.0 HQ is considered the standard for safety. A HQ of less than 1.0 denotes a small or nonexistent danger. Modest concerns exist when the HQ values fall between 1.1 and 10. There are significant hazards present when the HQ values are higher than 10 (US EPA, 1989; Lina Thabethe et al., 2014; Heydari et al., 2019;Yunesian et al., 2019). Table 5.2 lists the parameters that were applied to this study's health risk estimation.

Table 5.2 Risk parameters used for calculating HQ and ELCR for $PM_{2.5}$ and PM_{10} in indoor and ambient air

Parameters	**Adults**	**Reference:**
Inhalation rate (m^3/day)	20	(US EPA, 2011)
Body weight (kg)	60.7	(Walpole et al., 2012)
Exposure duration (year)	50	(US EPA, 2011)
Exposure frequency (day/year)	365	(US EPA, 2011)
Averaging time (day) for		
- Non-carcinogens	18,250	
- Carcinogens	25550	
Unit risk (UR)	0.008 (μg/m^3)$^{-1}$ for $PM_{2.5}$	(Greene & Morris, 2006)
Inhalation reference concentration (RfC)	10 μg/m^3 for $PM_{2.5}$	
	20 μg/m^3 for PM_{10}	(WHO, 2021)

RfD = RfC (inhalation reference concentration μg/m^3) × Assumed inhalation rate (m^3/day) × 1 / BW (kg); Slope factor or carcinogenic potency slope (SF) = (BW × UR)/IR; Averaging time (days) for carcinogens = 70 years × 365 days per year, for carcinogens = ED × 365 days per year; BW for RfD and SF = 70kg

5.2.4.2 Air quality index (AQI) of NO_2 and CO

The air quality index (AQI) is an indicator of the quality of the ambient air. Air pollution levels and associated health risks increase with increasing AQI values (US EPA, 2023a). The AQI for NO_2 and CO at the outdoor sampling sites was calculated. The AQI for each pollutant were derived using Equation (5.5), as described in (Kasim et al., 2018a; Mopa Wambebe & Duan, 2020; ACT Government, 2022). The WHO guidelines (1 hour averaging time) used for this calculation was for NO_2 (200 µg/m^3) and for CO (35000 µg/m^3) (WHO, 2021).

$$AQI_{Pollutant} = \frac{Pollutnat\ Concentration}{WHO\ Standard} \times 100 \qquad (5.5)$$

The six levels of AQI and health concern are presented in Table 5.3, and they were taken from the USEPA (USEPA, 2020) and described as follows:

Level 1 air pollution is considered to have satisfactory air quality as it poses minimal risk to human health. Level 2 pollution is deemed acceptable, but small number of individuals may perceive it as a moderate health concern.

Table 5.3 The six levels of AQI, health concern, and break point concentrations of NO_2 and CO (US EPA, 2020)

Air Quality Index (AQI) Values	Levels of Health Concern	NO_2 (µg/m^3)	CO (ppm)	Colors	Air pollution level
0 to 50	Good	0–53	0–4.4	Green	Level 1
51 to 100	Moderate	54–100	4.5–9.4	Yellow	Level 2
101 to 150	Unhealthy for Sensitive Groups	101–360	9.5–12.4	Orange	Level 3
151 to 200	Unhealthy	361–649	12.5–15.4	Red	Level 4
201 to 300	Very Unhealthy	650–1249	15.5–30.4	Purple	Level 5
301 to 500	Hazardous	1250–2049	30.5–50.4	Maroon	Level 6

Level 3 is labeled as unhealthy for sensitive groups, with the general population less likely to be affected, but individuals from sensitive groups may experience health issues. Level 4 is classified as unhealthy, with potential health consequences for anyone and more severe effects on vulnerable groups. Level 5 is extremely harmful, triggering a health alert and leading to more severe health impacts for everyone. Level 6 poses a public health risk, resulting in emergency situations and health alerts, with a higher likelihood of serious health repercussions for the entire population.

5.2.5 Statistical analysis

Both Microsoft Excel and IBM SPSS (Version 25) were used for the statistical data analysis. Using the Shapiro-Wilks test, the data's normality was tested. The data for all pollutants in the dry and wet seasons were not normally distributed except for the data on NO_2 in the rainy season. Therefore, the NO_2 concentration data was tested for homogeneity using Levene's test, and the result showed a lack of homogeneity. Consequently, a post-hoc test was conducted after the independent sample Kruskal-Wallis test to assess statistical differences in the measured concentration levels. The correlation coefficients between temperature, relative humidity, NO_2, CO, $PM_{2.5}$, PM_{10}, and NO_2 were determine using Spearman's rho correlation.

5.3 Results and Discussion

5.3.1 Concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, and SO_2

In this study, temperature and relative humidity, as well as the concentrations of $PM_{2.5}$, PM_{10}, SO_2, NO_2, and CO, were measured in urban and industrial areas in the rainy and dry seasons. The arithmetic mean concentrations of $PM_{2.5}$, PM_{10}, NO_2, CO, SO_2, and values of temperature and relative humidity in all sampling sites during dry and wet seasons are given in Table 5.4.

The percentiles P25 and P75 of $PM_{2.5}$, PM_{10}, NO_2, CO, temperature, and relative humidity are shown in Supplementary Table S8. $PM_{2.5}$, PM_{10}, and NO_2 were detected during both seasons and at all sampling sites. Carbon monoxide was detected during the wet season but not detected at all during the dry season at any of the sites. SO_2 was detected only at site S17 during both studied seasons.

Table 5.4 Arithmetic mean concentration ($\mu g/m^3$) values of $PM_{2.5}$, PM_{10}, NO_2, CO, SO_2, temperature (T), and relative humidity (RH) in all sampling locations during the dry and wet seasons

	Dry season							**Wet season**						
Sampling site	**$PM_{2.5}$**	**PM_{10}**	**NO_2**	**CO**	**SO_2**	**T (°C)**	**RH (%)**	**$PM_{2.5}$**	**PM_{10}**	**NO_2**	**CO**	**SO_2**	**T (°C)**	**RH (%)**
S1	25.3	57.5	93.0	ND	ND	30.0	31.1	87.2	115.4	88.0	2695	ND	20.8	69.3
S2	43.5	85.3	104.0	ND	ND	29.2	34.3	44.1	85.5	31.8	77	ND	21.5	64.7
S3	25.3	40.0	94.7	ND	ND	30.3	30.7	49.1	74.7	111.3	7948	ND	21.3	64.3
S4	14.3	35.2	101.2	ND	ND	29.7	28.4	26.6	35.7	83.0	1632	ND	23.5	60.3
S5	17.4	33.5	99.0	ND	ND	29.8	30.6	28.3	59.7	81.7	475	ND	21.5	64.5
S6	20.7	60.2	92.3	ND	ND	29.4	30.8	40.4	75.0	95.2	1637	ND	20.7	65.8
S7	8.8	20.1	51.8	ND	ND	30.2	29.4	25.3	37.2	68.2	ND	ND	21.5	64.2
S8	10.0	33.4	65.0	ND	ND	30.2	30.3	17.2	24.3	82.5	1350	ND	22.3	60.0
S9	32.6	79.4	62.8	ND	ND	28.5	35.2	117.1	159.1	79.7	271	ND	20.5	69.0
S10	310.7	515.8	64.3	ND	ND	28.9	38.0	113.3	131.8	75.2	138	ND	21.0	67.2
S11	17.5	36.4	92.0	ND	ND	28.5	36.3	64.9	92.5	86.7	8920	ND	20.7	66.5
S12	21.0	70.5	71.0	ND	ND	29.0	34.4	98.8	167.5	71.7	299	ND	22.5	64.3
S13	44.9	108.4	59.7	ND	ND	27.4	34.9	91.8	135.3	59.3	888	ND	22.5	61.8
S14	21.7	40.8	40.0	ND	ND	27.5	36.0	112.0	151.4	62.3	370	ND	21.8	55.2
S15	60.2	132.4	54.0	ND	ND	28.8	34.4	117.4	189.7	50.0	1495	ND	21.0	66.7
S16	34.8	75.7	76.5	ND	ND	28.5	34.9	100.5	167.2	57.8	493	ND	22.5	62.8
S17	142.5	270.0	80.3	ND	9.0	26.9	31.8	22.6	37.0	66.2	33312	16.7	20.3	68.3
S18	23.7	89.6	123.7	ND	ND	29.0	30.8	30.8	42.5	41.2	11974	ND	20.8	70.0
S19	22.7	105.7	99.6	ND	ND	30.2	24.3	27.4	93.6	35.3	16143	ND	21.3	67.0
S20	78.3	129.6	68.2	ND	ND	28.4	31.3	107.2	128.8	62.3	11336	ND	21.0	68.7
S21	32.8	148.9	92.3	ND	ND	30.0	30.0	63.3	90.7	45.5	11728	ND	21.0	69.8
S22	19.8	55.0	64.8	ND	ND	28.1	32.0	47.1	138.0	51.2	1489	ND	21.5	67.7

The levels of $PM_{2.5}$, PM_{10}, and NO_2 in the dry season in all sampling sites ranged from 8.8–310.7, 20.1–515.8, and 40.0–123.7 μg/m^3, respectively. The concentration of $PM_{2.5}$ in the dry season in the urban outdoors ranged from 8.8–43.5 μg/m^3, which was similar to the concentrations of $PM_{2.5}$ (20.1–41.2 μg/m^3) at roadsides in Addis Ababa (Embiale et al., 2019a) and 28.3–35.1 μg/m^3 in the Megenagna area in Addis Ababa (Bizualem et al., 2023). However, it was lower than the daily $PM_{2.5}$ concentration (19.1–127.0 μg/m^3) in the city center of Addis Ababa (Tefera et al., 2020) and the $PM_{2.5}$ concentration (39.6–85.3 μg/m^3) at roadside in Addis Ababa, Ethiopia (Jida et al., 2021). The PM_{10} level in the dry season in the urban outdoors ranged 20.1–85.3 μg/m^3 which was comparable with the mean of PM_{10} (54.4–65.8 μg/m^3) in the Megenagna area of Addis Ababa (Bizualem et al., 2023). However, it was lower than the GM of PM_{10} (148–300 μg/m^3) at roadsides in Addis Ababa (Embiale et al., 2019a) and PM_{10} concentration (54.2–247.4 μg/m^3) at roadside vehicles in Addis Ababa, Ethiopia (Jida et al., 2021). The NO_2 level in the dry season in the outdoor urban area was ranged from 51.8–104.0 μg/m^3.

The levels of $PM_{2.5}$, PM_{10}, and NO_2 in the dry season in indoor urban areas ranged from 21.0–310.7, 36.4–515.8, and 40.0–92.0 μg/m^3 respectively. The findings of this investigation have shown that the highest concentrations of $PM_{2.5}$ (310.7 μg/m^3) and PM_{10} (515.8 μg/m^3) in S10 (a residential house) pose a major risk to health. During all the sampling times, Injera (a staple food in many parts of Ethiopia) was being baked using biomass wood in a separate kitchen close to the living room. The reason for the higher concentrations of $PM_{2.5}$ and PM_{10} in S10 may be due to the baking of Injera using biomass wood, as indicated by Embiale et al. (2021). These authors reported $PM_{2.5}$ concentrations of 174±2.9 μg/m^3 and PM_{10} of 594±2.5 μg/m^3 in the dry season during baking Injera using a traditional stove (Embiale et al., 2021).

The lowest levels of $PM_{2.5}$ (8.8 μg/m^3) and PM_{10} (20.1 μg/m^3) in this study were measured at S7, which is a recreation area. The concentration of $PM_{2.5}$, PM_{10}, and NO_2 in the dry season in the outdoor industrial ranged from 22.7–142.5, 89.6–270.0, and 80.3–123.7 μg/m^3, respectively. The concentration range of $PM_{2.5}$ (22.7–142.5 μg/m^3) in the dry season at outdoor industrial area reported in this study was consistent with the ambient $PM_{2.5}$ concentration (27.8–75.9 μg/m^3) reported within the range of 400–800 meters of at Mugher Cement Factory in Ethiopia (Mekasha et al., 2018). Furthermore, it was also comparable with 50.1–96.8 μg/m^3 of $PM_{2.5}$ in industries and main transportation stations in the city of Addis Ababa, Ethiopia (Bikis, 2023).

The levels of $PM_{2.5}$, PM_{10}, and NO_2 in the dry season in the indoor industrial ranged from 19.8–78.3, 55.0–148.9, and 64.8–92.3 μg/m^3, respectively. The World Health Organization's (WHO) 24-hour and annual mean guidelines for $PM_{2.5}$ and PM_{10} are 25 and 10 μg/m^3 and 50 and 20 μg/m^3, respectively (WHO, 2020). The findings of this study have shown that the $PM_{2.5}$ concentrations in the dry season in 50% of the sampling sites were above the WHO 24-hour mean guidelines for $PM_{2.5}$ (25 μg/m^3). The concentrations of PM_{10} were above WHO 24-hour mean guidelines for PM_{10} (50 μg/m^3) in 68.2% of sampling sites; this might pose a major risk to the local community in the study area.

The normality of the $PM_{2.5}$, PM_{10}, and NO_2 concentration data during the dry season was tested using the Shapiro-Wilks test. For every pollutant during the dry season, the data were not normally distributed. Consequently, the Kruskal-Wallis sample test was applied to the $PM_{2.5}$, PM_{10}, and NO_2 data in all the sampling sites during the dry season. The results revealed that there were significant differences in the levels of $PM_{2.5}$, PM_{10}, and NO_2 across all sampling sites ($p < 0.000$). It doesn't, however, specify the location of this difference.

Therefore, a pair comparison between the sampling sites was made using a post hoc test, and significance values have been adjusted by the Bonferroni correction. The results for $PM_{2.5}$ data from the post hoc test revealed that there were significant differences ($P \leq 0.038$) in 12 pairwise comparisons (i.e., S7 vs. S20; S7 vs. S21; S7 vs. S17; S7 vs. S10; S8 vs. S20; S8 vs. 21; S8 vs. S17; S8 vs. S10; S4 vs. S17; S4 vs. S10; S15 vs. S10; S5 vs. S10). Likewise, the results for PM_{10} data from the post hoc test revealed that there were significant differences ($P \leq 0.028$) in 15 pairwise comparisons (i.e., S7 vs. S17; S7 vs. S10; S7 vs. S20; S7 vs. S19; S11 vs. S10; S7 vs. S21; S5 vs. S17; S5 vs. S10; S4 vs. S17; S4 vs. S10; S8 vs. S10; S8 vs. S17; S11 vs. S17; S16 vs. S10; S3 vs. S10). Further more, the results for NO_2 data from the post hoc test shown that there were significant differences ($P \leq 0.000$) in seven pairwise comparisons (i.e., S16 vs. S11; S16 vs. S5; S16 vs. S19; S16 vs. S2; S16 vs. S18; S7 vs. S18; S12 vs. S18).

The levels of $PM_{2.5}$, PM_{10}, NO_2, and CO in the wet season ranged from 17.2–117.4, 24.3–167.2, 31.8–111.3, and 77–33312 μg/m^3, respectively (Table 5.4). The levels of $PM_{2.5}$, PM_{10}, NO_2, and CO in the wet season in the outdoor urban area ranged from 17.2–87.2, 24.3–115.4, 31.8–111.3, and 77–7948 μg/m^3, respectively. The concentrations of $PM_{2.5}$ and PM_{10} found in this study were comparable with the concentrations of $PM_{2.5}$, which varied from 15.30 to 70.20 μg/m^3, and PM_{10}, which varied from 16.3 to 77.5 μg/m^3 in Abuja Municipal Area, Nigeria (Mopa Wambebe & Duan, 2020). The concentrations of $PM_{2.5}$, PM_{10}, NO_2, and CO in the wet season in the indoor urban ranged from 64.9–117.4, 92.5–189.7, 50.0–86.7, and 138–8920 μg/m^3, respectively. The results of the present study have shown a higher concentration of $PM_{2.5}$ (117.4 μg/m^3) and PM_{10} (189.7 μg/m^3) in S15 (a residential house with a kitchen inside), which may pose a major risk to health.

S15 is a residential house with a kitchen inside, and there was a coffee ceremony during the measurement, which may be the main reason for the higher concentration of PM_{10}, as also reported in Addis Ababa homes during coffee ceremonies (Keil et al., 2010). The lower concentrations of $PM_{2.5}$ (17.2 μg/m^3) and PM_{10} (24.3 μg/m^3) were measured at S8, which is a recreation area. Likewise, the concentrations of $PM_{2.5}$, PM_{10}, NO_2, and CO in the wet season in the outdoor industrial area ranged from 22.6–30.8, 37.0–93.6, 35.3–66.2, and 11974–33312 μg/m^3, respectively.

The level of $PM_{2.5}$ in the wet season in the indoor industrial area ranged from 47.1–107.2 μg/m^3, which is greater than the concentration of $PM_{2.5}$ (12.9–27.3 μg/m^3) in living rooms in Addis Ababa (Embiale et al., 2022). The level of PM_{10} in the wet season in the indoor industrial area ranged from 90.7–138.0 μg/m^3, which was comparable with concentrations of PM_{10} ranging from 57.7–108 μg/m^3 in living rooms in Addis Ababa (Embiale et al., 2022). The findings of the current study revealed that in 90.9% of the sampling sites, the $PM_{2.5}$ levels during the wet season exceeded the WHO 24-hour mean guidelines for $PM_{2.5}$ (25 μg/m^3).

In 77.3% of sampling sites, the PM_{10} concentrations were above the WHO 24-hour mean guidelines for PM_{10} (50 μg/m^3), suggesting a potential significant risk to the surrounding population.

The normality of the concentration data of $PM_{2.5}$, PM_{10}, CO, and NO_2 throughout the rainy season was examined using the Shapiro-Wilks test. The result from the Shapiro-Wilks test indicated that the concentration data for NO_2 was normally distributed; however, the data were not normally distributed for $PM_{2.5}$, PM_{10}, and CO. Therefore, the concentration data of NO_2 was tested for homogeneity using Levene's test, and the result showed a lack of homogeneity.

Therefore, the Kruskal-Wallis sample test was applied to the $PM_{2.5}$, PM_{10}, NO_2, and CO data in all the sampling sites during the wet season, and the results revealed that there was no significant difference in the concentration of CO across all sampling sites ($p \leq 0.832$). However, there were significant differences in the concentrations of $PM_{2.5}$, PM_{10}, and NO_2 across all sampling sites ($p < 0.000$). However, it does not indicate where this difference occurred. Therefore, a pair comparison between the sampling sites was carried out using a post hoc test, and significance values have been adjusted by the Bonferroni correction. The results for $PM_{2.5}$ data from the post hoc test indicated that there were significant differences ($P \leq 0.036$) in 10 pairwise comparisons (i.e., S8 vs. S12; S8 vs. S1; S8 vs. S20; S8 vs. S15; S8 vs. S9; S8 vs. 14; S8 vs. S10; S17 vs. S9; S17 vs. S14; S17 vs. S10). The post hoc test results for PM_{10} data also revealed significant differences ($P \leq 0.038$) in nine pairwise comparisons (i.e., S8 vs. S20; S8 vs. S22; S8 vs. S10; S8 vs. S9; S8 vs. S16; S8 vs. S15; S8 vs. S14; S4 vs. S15; S4 vs. S14). The post hoc test results for NO_2 data also revealed significant differences ($P \leq 0.001$) in nine pairwise comparisons (i.e., S2 vs. S6; S2 vs. S3; S19 vs. S6; S19 vs. S3; S18 vs. S6; S18 vs. S3; S21 vs. S3; S15 vs. S3; S22 vs. S3).

As shown in Table 5.4, the concentration of $PM_{2.5}$ level at 90.9% of the sampling sites was found to be higher in the wet season. A similar trend of $PM_{2.5}$ concentration was reported in the city center of Addis Ababa (Tefera et al., 2020). The concentration of PM_{10} level at 77.3% of the sampling sites was found to be higher in the wet season. The concentration of NO_2 was higher in the dry season for most of (63.6%) the sampling sites. Table 5.5 depicts that the overall arithmetic mean of $PM_{2.5}$, $PM_{10,}$ and NO_2 in indoor urban areas in the dry season was 67.9, 132.4, and 65.0 $\mu g/m^3$, and in outdoor urban areas it was 20.7, 45.7, and 87.6 $\mu g/m^3$, respectively.

Similarly, the overall mean of $PM_{2.5}$, PM_{10}, and NO_2 in indoor industrial areas in the dry season was 43.6, 111.2, and 75.1 µg/m^3, and in outdoor industrial areas it was 63.0, 155.1, and 101.2 µg/m^3. The findings of the present study (Table 5.5) for $PM_{2.5}$ in the dry season in indoor urban (67.9 µg/m^3) and industrial (43.6µg/m^3) areas were comparable with the concentration of $PM_{2.5}$ (57.2±1.89) in Addis Ababa using charcoal in the dry season (Embiale et al., 2019b). However, it was greater than the concentration of $PM_{2.5}$ (18.1 µg/m^3) in living rooms in Addis Ababa, Ethiopia (Embiale et al., 2022) and the concentration of $PM_{2.5}$ 39.2±2.48 and 26.4±2.02 µg/m^3 in households using kerosene and electricity, respectively, in the dry season in indoor Addis Ababa, Ethiopia (Embiale et al., 2019b).

Table 5.5 Overall arithmetic mean (µg/m^3) of $PM_{2.5}$, PM_{10}, NO_2, CO, SO_2, temperature (T), and relative humidity (RH)

	Dry season					Wet season					
	$PM_{2.5}$	PM_{10}	NO_2	T (°C)	RH (%)	$PM_{2.5}$	PM_{10}	NO_2	CO	T (°C)	RH (%)
Urban outdoor	20.7	45.7	87.6	29.8	30.7	39.8	63.4	80.2	1976.8	21.6	64.1
Urban indoor	67.9	132.4	65.0	28.4	35.5	102.0	149.3	67.8	1609.4	21.6	64.2
Industrial outdoor	63.0	155.1	101.2	28.7	29.0	26.9	57.7	47.6	20476.4	20.8	68.4
Industrial indoor	43.6	111.2	75.1	28.8	31.1	72.5	119.1	53.0	8184.1	21.2	68.7

The concentration of PM_{10} in the dry season in indoor urban (132.4 µg/m^3) and industrial (111.2 µg/m^3) was greater than the concentration of PM_{10} (80.2 µg/m^3) in living rooms in Addis Ababa, Ethiopia (Embiale et al., 2022). However lower than the concentrations of the PM_{10} 144±1.87, 152±1.87, and 222±1.62 µg/m^3 in households using electricity, kerosene, and charcoal, respectively, in the dry season in indoor Addis Ababa, Ethiopia (Embiale et al., 2019b).

The findings of the present study for $PM_{2.5}$ and PM_{10} in the dry season in outdoor urban areas (20.7 μg/m^3 and 45.7 μg/m^3), respectively, were analogous with the concentrations of $PM_{2.5}$ (30.3±2.2 μg/m^3) and PM_{10} (58.6±3.1 μg/m^3) in the Megenagna area in Addis Ababa (Bizualem et al., 2023). The average concentrations of $PM_{2.5}$ and PM_{10} in the present study in the dry season in the outdoor industrial area were 63.0 μg/m^3 and 155.1 μg/m^3, respectively. The concentrations of $PM_{2.5}$ (63.0 μg/m^3) were comparable with the average concentrations of $PM_{2.5}$, 51.5 and 23.6 μg/m^3 in the cities of Beijing and Addis Ababa, respectively, but lower than 107.1 μg/m^3 in New Delhi (Bulto & Berkessa, 2022). The overall arithmetic mean of $PM_{2.5}$, PM_{10}, NO_2, and CO in indoor and outdoor in urban and industrial areas in the wet season is presented in Table 5.5.

The concentrations of $PM_{2.5}$ in indoor urban areas in the wet season was 102 μg/m^3, which was greater than the concentrations of $PM_{2.5}$, 25.8±2.18, 25.4±1.70, and 45.1±2.25 μg/m^3 in households using electricity, kerosene, and charcoal, respectively, in the wet season in indoor Addis Ababa, Ethiopia (Embiale et al., 2019b). The concentrations of $PM_{2.5}$ (102.0 μg/m^3) and PM_{10} (149.3 μg/m^3) in indoor urban areas in this study were comparable with the $PM_{2.5}$ (83.31 μg/m^3) and PM_{10} (103.71 μg/m^3) in the living room in Abuja, Nigeria (Abulude et al., 2022). However, the $PM_{2.5}$ and PM_{10} concentrations in the current study were lower than the mean concentrations of $PM_{2.5}$ (344.03 ± 21.7 μg/m^3) and PM_{10} (752.8 ± 52.3 μg/m^3) for households using biomass fuel in Jimma, Ethiopia (Addisu et al., 2021). The PM_{10} (149.3 μg/m^3) in indoor urban areas in the wet season in this study was comparable with the concentrations of the PM_{10}, 91.8±2.21, 102±1.64, and 151±2.17, in households using electricity, kerosene, and charcoal, respectively, in the wet season in indoor Addis Ababa, Ethiopia (Embiale et al., 2019b).

The $PM_{2.5}$ and PM_{10} in outdoor urban areas in the wet season were 39.8 and 63.4 µg/m^3, respectively. The concentration of $PM_{2.5}$ (39.8 µg/m^3) in the outdoor urban area of the present study was lower than the mean daily concentration of $PM_{2.5}$ (53.8 ±25.0 µg/m^3) in the city center of Addis Ababa (Tefera et al., 2020). The overall mean of $PM_{2.5}$ and PM_{10} in indoor industrial areas in the wet season was 72.5 and 119.1 µg/m^3, and in outdoor industrial areas it was 26.9 and 57.7 µg/m^3, respectively. The concentrations of NO_2 (80.2 µg/m^3) and CO (1976.8 µg/m^3) in the outdoor urban area of the current study were less than the concentrations of NO_2 (120 µg/m^3) and CO (4820 µg/m^3) in the ambient of Addis Ababa city (Tsegaye et al., 2019) and the concentrations of CO (3350 µg/m^3) and NO_2 (130 µg/m^3) in Dire Dawa, Ethiopia (Kasim et al., 2018).

The indoor-to-outdoor (I/O) ratio of the concentrations of $PM_{2.5}$, PM_{10}, NO_2, and CO in dry and wet seasons is indicated in Table 5.6. The I/O concentration ratio was calculated by dividing the concentrations of $PM_{2.5}$, PM_{10}, NO_2, and CO in each house near the roadside by concentrations in each roadside and concentrations in each house near the industries by concentrations in the ambient of each industry. The I/O concentration ratio of $PM_{2.5}$ and PM_{10} in S10 (a residential house near Roadside 2) was 7.1 and 6.0, respectively. This revealed that there were possible indoor sources and other outdoor sources (a kitchen) of $PM_{2.5}$ and PM_{10} in addition to traffic roadside sources. The results of the I/O ratio of $PM_{2.5}$ and PM_{10} in dry (62%) and wet (100%) seasons were greater than one, suggesting the presence of indoor sources. All the values of the I/O ratio of NO_2 in the dry season were less than or equal to one, 62% of the results in the wet season were less than one, and 50% of the I/O ratio of CO was less than one. This indicates that NO_2 and CO originated from outdoor sources.

Table 5.6 The I/O ratio of the arithmetic mean concentration (μg/m^3) of $PM_{2.5}$, PM_{10}, NO_2, and CO in dry and wet seasons at urban and industrial sampling sites

Sampling site		I/O ratio in dry season			I/O ratio in wet season			
		$PM_{2.5}$	PM_{10}	NO_2	$PM_{2.5}$	PM_{10}	NO_2	CO
Urban	S9/S1	1.3	1.4	0.7	1.3	1.4	0.9	0.1
	S10/S2	7.1	6.0	0.6	2.6	1.5	2.4	1.8
	S11/S3	0.7	0.9	1.0	1.3	1.2	0.8	1.1
	S12/S4	1.5	2.0	0.7	3.7	4.7	0.9	0.2
	S13/S5	2.6	3.2	0.6	3.2	2.3	0.7	1.9
Industrial	S20/S17	0.5	0.5	0.8	4.7	3.5	0.9	0.3
	S21/S18	1.4	1.7	0.7	2.1	2.1	1.1	1.0
	S22/19	0.9	0.5	0.7	1.7	1.5	1.4	0.1

5.3.2 Correlation of air pollutants with meteorological data

The correlation between $PM_{2.5}$, PM_{10}, and NO_2 concentration, temperature, and relative humidity in the dry season was assessed (Supplementary Table S9). According to the results of Spearman's rho correlation, the correlation between $PM_{2.5}$ and PM_{10} concentrations was found to be a positive statistically significant correlation ($r = 0.784$, p-value =0.01). There was no statistically significant correlation between $PM_{2.5}$ and temperature and relative humidity or between PM_{10} and temperature and relative humidity. Furthermore, there was no statistically significant correlation between NO_2 and $PM_{2.5}$ or between NO_2 and PM_{10}. There was positive correlation between NO_2 and temperature ($r= 0.189$, p-value =0.05) and negative correlation between NO_2 and relative humidity ($r=-0.175$, p-value = 0.05). Temperature was negatively correlated with relative humidity ($r = -0.718$, p-value = 0.01).

The correlation between $PM_{2.5}$, PM_{10}, NO_2, and CO concentration, temperature, and relative humidity in the wet season is indicated in Supplementary Table S10. The results of Spearman's rho correlation in the wet season show that the correlation between $PM_{2.5}$ and PM_{10} concentrations was found to be a positive statistically significant correlation (r = 0.898, p-value =0.01). There was no statistically significant correlation between $PM_{2.5}$ and temperature or relative humidity. However, there is a significant correlation between PM_{10} and relative humidity (r = 0.184, p-value = 0.05). Temperature was negatively correlated with relative humidity (r = -0.888, p-value = 0.01). There was no significant correlation of the concentrations of CO and NO_2 with the other variables.

5.3.3 Potential human health risk of detected pollutants

5.3.3.1 The cancer and non-carcinogenic risks of exposure to $PM_{2.5}$ and PM_{10}

By calculating the excess lifetime cancer risk as well as the non-carcinogenic risk, this study evaluated the health concerns related to $PM_{2.5}$ and PM_{10} exposure. The excess lifetime cancer risk (ELCR) was computed using Equation (5.1), the lifetime average daily dose (LADD) (μg kg^{-1} day^{-1}) using Equation (5.2), and the hazard quotient (HQ) using Equation (5.4). The USEPA advises against using ELCR values lower than 1×10^{-6}, while the World Health Organization (WHO) considered values between 1×10^{-5} and 1×10^{-6} to be tolerable for humans (US EPA, 2009; Baghani et al., 2018; Heydari et al., 2019). The HQ for $PM_{2.5}$ and PM_{10} indoors and outdoors in urban and industrial areas in the dry and wet seasons were greater than one (Table 5.7), which implies the likelihood of the non-carcinogenic impact occurring. An analogous outcome was reported when utilizing charcoal fuel alone; given that the HQ value of PM_{10} was greater than one, it seems probable that the individual cooking would suffer from detrimental health effects (Embiale et al., 2019b).

Similar results have been reported at roadsides at Addis Ababa HQ for $PM_{2.5}$ and PM_{10}, which showed a value larger than one, suggesting that exposure to $PM_{2.5}$ and PM_{10} could cause health issues (Embiale et al., 2019a). Furthermore, ELCR $PM_{2.5}$ in indoor and outdoor urban and industrial areas ranged from 0.1 to 0.4 in the dry season and from 0.2 to 0.7 in the wet season (Table 5.7), which is greater than the recommended values by the WHO (ranging from 1×10^{-5} to 1×10^{-6}) and the USEPA (less than 1×10^{-6}). This ELCR value of $PM_{2.5}$ implies a significant risk for the general population.

Table 5.7 Overall Arithmetic mean of $PM_{2.5}$, PM_{10}, LADD (μg kg^{-1} day^{-1}) and HQ of $PM_{2.5}$ and PM_{10} and ELCR $PM_{2.5}$ in indoor and outdoor urban and industrial areas in the dry and wet season

		$PM_{2.5}$	PM_{10}	LADDPM2.5	LADDPM10	HQPM2.5	HQPM10	ELCRPM2.5
Dry Season	Urban outdoor	20.7	45.7	6.8	15.0	2.4	2.6	0.1
	Urban indoor	67.9	132.4	22.4	43.6	7.8	7.6	0.4
	Industrial outdoor	63.0	155.1	20.7	51.1	7.3	9.0	0.4
	Industrial indoor	43.6	111.2	14.4	36.6	5.0	6.4	0.3
Wet Season	Urban outdoor	39.8	63.4	13.1	20.9	4.6	3.7	0.3
	Urban indoor	102.0	149.3	33.6	49.2	11.7	8.6	0.7
	Industrial outdoor	26.9	57.7	8.9	19.0	3.1	3.3	0.2
	Industrial indoor	72.5	119.1	23.9	39.3	8.4	6.9	0.5

5.3.3.2 Air quality index of NO_2 and CO

The WHO standards for CO (35000 μg/m^3) and NO_2 (200 μg/m^3), as well as the mean concentration in Table 5.4, were used to calculate the AQI pollutant value. Equation (5.5) was used to construct the air quality index (AQI) of CO and NO_2. The results and findings of the present study revealed that in 72.7% of the outdoor sampling locations (8 out of 11 sites are with green color code in Figure 5.1) in the dry season had good level of air pollution. The air quality is considered acceptable, and there is minimal to no risk to human health from NO_2 exposure.

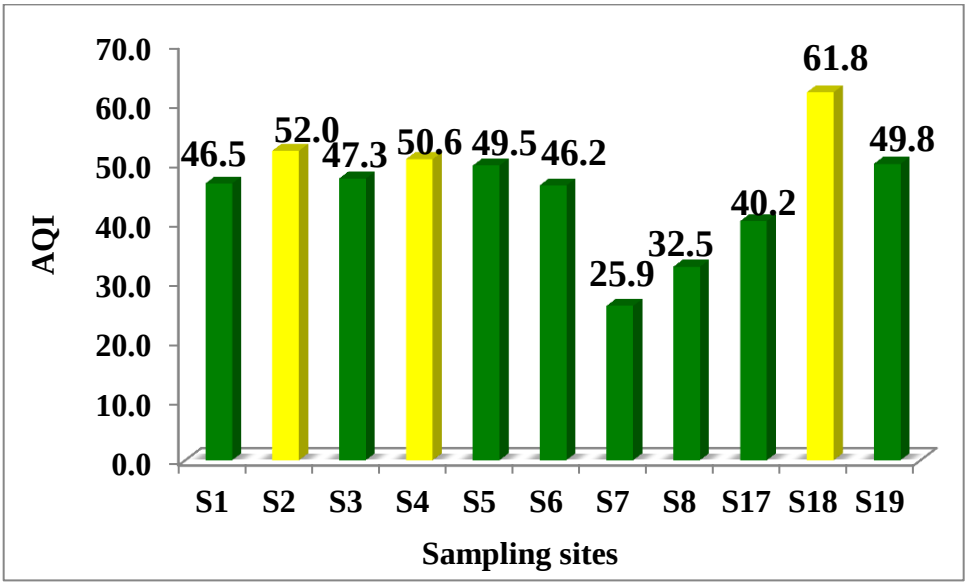

Figure 5.1. Air quality index (AQI) for NO_2 in 11 outdoor sampling sites and corresponding AQI color code in the dry season

In another way, the air quality at 27.3% of the outdoor sampling sites (3 out of 11 have a yellow color code in Figure 5.1) were acceptable; but, it may cause a sensible health distress for a small number of persons. In similar way, wet season results (Figure 5.2) and results of the present study revealed that the level of air pollution is good, the air quality is satisfactory, and there is little or no health risk due to NO_2 exposure in 90.9% of the outdoor sampling locations in the wet season. In addition, the air quality at 9.1% of the outdoor sampling sites was acceptable; however, it may pose a moderate health concern for a very small number of individuals.

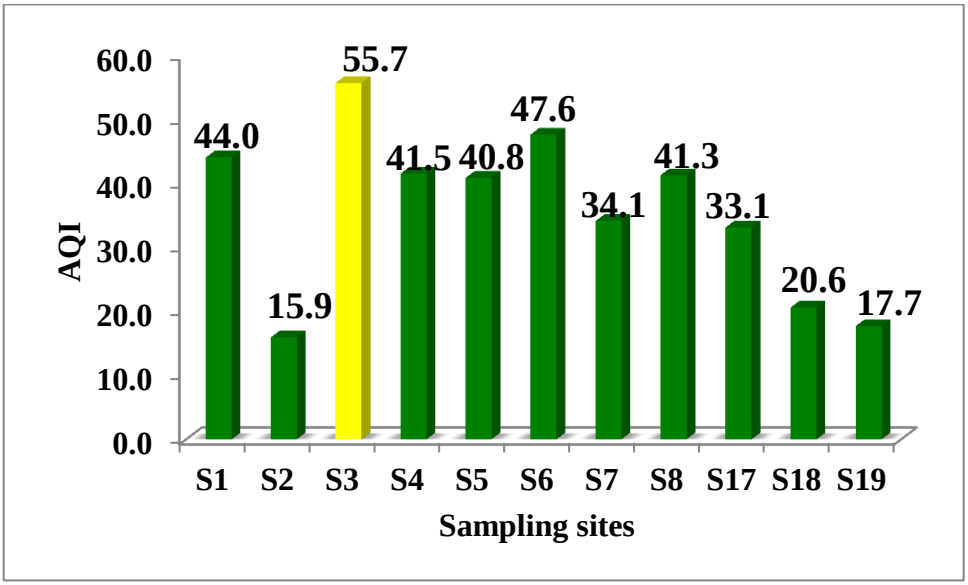

Figure 5.2. Air quality index (AQI) for NO_2 in 11 outdoor sampling sites and corresponding AQI color code in the wet season

The AQI of CO in the outdoor sampling locations in the wet season are indicated in Figure 5.3. The findings of this study shown that there is minimal to no risk to health from CO exposure, and the air quality is adequate in 90.9% of the outdoor sampling locations in the wet season. While 9.1% of the outdoor sampling sites had acceptable air quality, a very tiny percentage of people may have moderate health concerns.

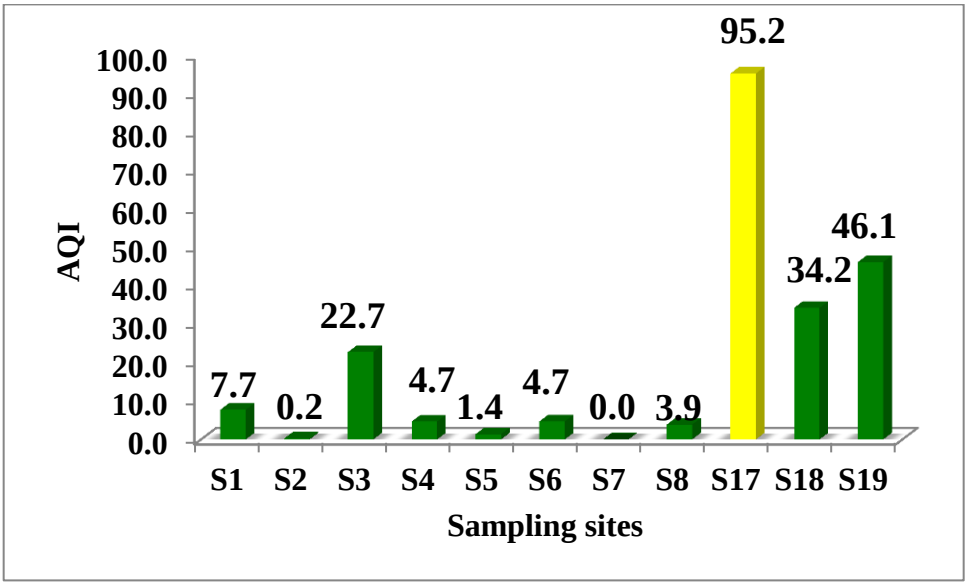

Figure 5.3. Air quality index (AQI) for CO in 11 outdoor sampling sites and corresponding AQI color code in the wet season

Conclusions and Recommendations

This was the first study of its type to look at the indoor and outdoor air quality in dry and wet seasons in urban and industrial areas of Hawassa, Ethiopia. In most of the sampling sites, the general trend for $PM_{2.5}$ and PM_{10} concentrations was found to be higher in the wet season than in the dry season. The findings of this research showed that $PM_{2.5}$ and PM_{10} levels exceeded WHO guidelines at 50% and 68.2% of sites in the dry season, and 90.9% and 77.3% of sites in the wet season, respectively. These results indicate a potential risk to the surrounding population. During the dry season, every I/O ratio for NO_2 was equal to or below one, while 62% of I/O ratios during the wet season were less than one. Additionally, 50% of the I/O ratio of CO was less than one. This indicates that NO_2 and CO may have originated from outdoor sources. The air quality index (AQI) of NO_2 and CO computed in the wet season revealed that the air quality is satisfactory (90.9%) and acceptable, however, may cause a moderate health worry for small number of persons (9.1%).

The HQ for $PM_{2.5}$ and PM_{10} in urban and industrial areas in the dry and wet seasons was greater than one, which suggests that the non-carcinogenic effect is likely to appear. The ELCR of $PM_{2.5}$ in urban and industrial areas exceeded WHO and USEPA recommendations, posing a significant risk to the general population during both wet and dry seasons. Therefore, respective government agencies, and all the relevant bodies should take remedial environmental measures to decrease the levels of $PM_{2.5}$ and PM_{10} in the city. Governments and academic experts can use the vital data set provided by this study to intensify their efforts to improve the city's air quality. The results would also add to the scant data on $PM_{2.5}$ and PM_{10} in developing countries and contribute to future global efforts to minimize air pollution. Based on our study, a policy recommendation to improve air pollution quality could be to implement more stringent regulations on emissions from vehicles and industries. Additionally, investing in green infrastructure and promoting public awareness about the importance of reducing air pollution could also be effective measures to improve the air quality of the urban and industrial environments.

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CHAPTER 6. GENERAL CONCLUSIONS AND RECOMMENDATIONS

6.1 General Conclusions

This study was the first to examine 76 VOCs in eight primary schools in Ethiopia. In most of the primary schools, the concentrations of TVOCs in the classrooms were higher than the concentrations in the playgrounds, signifying that there were possible sources of the measured VOCs in the classrooms. The I/O ratios of individual compounds also suggested the occurrence of possible indoor sources. The T/B ratios in all schools were less than two, indicating that vehicular sources may have an important effect on aromatic VOC concentrations. The cumulative cancer risk and total hazard ratio indicators showed that the exposure of children to the measured concentrations of benzene might have harmful effects. This study offers a crucial data set that governments and academic experts may use to step up efforts to enhance the air quality in school settings. Similarly, the concentrations of $PM_{2.5}$ and PM_{10} in primary schools were found to be above the WHO mean guidelines in 55% and 85% of sampling sites, respectively. The I/O concentration ratios of $PM_{2.5}$, PM_{10}, and NO_2 were greater than one in 50%, 50%, and 30%, respectively, of the primary schools, which revealed that there were possible indoor sources. The Air Quality Index (AQI) at 40% and 30% of the outdoor sampling sites could be unhealthy for sensitive groups due to exposure to $PM_{2.5}$ and PM_{10}, respectively. The AQI at 20% of the outdoor sampling sites was very unhealthy and will trigger a health alert due to exposure to $PM_{2.5}$. The AQI in 20% of the outdoor sampling sites was hazardous and will trigger health warnings of emergency conditions, and the entire population is even more likely to be affected by serious health effects due to exposure to PM_{10}.

Thus, the AQI value and the concentration levels of $PM_{2.5}$ and PM_{10} indicated poor air quality in the schools and suggest a significant health risk for the students and all populations around the schools. Governments and experts can use the vital data provided by this study to intensify their efforts to improve the air quality of the school environment. The results would also add to the scarce data on $PM_{2.5}$ and PM_{10} in developing countries and contribute to future global efforts to minimize air pollution. This was the first study of its type to look at the indoor and outdoor air quality in dry and wet seasons in urban and industrial areas of Hawassa, Ethiopia. In the majority of the sampling sites, the general trend for $PM_{2.5}$ and PM_{10} concentrations was found to be higher in the wet season than in the dry season. The results of this study revealed that the levels of $PM_{2.5}$ and PM_{10} at 50% and 68.2% of the sampling locations, respectively, during the dry season and 90.9% and 77.3% of the sampling locations, respectively, during the wet season were above the WHO guidelines. These results point to a significant potential risk to the surrounding population. All the values of the I/O ratio of NO_2 in the dry season were less than or equal to one, 62% of the results in the wet season were less than one, and 50% of the I/O ratio of CO was less than one. These indicate that NO_2 and CO probably originated from outdoor sources. The air quality index (AQI) of NO_2 and CO computed in the wet season revealed that the air quality was satisfactory (90.9%) and acceptable; however, it may cause a moderate health concern for a small number of people (9.1%). The HQ for $PM_{2.5}$ and PM_{10} in urban and industrial areas in the dry and wet seasons were greater than one, which suggests that a non-carcinogenic effect is likely to appear. The ELCR of $PM_{2.5}$ in urban and industrial areas exceeded the WHO and USEPA recommendations, posing a significant risk to the general population during both wet and dry seasons.

Governments and academic experts can use the vital data set provided by this study to intensify their efforts to improve the city's air quality. The results of this study would also add to the limited data on $PM_{2.5}$ and PM_{10} in developing countries and contribute to future global efforts to minimize air pollution.

6.2 Recommendations

The current study can be viewed as a first step in many aspects of air pollutants in the environments of Hawassa City and the possible human health risks associated with the pollutants. Since the cumulative cancer risk and total hazard ratio indicators indicated that children's exposure to measured benzene levels could be harmful, schools, government agencies, and relevant bodies should implement environmental measures to reduce benzene levels in educational environments. Additionally, schools, respective government agencies, and all the relevant bodies should take remedial environmental measures to decrease the levels of $PM_{2.5}$ and PM_{10} in schools, urban, and industrial environments. Based on our study, a policy recommendation to improve air pollution quality could be to implement more stringent regulations on emissions from vehicles and industries. Additionally, investing in green infrastructure and promoting public awareness about the importance of reducing air pollution could also be effective measures to improve the air quality of the schools, urban, and industrial environments. While many of the findings of the study can stand on their own, future studies can build upon the findings of the study and further examine the following:

- Sampling and monitoring in more locations over a longer period of time should be considered to further substantiate the initial findings of this and to have an appropriate data set for human health risk assessment on exposure to air pollutants.

- This study focused on 76 VOCs, two diameter sizes of particulate matter ($PM_{2.5}$ and PM_{10}), and three inorganic gaseous pollutants (CO, NO_2, and SO_2). In order to give a more complete picture, air pollutants like $PM_{0.1}$, $PM_{1.0}$, and ozone (O_3) should also be considered.
- The effects of seasonal variation should also be considered, as these could provide useful and practical information for air pollution assessment in Ethiopia.

APPENDIX: SUPPLEMENTARY DATA

Supplementary Table S1. Calibration Mixture A; the standard VOCs used for calibration of the TD-GC-MS with their characterizing ions (SIM), loaded mass, retention time and RSRF-Tol-d8.

Compound Name	Ions (SIM)	Density (kg/l)	MW (g/mol)	Conc STOCK (ng/µ)	Conc. (1:20) (ng/µl)	mass (ng)	RT (min)	RSRF
Acetonitrile	39.0, 40.0, 41.0	0.786	41.05	786	39.3	39.3	3.26	0.44
1-Pentene	55.0, 70.0	0.64	70.13	640	32	32	3.69	0.11
n-Pentane	39.0, 42.0, 43.0, 57.0, 72.0	0.626	72.15	626	31.3	31.3	3.90	0.16
Methylacetate	29.0, 43.0, 59.0, 74.0	0.93	74.08	930	46.5	46.5	4.32	0.43
1,1,2-Trichloortrifluorethane	101.0, 103.0, 151.0, 153.0	1.57	187.38	1570	78.5	78.5	4.59	0.02
Isobutyraldehyde	41.0, 43.0, 72.0	0.79	72.11	790	39.5	39.5	4.99	0.44
n-Butyraldehyde	44.0, 57.0, 72.0	0.817	72.11	817	40.85	40.85	6.10	0.22
1-hexene	56.0, 69.0, 84.0	0.678	84.16	678	33.9	33.9	6.69	0.26
n-Hexane	41.0, 71.0, 86.0	0.659	86.18	659	32.95	32.95	7.24	0.24
Chloroform	47.0, 83.0, 85.0	1.492	119.38	1492	74.6	74.6	7.54	0.40
2-Methyl-1-Propanol	31.0, 33.0, 43.0, 74.0	0.803	74.12	803	40.15	40.15	8.48	0.36
1,2-Dichloorethane	62.0, 64.0, 98.0	1.253	98.96	1253	62.65	62.65	9.02	0.27
Benzene	52.0, 63.0, 77.0, 78.0	0.874	78.11	874	43.7	43.7	10.74	0.82
CCl4	117.0, 119.0, 121.0	1.594	153.82	1594	79.7	79.7	11.14	0.23
1,2_Dichloorpropane	62.0, 63.0, 76.0	1.156	112.99	1156	57.8	57.8	13.11	0.38
Trichloorethylene	95.0, 97.0, 130.0, 132.0	1.46	131.39	1460	73	73	13.88	0.66
n-Propylacetate	61.0, 73.0	0.88	102.13	880	44	44	15.11	0.22
3-Methyl-1-butanol	29.0, 31.0, 42.0, 70.0	0.8	88.15	800	40	40	17.48	0.32
1,1,2_Trichloorethane	61.0, 97.0, 99.0, 132.0	1.435	133.4	1435	71.75	71.75	19.56	0.41
Toluene-d8_(A)	98.0, 100.0	0.94	100.19	940	47	47	20.02	1.00
Toluene	65.0, 91.0, 92.0	0.866	92.14	866	43.3	43.3	20.40	1.33
2-Hexanon	43.0, 71.0, 85.0, 100.0	0.812	100.16	812	40.6	40.6	21.92	0.40
n-Octane	71.0, 85.0, 114.0	0.703	114.23	703	35.15	35.15	24.43	0.29
Chlorobenzene	77.0, 112.0, 114.0	1.1075	112.56	1107.5	55.375	55.38	26.45	0.60
Ethylbenzene-d10_(A)	98.0,116.0	0.949	116.23	949	47.45	47.45	27.14	0.87
Ethylbenzene	91.0, 106.0	0.867	106.17	867	43.35	43.35	27.44	1.06
p-Xylene	91.0, 105.0, 106.0	0.866	106.17	866	43.3	43.3	27.85	1.04
Styrene	51.0, 78.0, 104.0	0.909	104.15	909	45.45	45.45	28.70	0.71
o-Xylene	91.0, 105.0, 106.0	0.878	106.17	878	43.9	43.9	28.90	1.08
1-Bromo-4-Fluorobenzene	75.0, 95.0, 174.0, 176.0	1.593	175	1593	79.65	79.65	29.91	0.68
Alfa-Pinene	92.0, 93.0, 121.0, 136.0	0.858	136.23	858	42.9	42.9	30.92	0.79
Propylbenzene	91.0, 92.0, 120.0	0.862	120.19	862	43.1	43.1	31.26	1.41
2-Octanon	58.0, 113.0, 128.0	0.819	128.21	819	40.95	40.95	32.02	0.40
1,3-Dichloorbenzene	75.0, 111.0, 146.0, 148.0	1.288	147	1288	64.4	64.4	32.86	0.72
3-Carene	77.0, 93.0, 121.0, 136.0	0.864	136.23	864	43.2	43.2	33.30	0.71
2-Ethyl-1-hexanol	31.0, 56.0, 70.0, 83.0, 112.0	0.833	130.23	833	41.65	41.65	33.40	0.29
Acetophenone	51.0, 77.0, 105.0, 120.0	1.03	120.15	1030	51.5	51.5	34.28	0.67
1-Octanol	68.0, 69.0, 70.0, 83.0, 84.0, 112.0	0.827	130.23	827	41.35	41.35	34.46	0.30
Nonanal	57.0, 70.0, 82.0, 98.0	0.827	142.24	827	41.35	41.35	35.24	0.11
Undecane	57.0, 85.0, 156.0	0.74	156.31	740	37	37	35.49	0.63
Dodecane	57.0, 85.0, 170.0	0.753	170.34	753	37.65	37.65	37.64	0.65
1,3,5-Triisopropylbenzene	161.0, 189.0, 204.0	0.854	204.36	854	42.7	42.7	39.76	0.96

Supplementary Table S2. Calibration Mixture B; the standard VOCs used for calibration of the TD-GC-MS with their characterizing ions (SIM), loaded mass, retention time and RSRF-Tol-d8.

Compound Name	Ions (SIM)	Density (kg/l)	MW (g/mol)	Conc STOCK (ng/µl)	Conc. (1:20) (ng/µl)	mass (ng)	RT (min)	RSRF
Isopropanol	29.0, 31.0, 45.0, 59.0	0.785	60.1	785	39.25	39.25	3.71	0.42
Furan	68.0, 69.0	0.936	68.08	936	46.8	46.8	3.77	0.18
Dimethylsulfide	61.0, 62.0	0.84	62.13	840	42	42	4.16	0.21
Dichloormethane	49.0, 84.0, 86.0	1.325	84.93	1325	66.25	66.25	4.37	0.28
Carbondisulfide	44.0, 76.0	1.26	76.13	1260	63	63	4.67	0.22
2-Methylpentane	43.0, 57.0, 71.0	0.653	86.18	653	32.65	32.65	5.86	0.23
2-Butanon	71.0, 72.0, 73.0	0.806	72.11	806	40.3	40.3	6.32	0.14
2-Methyl-furan	53.0, 81.0, 82.0	0.91	82.1	910	45.5	45.5	7.05	0.44
Ethylacetate	61.0, 70.0, 88.0	0.902	88.11	902	45.1	45.1	7.45	0.10
Tetrahydrofuran	41.0, 71.0, 72.0	0.889	72.11	889	44.45	44.45	8.28	0.27
Methylcyclopentane	55.0, 56.0, 69.0, 84.0	0.749	84.16	749	37.45	37.45	8.91	0.42
3-Methylbutyraldehyde	41.0, 42.0, 43.0, 58.0, 71.0, 86.0	0.796	86.13	796	39.8	39.8	9.61	0.29
1-Butanol	31.0, 41.0, 43.0, 56.0	0.81	74.12	810	40.5	40.5	11.17	0.55
Cyclohexane	69.0, 84.0	0.779	84.16	779	38.95	38.95	11.38	0.17
Hexamethyldisiloxane	73.0, 147.0, 148.0, 149.0	0.764	162.38	764	38.2	38.2	13.82	0.03
n-Heptane	70.0, 71.0, 100.0	0.684	100.2	684	34.2	34.2	14.91	0.31
Trimethoxymethylsilane	91.0, 105.0, 121.0	0.96	136.22	960	48	48	16.36	0.01
Dimethyldisulfide	45.0, 79.0, 94.0	1.0625	84.19	1062.5	53.125	53.125	17.74	0.70
Toluene-d8_(B)	98.0, 100.0	0.94	100.19	940	47	47	20.02	1.00
1-Pentanol	29.0, 31.0, 55.0, 57.0, 70.0	0.811	88.15	811	40.55	40.55	20.74	0.29
Hexanal	44.0, 56.0, 72.0, 82.0	0.815	100.16	815	40.75	40.75	22.87	0.16
n-Butylacetate	41.0, 43.0, 56.0, 73.0	0.88	116.16	880	44	44	24.51	0.42
Tetrachloorethylene	131.0, 164.0, 166.0, 168.0	1.623	165.83	1623	81.15	81.15	24.53	0.49
1,1,1,2-Tetrachloroethane	95.0, 117.0, 119.0, 131.0, 133.0	1.598	167.85	1598	79.9	79.9	26.46	0.46
Ethylbenzene-d10_(B)	98.0,116.0	0.949	116.23	949	47.45	47.45	27.15	0.89
m-Xylene	91.0, 105.0, 106.0	0.868	106.17	868	43.4	43.4	27.85	1.04
2-Heptanon	58.0, 71.0, 114.0	0.82	114.19	820	41	41	28.41	0.34
Heptaldehyde	44.0, 70.0, 96.0	0.82	114.19	820	41	41	28.83	0.09
n-Nonane	57.0, 85.0, 128.0	0.718	128.26	718	35.9	35.9	29.53	0.46
5-Methyl-3-heptanon	71.0, 99.0, 128.0	0.823	128.22	823	41.15	41.15	30.53	0.31
Benzaldehyde	77.0, 105.0, 106.0	1.05	106.12	1050	52.5	52.5	30.99	0.59
Benzonitrile	76.0, 103.0	1.01	103.12	1010	50.5	50.5	31.60	0.60
Fenol	66.0, 94.0	1.07	94.11	976	48.8	48.8	31.91	0.46
1,2,4-Trimethylbenzene	105.0, 120.0	0.88	120.19	880	44	44	32.59	0.90
n-Decane	57.0, 85.0, 142.0	0.73	142.28	730	36.5	36.5	32.86	0.49
Limonene	68.0, 93.0, 107.0, 121.0, 136.0	0.842	136.23	842	42.1	42.1	33.77	0.64
5-Nonanone	85.0, 100.0, 142.0	0.82	142.24	820	41	41	34.46	0.35
Methylbenzoate	77.0, 105.0, 136.0	1.08	136.15	1080	54	54	35.13	0.70
Linalool	71.0, 93.0, 121.0, 136.0	0.87	154.25	870	43.5	43.5	35.25	0.37
decamethylcyclopentasiloxane	73.0, 267.0 (355)	0.958	370.77	958	47.9	47.9	36.59	0.25
1,2,4-Trichlorobenzene	145.0, 180.0, 182.0, 184.0	1.454	181.45	1454	72.7	72.7	37.38	0.64
Tridecane	43.0, 57.0, 71.0, 85.0	0.75	184.36	750	37.5	37.5	39.31	1.18
Tetradecane	43.0, 57.0, 71.0, 85.0	0.762	198.4	762	38.1	38.1	40.68	1.28

Supplementary Table S3. The values of the used uptake rates (URs) with their source: 1 = (Walgraeve et al., 2011); 2 = (Jia & Fu, 2017); 3 = average class-based UR (for 2- methyl-butane, n-pentane n = 11, for linalool n = 2, Dichloromethane, 1,3,5-Triisopropylbenzene, 1,1,2-Trichlorotrifluoroethane n = 12); 4 = average calculated UR (n = 41) based on all the UR values in this table with source 1 and 2.

Compound Name	UR (mL/min)	Source	Compound Name	UR (mL/min)	Source
(Cyclo-) Alkanes					
n-Pentane	0.26	3	**Esters**		
n-Hexane	0.16	1	Methylacetate	0.30	4
n-Heptane	0.26 ± 0.05	1	Ethyl acetate	0.30	4
n-Octane	0.27 ± 0.10	1	n-Propylacetate	0.23 ± 0.03	1
n-Nonane	0.34 ± 0.07	1	Methylbenzoate	0.30	4
n-Decane	0.28 ± 0.02	1	n-Butylacetate	0.30	4
Undecane	0.28	1	**Other oxygenated compounds**		
Dodecane	0.26	1	Furan	0.30	4
Methylcyclopentane	0.20	1	2-Methylfuran	0.30	4
Cyclohexane	0.25 ± 0.02	1	Tetrahydrofuran	0.22	2
2-Methylpentane	0.26	3	**Halogenated compounds**		
Tridcane	0.30	2	Chloroform	0.19	2
Tetradecane	0.31	2	Carbon tetrachloride	0.22	2
Alkene			Chlorobenzene	0.34	2
1-Pentene	0.30		1,3-Dichlorobenzene	0.36	2
1-Hexene	0.30		1,2,4-Trimethylbenzeen	0.35	2
Aromatic compounds			1,1,2-Trichlorethane	0.31	2
Benzene	0.27 ± 0.03	1	1,2-Dichloroethane	0.20	1
Toluene	0.32 ± 0.04	1	1,2 Dichloorpropane	0.33	2
Ethylbenzene	0.35 ± 0.04	1	1,1,1,2 Tetrachloorethane	0.32	2
p-Xylene	0.36 ± 0.04	1	Trichloroethylene	0.28	2
m-Xylene	0.36 ± 0.05	1	Tetrachloroethylene	0.28	1
o-Xylene	0.34	2	1,2,4-Trichlorobenzene	0.38	2
Styrene	0.36 ± 0.05	1	Dichloromethane	0.30	3
Propylbenzene	0.36 ± 0.06	1	1,3,5-Triisopropylbenzene	0.30	3
1,2,4-Trimethylbenzene	0.35 ± 0.04	1	1,1,2-Trichlorotrifluoroethane	0.30	3
Oxygenated compounds			**Sulfur Containing Compounds**		
Aldehydes			Dimethyldisulfide	0.30	4
Hexanal	0.17	1	Carbondisulfide	0.30	4
Heptanal	0.30	4	**Nirogen Containing Compounds**		
Nonanal	0.30	4	Acetonitrile	0.30	4
Benzaldehyde	0.41 ± 0.06	1	Benzonitrile	0.30	4
n-Butyraldehyde (butanal)	0.30	4	**Silicon Containing Compounds**		
Isobutyraldehyde	0.30	4	Trimethoxymethylsilane	0.30	4
3-Methylbutyraldehyde	0.30	4	Hexamethyldisiloxane	0.30	4
Alcohols	0.30	4	Decamethylcyclopentasiloxane	0.30	4
Isopropanol	0.30	4	**Terpenes**		
1-Butanol	0.30	4	α-Pinene	0.20	1
1-Pentanol	0.30	4	Limonene	0.27	1
2-Methyl-1-Propanol	0.30	4	Linalool	0.24	3
2-Ethyl-1-hexanol	0.30	4			
1-Octanol	0.30	4			
3-Methyl-1-butanol	0.30	4			
Phenol	0.43 ± 0.03	1			
Ketones					
2-Butanone	0.30	4			
2-Hexanone	0.30	4			
2-Heptanone	0.30	4			
2-Octanone	0.30	4			
5-Nonanone	0.30	4			
5-Methyl-3-heptanone	0.30	4			
Acetophenone	0.30	4			

Supplementary Table S4. VOCs concentration (μg/m^3) measured in the eight primary schools of Hawassa, Ethiopia (D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds).

Component Name	Debub CR	Debub PG	Hayole CR	Hayole PG	Alito CR	Alito PG	Adare CR	Adare PG	Comboni CR	Comboni PG	StGebriel CR	StGebriel PG	Tabor PG	Silase CR	Silase PG
(Cyclo-) Alkanes															
n-Pentane	4.30	2.99	3.74	3.54	4.02	3.75	3.76	2.88	2.51	2.59	3.17	2.99	3.43	1.81	2.08
n-Hexane	1.41	1.08	1.34	0.98	1.15	1.26	1.31	0.90	D	1.12	1.00	0.94	1.20	D	D
n-Heptane	0.89	0.68	0.76	0.68	0.89	0.82	1.16	0.90	0.52	0.57	0.64	0.70	0.68	0.41	0.47
n-Octane	0.76	0.48	0.99	0.49	0.77	0.54	0.88	0.55	0.58	0.38	0.64	0.48	0.42	0.50	0.35
n-Nonane	0.50	0.32	0.38	0.33	0.53	0.41	1.18	0.86	0.25	0.25	0.35	0.40	0.39	0.30	0.22
n-Decane	0.64	0.75	0.51	0.52	0.67	0.81	2.16	1.54	0.31	0.32	0.45	0.47	0.57	0.24	0.24
Undecane	0.58	0.41	0.54	0.44	0.57	0.55	1.91	1.39	0.34	0.30	0.51	0.54	0.44	0.24	0.25
Dodecane	0.48	0.36	0.46	0.36	0.50	0.48	2.13	2.01	0.30	0.26	0.46	0.49	0.43	0.26	0.21
Methylcyclopentane	1.06	0.82	1.00	0.86	1.14	1.01	1.25	0.96	0.60	0.68	0.81	0.81	0.89	0.42	0.52
Cyclohexane	D	D	D	D	D	D	D	D	D	D	D	D	D	ND	ND
2-Methylpentane	6.79	5.39	6.13	4.99	6.44	5.89	6.37	4.96	3.99	4.00	4.92	4.62	5.17	2.74	3.19
Tridcane	0.43	D	0.35	0.33	0.37	0.31	1.26	1.40	D	D	0.33	0.45	0.30	D	D
Tetradecane	0.44	0.24	0.34	0.24	0.28	0.24	0.46	0.44	D	D	0.41	0.31	0.24	0.27	D
∑ (Cyclo-) Alkanes	**18.29**	**13.51**	**16.54**	**13.75**	**17.34**	**16.06**	**23.82**	**18.79**	**9.41**	**10.46**	**13.69**	**13.21**	**13.91**	**7.20**	**7.52**
Alkene															
1-Pentene	0.33	0.30	0.45	0.33	0.24	0.26	0.22	0.24	0.27	0.25	0.30	0.27	0.23	0.23	0.26
1-Hexene	0.33	0.27	0.33	0.29	0.29	0.28	0.32	0.21	0.25	0.21	0.25	0.27	0.31	0.19	0.18
∑ Alkene	**0.66**	**0.56**	**0.78**	**0.63**	**0.54**	**0.54**	**0.54**	**0.45**	**0.51**	**0.45**	**0.54**	**0.54**	**0.54**	**0.42**	**0.44**
Aromatic compounds															
Benzene	3.28	2.98	3.21	3.06	3.20	3.34	3.46	3.42	2.40	2.46	2.68	2.56	3.22	1.76	2.15
Toluene	6.29	4.36	4.78	4.30	5.33	5.24	4.96	4.16	2.95	3.09	4.03	3.89	4.30	2.26	2.73
Ethylbenzene	1.30	0.95	1.18	1.02	1.18	1.15	1.39	1.10	0.65	0.69	0.91	0.91	0.96	0.50	0.60
p+m-Xylene	3.81	2.79	3.30	2.81	3.25	3.34	3.47	2.83	1.84	1.93	2.56	2.64	2.70	1.34	1.64
o-Xylene	1.81	1.28	1.48	1.29	1.48	1.46	1.55	1.24	0.78	0.86	1.13	1.15	1.20	0.59	0.74
Styrene	0.60	0.26	0.35	0.22	0.29	0.24	0.28	0.31	0.17	0.16	0.24	0.23	0.38	0.18	0.15
Propylbenzene	0.23	0.17	0.19	0.17	0.20	0.19	0.23	0.18	0.10	0.11	0.16	0.15	0.16	0.08	0.10
1,2,4-Ttrimethylbenzene	1.45	1.05	1.29	1.13	1.31	1.24	1.53	1.18	0.65	0.75	1.05	1.06	1.09	0.51	0.61
1,3,5-Ttriisopropylbenzene	ND	ND	ND	ND	ND	ND	0.00	0.00	ND	ND	0.00	0.00	0.00	ND	ND
∑ Aromatic compounds	**18.76**	**13.84**	**15.78**	**13.99**	**16.22**	**16.20**	**16.86**	**14.42**	**9.54**	**10.07**	**12.75**	**12.60**	**14.01**	**7.22**	**8.74**
Oxygenated compounds															
Aldehydes															
Hexanal	1.08	D	2.73	D	D	ND	D	1.06	D	ND	1.08	D	ND	1.19	ND
Heptanal	1.34	D	1.68	D	1.62	D	D	D	D	D	D	D	D	D	D
Nonanal	6.63	2.29	17.52	1.90	6.82	2.41	2.44	1.29	5.33	2.43	7.27	2.09	D	7.68	1.32
Benzaldehyde	5.51	4.76	4.98	4.64	4.55	4.42	3.21	6.81	3.56	4.18	3.81	4.11	4.37	2.57	3.67
Butanal	ND	ND	D	ND	ND	ND	ND	ND	ND	ND	D	ND	ND	ND	ND
Isobutyraldehyde	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D
3-Methylbutyraldehyde	0.18	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
∑ Aldehydes	**14.74**	**7.22**	**26.91**	**6.54**	**12.99**	**6.84**	**5.65**	**9.16**	**8.89**	**6.61**	**12.17**	**6.19**	**4.37**	**11.44**	**4.98**
Alcohols															
Isopropanol	0.11	0.18	ND	ND	0.08	0.05	0.16	0.13	ND	0.06	0.09	0.12	0.11	0.09	0.10

Component Name	Debub CR	Debub PG	Hayole CR	Hayole PG	Alito CR	Alito PG	Adare CR	Adare PG	Comboni CR	Comboni PG	StGebriel CR	StGebriel PG	Tabor PG	Silase CR	Silase PG
1-Butanol	ND	ND	ND	ND	ND	ND	0.30	ND	ND	ND	0.32	0.22	0.19	0.62	0.15
1-Pentanol	ND	ND	0.45	ND	0.31	ND	ND	ND	0.22	ND	ND	ND	ND	0.23	ND
2-Methyl-1-Propanol	ND	ND	ND	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	0.42	ND
2-Ethyl-1-hexanol	0.53	0.22	0.74	0.17	0.59	0.19	0.22	0.12	0.32	0.26	0.39	0.26	0.28	0.83	0.21
1-Octanol	0.45	0.19	0.52	0.18	0.31	0.19	0.38	0.22	0.26	0.16	0.32	0.20	0.22	0.28	0.14
3-Methyl-1-butanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenol	3.27	3.28	3.44	2.75	3.28	3.42	2.09	2.98	2.40	3.01	2.48	2.69	2.65	1.89	2.29
∑Alcohols	**4.36**	**3.87**	**5.15**	**3.10**	**4.58**	**3.85**	**3.15**	**3.44**	**3.31**	**3.49**	**3.61**	**3.50**	**3.46**	**4.35**	**2.89**
Ketones															
2-Butanone	0.94	0.85	0.93	0.83	0.91	0.83	0.87	D	D	D	0.77	0.81	D	D	D
2-Hexanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Heptanone	0.17	0.11	0.19	0.13	0.14	0.13	0.20	0.16	0.10	0.10	0.13	0.10	0.13	0.12	0.08
2-Octanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5-Nonanone	0.05	0.03	0.03	0.04	0.06	0.04	0.16	0.10	0.03	0.03	0.04	0.04	0.04	0.02	ND
5-Methyl-3-heptanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetophenone	5.75	6.61	6.42	6.80	5.53	6.71	4.55	10.33	4.89	6.16	5.41	6.37	5.19	3.51	5.30
∑ ketones	**6.91**	**7.61**	**7.57**	**7.80**	**6.63**	**7.71**	**5.77**	**10.58**	**5.02**	**6.29**	**6.35**	**7.31**	**5.36**	**3.65**	**5.38**
Esters															
Methylacetate	0.78	0.70	0.80	D	0.72	0.70	D	D	D	D	0.65	0.63	D	D	D
Ethyl acetate	2.06	1.10	0.97	0.64	1.29	1.19	1.15	1.19	0.69	0.79	0.93	0.89	0.83	0.52	0.59
n-Propylacetate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylbenzoate	0.13	D	0.11	D	D	0.11	0.10	0.12	D	D	D	0.12	0.11	D	D
n-Butylacetate	1.56	0.59	0.29	0.37	0.73	0.81	0.59	0.66	0.30	0.31	0.33	0.34	0.25	0.16	0.20
∑ Esters	**4.53**	**2.39**	**2.17**	**1.02**	**2.74**	**2.80**	**1.84**	**1.97**	**1.00**	**1.10**	**1.90**	**1.97**	**1.20**	**0.68**	**0.79**
Other oxygenated compounds															
Furan	D	D	D	0.60	D	D	D	D	D	D	D	D	D	D	D
2-Methylfuran	0.48	0.43	0.49	0.42	0.48	0.44	0.40	0.34	0.29	0.29	0.34	0.33	0.46	0.25	0.25
Tetrahydrofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
∑ Other oxygenated compounds	**0.48**	**0.43**	**0.49**	**1.02**	**0.48**	**0.44**	**0.40**	**0.34**	**0.29**	**0.29**	**0.34**	**0.33**	**0.46**	**0.25**	**0.25**
Halogenated compounds															
Chloroform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.53	0.53	0.60	0.55	0.56	0.58	0.54	0.51	0.48	0.50	0.55	0.55	0.55	0.41	0.50
Chlorobenzene	0.03	0.03	0.04	0.04	0.04	0.03	0.04	0.04	0.03	0.02	0.03	0.03	0.04	0.02	0.03
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichlorethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2 Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,2 Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	0.01	0.01	ND	ND	ND	ND	0.02	0.12	0.13
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloromethane	0.14	0.09	D	D	0.10	0.08	0.14	0.07	0.17	D	D	D	D	D	D
1,1,2-Trichlorotrifluoroethane	3.05	3.04	2.92	2.84	2.78	2.91	3.00	2.83	2.74	2.62	3.11	3.07	2.73	2.24	2.98
∑ Halogenated compounds	**3.75**	**3.68**	**3.56**	**3.43**	**3.47**	**3.60**	**3.73**	**3.47**	**3.42**	**3.15**	**3.69**	**3.65**	**3.33**	**2.79**	**3.63**

Component Name	Debub CR	Debub PG	Hayole CR	Hayole PG	Alito CR	Alito PG	Adare CR	Adare PG	Comboni CR	Comboni PG	StGebriel CR	StGebriel PG	Tabor PG	Silase CR	Silase PG
Sulfur containing compounds															
Dimethyldisulfide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbondisulfide	ND	0.39	ND	ND	ND	D	ND	D	ND	ND	ND	D	ND	ND	ND
∑ Sulfur containing compounds		**0.39**													
Nirogen containing compounds															
Acetonitrile	0.87	D	0.91	0.82	D	D	D	ND	D	D	D	D	D	ND	D
Benzonitrile	0.73	0.63	0.66	0.73	0.66	0.54	0.57	0.71	0.47	0.46	0.47	0.45	0.58	0.35	0.46
∑ Nitrogen containing compounds	**1.60**	**0.63**	**1.56**	**1.56**	**0.66**	**0.54**	**0.57**	**0.71**	**0.47**	**0.46**	**0.47**	**0.45**	**0.58**	**0.35**	**0.46**
Silicon containing compounds															
Trimethoxymethylsilane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexamethyldisiloxane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Decamethylcyclopentasiloxane	1.40	D	1.99	D	D	ND	D	ND	D	ND	D	D	D	ND	1.42
∑ Silicon containing compounds	**1.40**		**1.99**												**1.42**
Terpenes															
α-Pinene	0.25	0.19	0.27	0.16	0.24	0.20	0.16	0.19	0.13	0.12	0.15	0.14	0.17	0.13	0.13
Limonene	0.48	D	ND	D	D	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Linalool	0.21	0.06	0.52	0.12	0.25	0.11	ND	ND	0.19	0.09	0.26	0.10	ND	0.26	0.09
∑ Terpenes	**0.95**	**0.25**	**0.79**	**0.28**	**0.49**	**0.31**	**0.16**	**0.19**	**0.32**	**0.21**	**0.41**	**0.24**	**0.17**	**0.38**	**0.22**
TVOC	**76.44**	**54.38**	**83.28**	**53.11**	**66.15**	**58.90**	**62.51**	**63.52**	**42.17**	**42.58**	**55.93**	**50.00**	**47.40**	**38.71**	**36.71**

Supplementary Table S5, Pearson correlation coefficients of Alkanes and Alkenes (n= 15)

	n-Pen	n-Hep	n-Oct	n-Non	n-Dec	Unde	Dode	MCP	2-MP	1-Pen	1-He
n-Pentane (n-Pen)	1.0										
n-Heptane (n-Hep)	**0.8**	1.0									
n-Octane (n-Oct)	*0.6*	**0.6**	1.0								
n-Nonane (n-Non)	0.4	**0.9**	0.5	1.0							
n-Decane (n-Dec)	0.4	**0.9**	0.4	**1.0**	1.0						
n-Undecane (Unde)	0.4	**0.8**	0.5	**1.0**	**1.0**	1.0					
n-Dodecane (Dode)	0.2	**0.8**	0.4	**1.0**	**1.0**	**1.0**	1.0				
Methylcyclopentane (MCP)	**0.9**	**1.0**	**0.7**	**0.7**	**0.7**	**0.7**	*0.6*	1.0			
2-Methylpentane (2-MP)	**1.0**	**0.9**	**0.7**	*0.5*	*0.5*	0.5	0.3	**1.0**	1.0		
1-Pentene (1-Pen)	0.4	0.0	0.5	-0.3	-0.3	-0.2	-0.3	0.2	0.3	1.0	
1-Hexene (1-He)	**0.9**	**0.7**	**0.7**	0.3	0.3	0.3	0.1	**0.8**	**0.9**	0.5	1.0

Bold Correlation is significant at the 0.01 level (2-tailed
Italic Correlation is significant at the 0.05 level (2-tailed)

Supplementary Table S6, Pearson correlation coefficients of Aromatic compounds (n=15)

	B	T	EB	p,m-X	o-X	S	PB	1,2,4-TMB
Benzene (B)	1.0							
Toluene (T)	**0.9**	1.0						
Ethylbenzene (EB)	**0.9**	**0.9**	1.0					
p,m-Xylene (P,m-X)	**0.9**	**1.0**	**1.0**	1.0				
o-Xylene (O-X)	**0.9**	**1.0**	**1.0**	**1.0**	1.0			
Styrene(S)	*0.6*	**0.8**	**0.7**	**0.7**	**0.8**	1.0		
Propylbenzene (PB)	**0.9**	**1.0**	**1.0**	**1.0**	**1.0**	**0.7**	1.0	
1,2,4-Trimethylbenzene (1,2,4-TMB)	**0.9**	**0.9**	**1.0**	**1.0**	**1.0**	**0.7**	**1.0**	1.0

Bold Correlation is significant at the 0.01 level (2-tailed)
Italic Correlation is significant at the 0.05 level (2-tailed)

Supplementary Table S7, Person correlation coefficients of terpenes, oxygenated and nitrogen compounds (n= 15)

	No	**BA**	**2-E-1-H**	**1-O**	**Ph**	**2-H**	**Ac**	**EAc**	**n-BuAc**	**2-MF**	**CCl_4**	**ClB**	**1,1,2-TCTFE**	**BN**	**α-P**
Nonanal (No)	1.0														
Benzaldehyde (BA)	0.0	1.0													
2-Ethyl-1-hexanol (2-E-1-H)	**0.8**	-0.3	1.0												
1-Octanol (1-O)	**0.8**	0.1	**0.7**	1.0											
Phenol (Ph)	0.2	**0.7**	0.0	0.2	1.0										
2-Heptanone (2-H)	0.4	0.3	0.3	**0.8**	0.2	1.0									
Acetophenone (Ac)	-0.2	**0.9**	-0.5	-0.2	*0.6*	0.1	1.0								
Ethyl acetate (EAc)	0.1	*0.6*	0.1	*0.5*	*0.6*	*0.6*	0.3	1.0							
n-Butylacetate (n-BuAc)	0.0	*0.5*	0.0	0.4	*0.5*	0.4	0.2	**1.0**	1.0						
2-Methylfuran (2-MF)	0.3	0.5	0.1	0.5	**0.7**	*0.6*	0.2	*0.6*	*0.5*	1.0					
Carbon tetrachloride (CCl_4)	0.2	0.4	-0.2	0.3	**0.7**	0.5	0.3	0.4	0.3	**0.8**	1.0				
Chlorobenzene (ClB))	-0.1	*0.5*	-0.3	0.3	0.3	**0.7**	0.5	0.4	0.3	*0.6*	*0.6*	1.0			
1,1,2-Trichlorotrifluoroethane(1,1,2-TCTFE))	-0.1	0.3	-0.4	0.2	0.3	0.2	0.3	0.5	0.4	0.4	**0.7**	0.4	1.0		
Benzonitrile (BN)	0.1	**0.8**	-0.1	0.3	*0.6*	*0.6*	*0.6*	*0.6*	*0.6*	**0.8**	*0.6*	**0.7**	0.4	1.0	
α-Pinene (α-P)	*0.5*	*0.6*	0.4	**0.7**	**0.7**	**0.7**	0.3	**0.7**	*0.6*	**0.9**	*0.6*	0.5	0.3	**0.7**	1.0

Bold Correlation is significant at the 0.01 level (2-tailed)
Italic Correlation is significant at the 0.05 level (2-tailed)

Supplementary Table S8. Percentiles (P25 and P75) of $PM_{2.5}$, PM_{10}, NO_2, CO, temperature, and relative humidity (n = 132) in the dry and wet seasons

	Dry season			Wet season		
	P25	P50	P75	P25	P50	P75
$PM_{2.5}$ (μg/m^3)	15.4	21.0	27.9	26.6	40.5	96.8
PM_{10} (μg/m^3)	39.7	56.0	95.1	45.8	82.4	143.9
NO_2 (μg/m^3)	60.0	73.0	91.0	51.5	66.0	84.5
CO	-	-	-	0.0	0.0	1910.0
Temperature (°C)	27.4	29.0	30.9	20.0	22.0	24.0
Relative humidity (%)	27.0	32.0	39.0	59.0	65.0	73.0

Supplementary Table S9. Spearman's rho correlation coefficients of $PM_{2.5}$, PM_{10}, temperature (T), and relative humidity (RH) (n = 132) in the dry season

	$PM_{2.5}$ ($\mu g/m^3$)	**PM_{10} ($\mu g/m^3$)**	**NO_2 ($\mu g/m^3$)**	**T (°C)**	**RH (%)**
$PM_{2.5}$ ($\mu g/m^3$)	1.000				
PM_{10} ($\mu g/m^3$)	.784**	1.000			
NO_2 ($\mu g/m^3$)	.101	.124	1.000		
Temperature (°C)	-.101	-.053	.189*	1.000	
RH (%)	.128	.023	-.175*	-.718**	1.000

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Supplementary Table S10. Spearman's rho correlation coefficients of $PM_{2.5}$, PM_{10}, temperature (T), and relative humidity (RH) (n = 132) in the wet season

	$PM_{2.5}$ ($\mu g/m^3$)	**PM_{10} ($\mu g/m^3$)**	**NO_2 ($\mu g/m^3$)**	**CO ($\mu g/m^3$)**	**T (°C)**	**RH (%)**
$PM_{2.5}$ ($\mu g/m^3$)	1.000					
PM10 ($\mu g/m^3$)	.898**	1.000				
NO_2 ($\mu g/m^3$)	.014	-.083	1.000			
CO ($\mu g/m^3$)	.057	.051	.042	1.000		
Temperature (°C)	-.119	-.155	-.092	.064	1.000	
RH (%)	.143	.184*	.046	-.034	-.888**	1.000

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).