

**MONITORING AND ASSESSMENT OF INDOOR
AIR VOLATILE ORGANIC COMPOUND
CONCENTRATIONS IN PRIMARY SCHOOLS**

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ABSTRACT

MONITORING AND ASSESSMENT OF INDOOR AIR VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN PRIMARY SCHOOLS

Indoor air quality (IAQ) is important mainly because, poor IAQ may cause variety of adverse health effects and people spend majority of their time indoors. One of the most susceptible groups to air pollution is considered as children. Children spend approximately six to eight hours a day in school buildings, therefore the indoor air quality of school buildings should be given utmost importance. Formaldehyde and volatile organic compounds (VOCs) have been receiving considerable interest in indoor air field studies because of their high emission rates from products used indoor environments. Thus, their concentrations have been measured in school buildings in many different countries.

Indoor and outdoor air samples were collected from three primary schools in İzmir (School 1, School 2, and School 3). Sampling was performed in spring and winter terms. Active sampling was applied for VOCs and formaldehyde by using Tenax TA and DNPH silica gel sorbent tubes, respectively. VOCs were analyzed by using a thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS) system. Formaldehyde analysis was performed by using an HPLC instrument.

Benzene, toluene, ethyl benzene and xylenes, which have high toxicity, were detected at high concentrations. In addition, the indoor/outdoor (I/O) concentration ratios of VOCs were investigated. Mean Total VOC (TVOC) and formaldehyde concentrations were calculated for the three schools in winter and spring terms. TVOC and formaldehyde concentrations were $104 \mu\text{g}/\text{m}^3$ and $44.36 \mu\text{g}/\text{m}^3$ in winter, and $66.42 \mu\text{g}/\text{m}^3$ and $43.73 \mu\text{g}/\text{m}^3$ in spring terms for School 1; and $50.86 \mu\text{g}/\text{m}^3$ and $30.78 \mu\text{g}/\text{m}^3$ in winter, and $32.1 \mu\text{g}/\text{m}^3$ and $35.82 \mu\text{g}/\text{m}^3$ in spring term for School 2, and $51.09 \mu\text{g}/\text{m}^3$ and $36.53 \mu\text{g}/\text{m}^3$ in spring term for School 3 primary schools, respectively. These concentration values are generally higher than or parallel to the values reported in the literature. The TVOC concentrations in kindergartens were higher than the concentrations in classrooms.

ÖZET

İLKÖĞRETİM OKULLARINDA BİNA-İÇİ UÇUCU ORGANİK MADDE DERİŞİMLERİNİN İZLENMESİ VE DEĞERLENDİRİLMESİ

Bina-içi hava kirleticileri çeşitli olumsuz sağlık sorunlarına sebep olabildiklerinden dolayı, bina-içi hava kalitesi önemlidir. Hava kirleticilerinden en fazla etkilenen hassas gruplardan biri çocuklar olarak düşünülmektedir. Çocukların günde yaklaşık altı ila sekiz saatlerini okul binaları içerisinde geçirdikleri düşünüldüğünde, bina-içi hava kalitesinin okullarda incelenmesi gerekliliği ortaya çıkmaktadır. Bina-içerisinde kullanılan malzemelerden yüksek oranda emisyonu sahip olan formaldehit (HCHO) ve uçucu organik bileşikler (UOB) bina-içi hava kalitesi açısından önem taşımaktadır. UOB ve HCHO'nun önemi nedeniyle, bu bileşiklerin derişimleri birçok ülkede okul binalarında ölçülmektedir.

UOB ve HCHO'nun ilköğretim okullarında, bina-içi ve bina-dışı derişimlerini belirlemek için, İzmir ilinde, seçilen üç ilköğretim okulunda (Okul 1, Okul 2 ve Okul 3), 2007 yılı kış ve bahar mevsimlerinde aktif örnekleme yöntemi ile UOB ve HCHO örnekleme yapılmıştır. UOB ve HCHO analizleri, sırasıyla, termal desorber ünitesi bulunan GC/MS ve HPLC cihazları ile gerçekleştirilerek derişimleri belirlenmiştir.

Çalışmanın sonucunda, yüksek toksisiteli sebebiyle en zararlı UOB'ler olarak gruplandırılan benzen, toluen, etil benzen ve ksilenler, iç havada en yüksek derişimlerde ölçülmüştür. Ayrıca, örneklerin genelinde saptanan bileşikler için iç-dış hava (İ/D) derişim oranları hesaplanmıştır. Ortalama Toplam UOB (TUOB) ve HCHO derişim değerleri her üç okul için hesaplanmıştır. Okul 1 için ortalama TUOB ve HCHO derişimleri sırasıyla, kış dönemi için; 104 $\mu\text{g}/\text{m}^3$ ve 44,36 $\mu\text{g}/\text{m}^3$, bahar dönemi için 66,42 $\mu\text{g}/\text{m}^3$ ve 43,73 $\mu\text{g}/\text{m}^3$; Okul 2 için kışın 50,86 $\mu\text{g}/\text{m}^3$ ve 30,78 $\mu\text{g}/\text{m}^3$, baharda 32,1 $\mu\text{g}/\text{m}^3$ ve 35,82 $\mu\text{g}/\text{m}^3$; Okul 3 için bahar da 51,09 $\mu\text{g}/\text{m}^3$ ve 36,53 $\mu\text{g}/\text{m}^3$ olarak ölçülmüştür. Genel olarak, bu derişimler literatürde olan çalışmaların sonuçlarıyla karşılaştırıldığında daha yüksektir ya da paralellik göstermiştir. Anasınıflarında hesaplanan TUOB derişimleri sınıflardaki derişimler ile karşılaştırıldığında daha yüksek olduğu görülmüştür.

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CHAPTER 1

INTRODUCTION

The quality of the air we breathe is important to human health. Most of our time is spent indoors, mainly in nonindustrial buildings, such as dwellings, offices, schools and caring institutions. Evidence indicates that indoor air can be more polluted than outdoor air. Various pollutants present in indoor environments may be harmful to human health.

Indoor air pollutants include volatile organic compounds (VOCs), inorganic gases, particulate matter (PM), biological agents and complex mixtures such as environmental tobacco smoke (ETS). Indoor concentrations of many pollutants are often higher than outdoor concentrations due to the use of indoor pollutant sources in a confined space.

There are many sources of indoor air pollution in any building. They are released from building materials, and furnishings as diverse as deteriorated, asbestos-containing insulation, wet or damp carpet, and cabinetry or furniture made of certain pressed wood products, generally over long periods of time. Furthermore, pollutants are released into the indoor air in connection with the use of products for household cleaning and maintenance, personal care, or hobbies. In addition, combustion processes are at the origin of a large number of indoor air pollutants. In addition to combustion processes, smoking is a major cause of indoor air pollution.

Indoor air pollution often effects the most susceptible people who may be exposed to indoor air pollutants for the longest periods of time. Such groups include the young, the elderly, and the chronically ill. One of the most susceptible groups to air pollution is considered as children. Indoor air quality (IAQ) should be considered a top priority in the school environment because of many reasons. One reason is that problems that occur in poor indoor environments may reduce the performance of occupants in buildings. Another reason is that children are still developing physically and are more likely to suffer the consequences of indoor pollutants. The other most important reason is that, the number of children suffering from asthma and allergic diseases is on the increase.

VOCs and formaldehyde are considered to be an important category of the compounds that exist in indoor air. Lots of products used indoor environments emit VOCs and formaldehyde so there have been considerable interest in indoor air field studies. Another reason for these compounds having priority importance in scientific research is that these compounds may be the potential causes of eye and airway irritation.

Many investigations examining school indoor air quality (IAQ) problems have been performed in different countries in which VOCs and formaldehyde were commonly measured. In our country, however, measurements of these pollutants have not been performed.

The overall goal of this study was to monitor and assess the IAQ in terms of VOCs and formaldehyde in primary schools. Specifically the objectives of this research were:

- To measure indoor VOC and formaldehyde concentrations in schools
- To measure outdoor VOC and formaldehyde concentrations at school playgrounds, and determine indoor/outdoor ratios which give an idea about the sources of the compounds
- To determine the seasonal variations in VOC and formaldehyde concentrations

This thesis is divided into five chapters. The first chapter is an overview and objectives of the study. The second chapter reviews concepts and previous studies in the literature. The third chapter presents site description and sampling program, sample preparation and analysis, and quality assurance/quality control applications. Results and discussions are presented in the fourth chapter. In the fifth chapter presents the conclusions drawn from this research.

CHAPTER 2

LITERATURE REVIEW

2.1. Indoor Air Quality (IAQ)

The quality of air inside enclosed spaces has become a matter of growing concern over the last twenty years. Scientists attached importance to the indoor air quality in work place and residential environments. Many studies have found indoor pollutant levels greater than outdoor levels, and that people spend more than 90 % of their time indoors; therefore indoor air quality is very important (Lee, et al. 2000). Various pollutants present in indoor environments may be harmful to human health (Righi, et al. 2002, Rehwagen, et al. 2003, Rivelino, et al. 2006). Thus, for many people, the risks to health may be greater due to exposure to air pollution indoors than outdoors. In addition, people who may be exposed to indoor air pollutants for the longest periods of time are often those most susceptible to the effects of indoor air pollution. Such groups include the young, the elderly, and the chronically ill, especially those suffering from respiratory or cardiovascular diseases (Maroni, et al. 1995).

There are many sources of indoor air pollution in any building. Eventually, all internally-generated air pollutants are results of human action or choice. Such pollutants can be categorized into two groups. In the first group, the pollutants are released only in connection with human activity or even presence; while in the second group, they are released from building materials, and furnishings as diverse as deteriorated, asbestos-containing insulation, wet or damp carpet, and cabinetry or furniture made of certain pressed wood products, generally over long periods of time. Furthermore, pollutants are released into the indoor air in connection with the use of products for household cleaning and maintenance, personal care, or hobbies. Also, combustion processes like those related to heating and cooking are at the origin of a large number of indoor air pollutants. In addition to combustion processes, smoking is a major cause of indoor air pollution. While smokers are exposed to mainstream smoke, nonsmokers in a space are exposed to increased concentrations of tobacco smoke constituents, especially respirable particulate matter, carbon monoxide, and a number of organic substances

known or suspected to be carcinogens (Maroni, et al. 1995). Human presence and activity bring further changes in the indoor atmosphere: reducing concentration of oxygen because of metabolic activity cause an increase in CO₂ concentration and production of variety of odors. Regardless of human presence or activity, a large number of organic pollutants are released from building materials.

The high ranking of indoor pollution relative to other environmental problems is not surprising, because there are numerous sources of pollutants indoors; indoor air concentrations of some pollutants are often high enough to pose a health risk. The total quantity of air pollutants emitted indoors is much less than that emitted by outdoor sources. However, once emitted, indoor pollutants are diluted much more slowly than pollutants from outdoor sources. When this factor is combined with the fact that people spend most of their time indoors, there is a much higher likelihood that people will be exposed to pollutants emitted indoors than those emitted outdoors. (Godish 2000).

The definition of good indoor air quality management includes control of airborne pollutants, introduction and distribution of adequate outdoor air, and maintenance of acceptable temperature and relative humidity. Temperature and humidity are important because thermal comfort concerns underlie many complaints about "poor air quality." Temperature and humidity can also affect indoor contaminant levels. Failure to respond quickly and effectively to IAQ problems can lead to numerous adverse health, cost, and educational process consequences (Pennsylvania Department of Health 2002).

Indoor air pollution can cause a variety of adverse impacts on human health, from irritant effects to respiratory disease, cancer, and death. The lung is the most common site of injury by airborne pollutants. Acute effects, however, may also include non-respiratory signs and symptoms, which may depend upon toxicological characteristics of the substances and host-related factors (EPA 1994). It is important to note that health effects are determined not only by the specific toxicology of the air pollutant, but also by the exposure and absorbed dose. The higher the exposure and dose, the higher the risk of adverse health effects. In addition, more severe effects generally occur with higher doses. The possibility of adverse effects is increased with the knowledge that people spend such a significant part of the day indoors.

Hundreds of substances representing a range of chemical, physical, and biological species have been identified as indoor air pollutants. The following sections

offer descriptions of some of the more common indoor air contaminants, sources and the major health effects that can occur from exposure to common indoor pollutants.

2.1.1. Pollutant Descriptions, Sources, and Health Effects

A variety of substances have been identified as indoor air pollutants as they are emitted from many sources. Table 2.1 lists groups of indoor air pollutants and their sources.

Table 2.1. Groups of Indoor Air Pollutants and Their Sources
(Source: Phillips, et al. 2006)

Pollutant	Sources
Volatile Organic Compounds (VOCs)	Paints, thinners, perfumes, hair sprays, furniture polish, cleaning solvents, carpet dyes, glues, dry cleaned clothing, air fresheners, candles, soaps, bath oils, molds, tobacco smoke, particle board, plywood, veneers, insulation, fuel combustion
Inorganic Compounds (CO, CO ₂ , NO _x)	Gas-fired stoves and ovens, candles, fireplaces, woodstoves, kerosene space heaters, tobacco smoke
Particles	Fireplaces, woodstoves, candles, tobacco smoke
Biological Contaminants	Pets, house plants, insects, molds, humans, pillows, bedding, wet or moist materials, HVAC systems, humidifiers

2.1.1.1. Organic Pollutants

A wide range of organic compounds is present in the indoor air. These occur as a result of indoor emissions from a range of sources, including: (1) people; (2) building and furnishing materials; (3) other materials and equipment in buildings; (4) use of consumer products such as paints and aerosol sprays; (5) combustion of fuel, and (6) unburnt fuel. They also occur indoors because of contaminants in the outdoor air that enter buildings by infiltration and planned ventilation. The indoor

sources result in concentrations of many chemicals in the indoor environment exceeding those in the outdoor air (Maroni, et al. 1995, Crump 2001).

In view of the large number of known organic chemicals in indoor air, there is a tendency to divide them into several classes for easier handling. The division can be made according to, e.g., their chemical character (alkanes, aromatic hydrocarbons, aldehydes, etc.), their physical properties (boiling point, vapour pressure, carbon number, etc.), or their potential health effects (irritants, neurotoxics, carcinogens, etc.). A World Health Organization (WHO) Group has categorized organic chemicals according to boiling point ranges to amongst discriminate Very Volatile Organic Compound (VVOC), Volatile Organic Compound (VOC), Semi Volatile Organic Compound (SVOC) and Particulate Organic Matter (POM) (European Collaborative Action Report No 19 1997). Despite the grouping by boiling ranges, there are no sharp limits between the four categories. Because, in practice the categories are defined by the different methods used to collect organic pollutants from air. Most of these methods rely on trapping organic compounds on adsorbent materials such as polymers, carbon molecular black or polyurethane foam. As a result, categories of compounds cannot be separated by a single boiling point value (Maroni, et al. 1995).

The classification of indoor organic pollutants and the sampling methods used typically in the field studies is summarized by WHO Working Group and it is given in Table 2.2.

Sampling and analysis of organic pollutants in air requires different instrumentation, volume, weight, and cost. Pollutants in different categories require different methods; so, there is a limitation to perform large scale surveys. The attention has been focused on the pollutants due to their widespread diffusion and sanitary significance. The compounds that are emitted from construction products have special importance in the indoor air field, because these compounds have the potential to impact indoor air quality. These tend to be within the WHO 'VOC' range because more volatile components are lost more rapidly from materials. Some very volatile organic compounds (VVOCs) such as formaldehyde are of particular interest because they are released from some common building products, but other VVOCs have not been the subject of research to the same extent as VOCs. Semivolatile organic compounds have relatively low vapour pressures, therefore, those tend to occur at lower concentrations in indoor air than the more volatile VOCs. These include plasticisers used in polymeric materials including vinyl floorings and paints, pesticides such as

DDT and polyaromatic hydrocarbons, produced during fuel combustion and present in coal tar and as a component of tobacco smoke.

Table 2.2. Classification of indoor organic pollutants

Source: Maroni, et al. 1995

Category	Description	Abbreviation	Boiling-point range*	Sampling media typically used in field studies
1	Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Batch sampling; adsorption on charcoal
2	Volatile organic compounds	VOC	50-100 to 240-260	Adsorption on Tenax, graphitized carbon black or charcoal
3	Semivolatile organic compounds	SVOC	240-260 to 380-400	Adsorption on polyurethane foam or XAD-2
4	Organic compounds associated with particulate matter or particulate organic matter	POM	>380	Collection on filters

* Polar compounds appear at the higher end of the range

Formaldehyde and VOCs have been receiving considerable interest in indoor air field studies because of their high emission rates from products used indoor environments. Additionally, adverse health effects of these compounds, such as potential causes of eye and airway irritation, and other health effects, can be shown as a reason for these compounds having priority importance (Godish 2000).

2.1.1.2. Inorganic Pollutants

A number of inorganic compounds can adversely affect indoor air quality, which includes carbon dioxide, carbon monoxide, nitrogen dioxide, sulfur dioxide, and ozone. Carbon dioxide (CO₂) is a colorless, odorless gas that is the main combustion product of natural gas use for cooking and heating purposes. CO₂ is a good indicator of human

bioeffluents in the indoor environment. CO₂ concentrations above 1.5% affect respiration and breathing becomes faster and more difficult. Higher levels of CO₂ can result in headaches, dizziness, nausea, and even death (Maroni, et al. 1995).

Carbon monoxide (CO) is also a colorless, odorless gas and is the product of incomplete combustion of carbon-containing materials. Common indoor sources of CO include unvented combustion appliances and environmental tobacco smoke (ETS) (Godish 2000). Overexposure to CO is dangerous since CO reacts with hemoglobin in the blood to form carboxyhemoglobin (COHb). Elevated levels of COHb result in decreased visual perception, manual dexterity, and mental activity. CO exposures exceeding several thousand ppm can result in death from CO poisoning (Cooper and Alley 2002).

Nitrogen dioxide (NO₂) is the most widely considered form of the nitrogen oxides (NO_x) for indoor air studies. NO₂ is a water soluble red to brown gas with a pungent, acrid odor that is produced during high temperature combustion from the combination of nitrogen and oxygen from air. NO₂ is an oxidizer and can be highly irritating to mucous membranes. Indoor sources of NO₂ include ETS, gas appliances, kerosene heaters, and fireplaces (Maroni, et al. 1995). Health effects of NO₂ exposure include respiratory symptoms, increased susceptibility to respiratory infections, and some impairment of lung function. Concentrations as low as 0.5 ppm have been shown to cause effects in people with asthma (Cooper, et al. 2002).

Sulfur dioxide (SO₂) is a colorless gas with a pungent smell resulting from the combustion of fossil fuels. It is often emitted to the indoor environment by oil and coal heaters and is related to the sulfur content of the fuel. SO₂ can be detected by the human nose at approximately 0.5 ppm. Health effects from exposure to SO₂ include sensitivities of the respiratory tract for short-term exposure to increased risk of chronic bronchitis with long-term exposure (Maroni, et al. 1995).

Ozone (O₃) is a photo-chemical product and there are no significant anthropogenic emissions of ozone into the atmosphere. Ambient levels of O₃ are typically because of in situ photo-chemical reactions. Similarly, ozone can also be formed indoors from the reactions of VOCs, NO_x, and light. Indoor sources of O₃ include air cleaners, UV lighting, photocopying machines, and laser printers. O₃ can also enter the indoor air from outdoors. Health effects resulting from exposures to O₃ include: respiratory and pulmonary impairment in the form of eye, nose, and throat irritation, chest discomfort, coughs, and headaches (Maroni, et al. 1995).

2.1.1.3. Physical Pollutants

Particulate Matter (PM), asbestos, and radon can be classified as the major important physical pollutants.

The term particulate matter (PM) is used to describe airborne solid particles and/or droplets. Particulates may vary in size, composition, and origin. Based on size, particulate matter tends to be divided into three principal groups: coarse, fine and ultra fine particles. The border between the coarse and fine particles usually lies between 1 μm and 2.5 μm , but is usually fixed by convention at 2.5 μm in aerodynamic equivalent diameter ($\text{PM}_{2.5}$) for measurement purposes. EPA scientists recommended 2.5 μm as the cut-point between fine and coarse particles and a National Ambient Air Quality Maximum contaminant level was assigned to $\text{PM}_{2.5}$ (NAAQ 2008). $\text{PM}_{2.5}$ fraction is frequently referred as “fine” particles; because of the wide use of this cut point. Fine particles can only be seen with the aid of a microscope. The coarse particles are with a diameter larger than 2.5 μm and smaller than 10 μm . The border between fine and ultrafine particles lies at about 0.1 μm . PM_{10} is used to describe particles with an aerodynamic diameter smaller than 10 μm (WHO 2008).

The major components of PM are sulfate, nitrates, ammonia, sodium chloride, carbon, mineral dust and water. Particles may be classified as primary or secondary, depending on how they are formed. *Primary particles* are emitted into the atmosphere through man-made (anthropogenic) and natural processes including combustion of fuels in vehicle engines or in households; industrial activities; erosion of road surfaces by road traffic and abrasion of brakes and tyres; and work in caves and mines. Others form in complicated reactions in the atmosphere of chemicals such as sulfur dioxides and nitrogen oxides that are emitted from power plants, industries and automobiles. These particles, known as *secondary particles*, make up most of the fine particle pollution. Particles produced by outdoor sources (industry and traffic) penetrate easily into indoor spaces and add to the burden of PM emitted indoors (WHO 2008, EPA 2008).

Particle pollution - especially fine particles - contains microscopic solids or liquid droplets that are so small that they can get deep into the lungs and cause serious health problems. EPA reported numerous scientific studies that have been linked to health problems, including:

- increased respiratory symptoms, such as irritation of the airways, coughing, or difficulty breathing,
- decreased lung function,
- aggravated asthma,
- development of chronic bronchitis,
- irregular heartbeat,
- nonfatal heart attacks, and
- premature death in people with heart or lung disease (EPA 2008).

The term “asbestos” designates a group of naturally occurring fibrous serpentine or amphibole minerals that have extraordinary tensile strength, conduct heat poorly and are relatively resistant to chemical attack. Asbestos is neither volatile nor soluble; however, small fibers may occur in suspension in both air and water. The thin fibers can be spun and woven together, and possess valuable heat-resistant properties that make asbestos suitable for insulation and other such products (EPA 2008, Maroni, et al. 1995). There are two kinds of asbestos. The serpentine variety is curly. Chrysotile asbestos, most commonly used for industrial purposes, is from the serpentine family. Other asbestos fibers, from the amphibole family, are very straight and needle-like. Amosite, crocidolite, tremolite, actinolite, and anthophyllite are amphibole asbestos varieties (WHO 2000).

The main uses of asbestos are in building materials, paper products, asbestos-cement products, friction products, textiles, packings and gaskets, and asbestos-reinforced plastics. Typical concentrations in indoor range from 1 to 200 ng/m³ (Maroni, et al. 1995).

Asbestos is made up of thin fibres. These can break down into much smaller and thinner fibres. The smallest fibres cannot be seen with the naked eye but they can be breathed in. The fibres that are breathed in can become stuck in the lungs and damage them. This can cause scars that stop the lungs working properly (asbestosis), or it can cause cancer. The main types of cancer caused by asbestos are cancer of the lung and cancer of the lining of the lung (mesothelioma) (Godish 2000).

Radon is a naturally occurring radioactive gas that is odorless and tasteless. It is formed from the radioactive decay of uranium. Uranium is found in small amounts in most rocks and soil. It slowly breaks down to other products such as radium, which breaks down to radon (ATSDR 2007).

Radon gas can enter a home from the soil through cracks in concrete floors and walls, floor drains, sump pumps, construction joints, and tiny cracks or pores in hollow-block walls. Radon levels are generally highest in basements and ground floor rooms that are in contact with the soil (EPA 2008).

Exposure to high levels of radon may result in an increased incidence of lung diseases, such as emphysema and pulmonary fibrosis. These diseases have been seen at a higher rate than normal among underground miners who were also exposed to arsenic, silica dust, diesel fumes, and cigarette smoke. Lung disease has been reported to increase with increasing exposure to radon and cigarette smoking (Maroni, et al. 1995).

The International Commission on Radiological Protection (ICRP) has recommended that the action level for intervention in the workplace where the occupancy of members of the public is low – e.g. in offices, libraries and theatres – should be in the range 500 to 1500 Bq/m³ (Maroni, et al. 1995). The acceptable value is 400 Bq/m³ in Turkey (TAEK 2007).

2.1.1.4. Biological Pollutants

Biological contaminants include bacteria, molds, mildew, viruses, animal dander, cat saliva, house dust, mites, cockroaches, and pollen. Biological contaminants are, or are produced by, living things. There are many sources of these pollutants. Biological contaminants are often found in areas that provide food and moisture or water. For example, damp or wet areas such as cooling coils, humidifiers, condensate pans, or unvented bathrooms can be moldy. Draperies, bedding, carpet, and other areas where dust collects may accumulate biological contaminants. Some biological contaminants trigger allergic reactions, including hypersensitivity pneumonitis, allergic rhinitis, and some types of asthma. Infectious illnesses, such as influenza, measles, and chicken pox are transmitted through the air. Molds and mildews release disease-causing toxins. Symptoms of health problems caused by biological pollutants include sneezing, watery eyes, coughing, and shortness of breath, dizziness, lethargy, fever, and digestive problems (Maroni, et al. 1995, EPA 2007).

The major types of indoor pollutants, their sources and health effects were introduced. It is clear that the indoor environment needs to be managed as seriously as

the outdoor. If this does not take place, the result will be human dissatisfaction, discomfort, illness, social problems and, consequently, reduced productivity.

2.2. Importance of Indoor Air Quality in Schools

Indoor air quality is important mainly because, poor indoor air quality may cause variety of adverse health effects. Public concern about these adverse effects has increased in recent decades, beginning with episodes during the 1970s in which occupants of residences and commercial and institutional buildings reported health problems associated with their buildings (Mendell and Heath 2005). One of the most susceptible groups to air pollution is considered as children. Studies on new episodes have continued unabated, particularly in commercial buildings and schools. Problems that occur in poor indoor environments may reduce the performance of occupants in buildings (Mendell and Heath 2005).

There are many reasons that IAQ should be considered a top priority in the school environment. One reason is that children are still developing physically and are more likely to suffer the consequences of indoor pollutants. The same concentration of pollutants can result in higher body burden in children than adults because children breathe a greater volume of air relative to their body weight. Another is that children, along with teachers, administrators, custodians, and other school staff, spend a significant amount of time in schools. Students spend approximately six hours per day for 35 weeks per year in primary and secondary schools (Atlantic Health Promotion Research Centre 2003). It is therefore critical that schools provide a healthy environment for learning. There are limited studies about the relation between human performance and indoor air quality. Mendell and Heath (2005) reviewed and summarized available scientific evidence on the relationship between selected aspects of indoor environments and academic performance of students. They showed that indoor pollutants and thermal conditions might impair performance and reduce attendance. So, reducing attendance may impair learning. According to the review, indoor air quality in schools might cause health effects that directly impair concentration or memory, or cause health effects that indirectly affect learning. Mendell and Heath (2005) also investigated the scientific findings concerning direct relationships in schools or non-school indoor environments between performance, attendance, and pollutant levels. Results showed that human performance was decreased

at higher organic pollutant concentrations. An experiment that was performed in a school resulted in decreased attendance at higher NO₂ concentrations.

The other important reason for making IAQ in schools a top priority is that, the number of children suffering from asthma. It was reported that, nearly 9.3 million children under age 18 have ever been diagnosed with asthma and more than 6.5 million children currently have asthma in the US (CDC 2005). Asthma is the principal cause of school absences in the US, accounting for 20% of lost school days in elementary and high schools (Bayer, et al. 1999). Asthma is an important chronic illness of childhood worldwide, including Turkey. The prevalence of asthma in childhood throughout the world varies between 1.6% and 36.8% according to the International Study of Asthma and Allergies in Childhood (ISAAC). The prevalence of childhood asthma in Turkey varies between 3.8% and 12.9% (Öneş, et al. 2005).

A number of epidemiological studies on allergic diseases have recently been conducted in different parts of Turkey. The first epidemiological survey of allergic diseases in school children was carried out in an urban area of Ankara in 1992 (Kalyoncu, et al. 1999). The authors instructed the same survey in 1997 and 2002 in the same school in Ankara (Kalyoncu, et al. 2004). The number of students that were enrolled in these studies was 1036, 738, and 621 in 1992, 1997, and 2002, respectively. According to their reports, prevalence of asthma was 8.3%, 9.8% and 6.4% in 1992, 1997 and 2002, respectively. There was a significant decrease in the prevalence of asthma in the latest study. Kalyoncu, et al. explained that, there could be a relation between air quality and the decrease in the prevalence of asthma. They supported this idea by explaining the improvements in ambient air quality within the last 10 years in Ankara. It was reported that the use of natural gas and increasing green area affected positively the air quality. To see the importance of the prevalence of allergic diseases, especially asthma, in Turkey, a study that was performed in Edirne by Selçuk, et al. (1997) should also be considered. Selçuk, et al. employed the same questionnaire used in the Ankara study, to determine the prevalence of asthma and other allergic diseases. 5412 primary school children were enrolled in their study. Selçuk, et al., found that allergic diseases are major health problems that affect 34.2% of primary school children at some time in their life. They reported that, prevalence of asthma in 1996 was found as 5.6% (Selçuk, et al. 1997). They concluded that, allergic diseases appear as a major health problem for children both in Ankara and Edirne, Turkey.

2.3. Volatile Organic Compounds

2.3.1. Definitions

Volatile Organic Compounds (VOCs) are organic chemicals that easily vaporize at room temperature. They are called organic because they contain the element carbon in their molecular structures. VOCs include substances with widely varying physicochemical properties and are nearly everywhere in the indoor environment (Phillips 2006). These chemicals are particularly important as indoor air pollutants, because they easily enter a gaseous phase at room temperature, thereby making them potential inhalation hazards. The list of volatile organic compounds is quite extensive. Several of the more commonly known compounds are benzene, chloroform, methylene chloride, octane, toluene, terpenes, and polycyclic aromatic hydrocarbons (Maroni, et al. 1995).

The number of VOCs detected indoors is often higher than outdoors, as they are released by almost all materials, consumer products, furnishings, pesticides, and fuels. Common household items such as cleaners, waxes, paints, adhesives, cosmetics, furnishings, and combustion appliances release VOCs (Maroni, et al. 1995). VOCs can enter the indoor environment from outdoor air, from human and biological origin (animal feces, pets, indoor plants), and through the volatilization of VOCs during showering, bathing, and other uses of potable water (Phillips 2006). As of 1989, over 900 different VOCs had been detected in the indoor environment (Maroni, et al. 1995). More recently, Spengler, et al. (2001) reported that over 1000 different VOCs had been found and identified indoors. Exposure to VOCs can result in both acute and chronic health effects. Many VOCs found indoors have been determined to be human carcinogens and/or they affect the central nervous system, but they can also cause irritation in the eyes and respiratory tract. At high concentrations, many VOCs have been shown to result in kidney and liver damage (Maroni, et al. 1995).

In many scientific publications, concentration of VOCs is not reported individually, they indicate the total concentration of VOCs under the "Total Volatile Organic Compounds" (TVOCs) (Molhave, et al. 1997). TVOCs generally refers to the sum of the mass concentrations of individual VOCs, exclusive of very volatile compounds and highly reactive compounds like formaldehyde (Hodgson 1995).

Detecting VOCs individually and reporting the results is a way to understand the compounds that are presenting indoor environment, but this way do not make easy to compare the concentrations of VOCs to the other studies. To overcome this problem, TVOCs term is used. Because, the interpretation of one single parameter is simpler and faster than the interpretation of the concentrations of several dozens of VOCs typically detected indoors.

The international working group 13 of the European Collaborative Action “Indoor air Quality and its Impact on Man” (ECA-IAQ) recommended an analytical procedure to determine TVOCs concentrations (Molhave, et al. 1997). The VOCs are sampled on Tenax TA, subsequently thermally desorbed and separated on a deactivated non-polar GC column (stationary phase: pure methyl-silicone or methyl-silicone with addition of not more than 8 % of phenyl-silicone). All compounds found with retention times between n-hexane and n-hexadecane have to be considered. This definition of an “analytical window” differs from the definition given by the WHO which is based on the range of boiling points (50–100 °C to 240–260 °C) (Maroni, et al. 1995). Based on individual response factors, as many VOC as possible should be quantified, including at least the 64 compounds listed in the ECA-IAQ recommendation and those representing the 10 largest peaks. The concentrations of unidentified compounds are determined using the response factor of toluene. The sum of the identified and unidentified compounds is defined as the TVOCs concentration.

2.3.2. Sources

Volatile organic compounds are ubiquitous in the indoor environment. The number of VOCs detected in indoor air is usually higher than in outdoor air and has continuously been increasing over the past decade (Maroni, et al. 1995, Yu, et al. 1998). It is difficult to distinguish the origin of indoor-air VOC because there are a great number of possible sources and each single compound may emanate from more than one source, including those outdoors (Johansson 1999).

Major sources are construction materials, furnishings, cosmetics and textiles, paints, carpets, architectural finishes, insulation, fabrics and paper, varnishes and solvents, adhesives, cleaning compounds, and combustion by-products. Combustion,

particularly tobacco smoking, but also photocopying or laser printing on paper, strongly influences the indoor concentrations of VOCs (Righi, et al. 2002, Khoder 2006).

Studies have been performed to find out the relation between VOCs emission and the indoor sources. Building materials that are widely used in homes, schools, and offices, are studied to detect the emissions of VOC. Polymeric materials are used widely in buildings; for construction, decorating and furnishing of homes, offices, schools and other non-industrial work places. VOC emissions from polymeric materials can be subdivided into two main groups: (i) emission from solid and cured materials, e.g. vinyl floorings and polymeric foam insulants; and (ii) emission from liquid (wet) materials, e.g. paints and wax polishes. A wide range of VOCs are emitted from vinyl/PVC floorings. These include plasticizers, solvent residues and their secondary reaction products. In the study by Yu and Crump (1998), TVOC emission rates varied from ca. 100 $\mu\text{g}/\text{m}^2\text{h}$ to more than 20,000 $\mu\text{g}/\text{m}^2\text{h}$ for less-than-two-year-old materials. Alkanes, aromatics, alcohols, ketones and esters were detected. Wall and floor adhesives emitted VOCs up to $\sim 300 \text{ mg}/\text{m}^2\text{h}$ tested after 24 hours.

Adhesives are widely used in architectural materials. The applications areas of adhesives can be summarized as bonding of carpets, vinyl floors and subfloor assemblies, and miscellaneous architectural applications. In residential buildings, especially homes, offices and schools, adhesives can be thought as a considerable source of VOCs due to the application area. Girman, et al. (1986) investigated the emissions of VOC from a broad range of architectural adhesives with indoor applications. They selected 15 both solvent- and water-based, that are used to construct and finish interiors of buildings. In the study, adhesives were applied to an inert substrate and dried for 7 to 14 days and vacuum extraction and cryogenic trapping of volatiles with analysis by gas chromatography/mass spectrometry were used for qualitative determination of emissions of VOC. The study showed that, the major compounds emitted by the adhesives were toluene, styrene, and a variety of cyclic branched and normal alkanes.

Another important material that is used in buildings is carpets. Carpets are important sources for emissions of volatile organic compounds. Especially fitted wall-to-wall carpets have significant effects on the indoor air quality. These fitted carpets are mostly used in office and also in school buildings especially in kindergardens. The materials that are commonly used to fix the carpets on the floor are water-based adhesives. An important study was carried out about determining the whether the

adhesives are sources of VOCs (Augustin, et al. 2000). In a series of investigations it has been established that in many cases the adhesives used were the primary cause of complaints. Volatile organic components from water based adhesives have a major influence on the indoor air quality. The emissions of these compounds are a major problem of indoor air pollution.

Finishing varnishes, a typical type of oil-based varnishes, are widely used to furnish interior walls and ceilings to prevent water seepage from such surfaces. Kwok, et al. (2003) performed a study to investigate VOC emissions from interior architectural coatings. In the study, a small dynamic environmental chamber with controlled temperature, relative humidity and air exchange rate was used to measure the emissions from a finishing varnish. Four different substrates (aluminium, plaster, gypsum and plywood) were used in the experiment. A finishing varnish was applied to four different substrates. It was reported that four major VOCs, including toluene, ethylbenzene, m,p-xylene and o-xylene, were identified and quantified in the varnish emissions.

Polishes are chemicals designed to shine furniture. Furniture polish may contain one or more of the following substances: nitrobenzene, petroleum distillates, phenol, and diethylene glycol (Guo, et al. 2001). Thus, these compounds can be detected in indoor air of homes, offices also schools because of present of furniture. Guo, et al. studied emission of volatile organic compounds from the different kind of furniture polish. They developed an environmental test chamber with controlled temperature, relative humidity, and airflow rate. They constructed TVOC concentration-time profiles. Headspace analysis indicated that the concentrations of TVOC for different polishes were between 41.25 and 10.60 mg/m³.

Construction materials are also one of the important sources of VOCs. Composite wood products are used in all aspects of construction, and are used in everything from furniture to cabinets to shelving. Especially in school buildings and libraries cabinets and shelving are made of composite wood products. Also, in modern housing, a majority of indoor surfaces are made from composite wood materials. Wood products such as furniture, cabinets and building materials may emit a variety of VOCs into the indoor air environment (Guo, et al. 2002). Glues and resins are used in composite wood materials in order to bond wood fibres together into a panel which are the sources of VOCs. Research identified that, formaldehyde, acetone, hexanal, propanol, butanone, benzene and benzaldehyde are the major VOCs emitted from a particleboard. Also from plywood, formaldehyde, terpenes, aromatic hydrocarbons and

aliphatic hydrocarbons were the main VOCs emitted (Guo, et al. 2002). A study was performed by Guo, et al. (2002) to investigate VOC emissions from the press wood products. They worked on three different types of widely used pressed wood products: plywood, particleboard and hardboards. Experiments were designed to generate TVOC concentration data from newly applied pressed wood products under controlled experimental conditions in an environmental chamber. The results showed that the maximum TVOC value ($28.5 \mu\text{g}/\text{m}^3$) was observed approximately after 1 day, and declined within 9 days to the 17% of the maximum value for plywood products. For particleboard, the maximum TVOC value ($154 \mu\text{g}/\text{m}^3$) was reached within 21 h, and decreased rapidly to 4.9% of the maximum after 165 h. The TVOC concentration increased to the maximum value of $408 \mu\text{g}/\text{m}^3$ within 24 h, and decreased to only 2.5% of the maximum within 1 week for hardboard.

Paints are used widely in buildings to protect surfaces, and to provide a decorative finish in homes, offices, schools and other non-industrial work places. They can be found on walls, ceilings, furniture and floors. Paints may emit significant quantities of VOCs, mainly aromatic hydrocarbons (Maroni, et al. 1995, Yu, et al. 1998). The US Environmental Protection Agency (EPA) has put paint on its top-five list of environmental hazards. Therefore, it is necessary to gain an understanding of the characteristics of VOCs emitted from paints. Paints can be categorized into two groups: organic solvent-soluble and water-soluble. Conventional organic solvent-based paints contain approximately 50% petroleum based solvents, while conventional water-based paints contain only 7% (Guo, et al. 2000).

Cleaning products are also important sources of VOC emissions (Maroni, et al. 1995). The cleaning of buildings and their contents is a major human activity that aims to promote hygiene, aesthetics, and material preservation. Nazaroff, et al. (2004) reviewed the studies about airborne chemicals resulting from cleaning products and air fresheners used in homes and in nonindustrial workplaces. Some of these chemicals are listed by the state of California as toxic air contaminants (TACs) (Nazaroff, et al. 2004). California's Proposition 65 list of species recognized as carcinogens or reproductive toxicants also includes constituents of certain cleaning products and air fresheners (Oehha 2008). In addition, many cleaning agents and air fresheners contain chemicals that can react with other air contaminants to yield potentially harmful secondary products. For example, terpenes can react rapidly with ozone in indoor air generating many secondary pollutants, including TACs such as formaldehyde. Furthermore,

ozone–terpene reactions produce the hydroxyl radical, which reacts rapidly with organics, leading to the formation of other potentially toxic air pollutants (Nazaroff, et al. 2004). General cleaning products were examined and the nature of these products was reported in William, et al. (2004) study. They demonstrated that, there were strong parallels between exposure from cleaning product/air freshener use and the broader concerns of air pollutant exposures from indoor sources. In addition to these products, a common cleaning agent is bleach. It is used in wide variety of cleaning products and many be applied directly especially in our country. Four commonly used bleach products were examined to see their effect on VOC concentrations indoor air (Odabasi 2007). VOCs were measured before, during and 30 min after product applications. According to the study, halogenated VOCs were detected and concentrations increased during product application measurements. In addition to halogenated VOCs, aromatics, aldehydes, and some oxygenated compounds were detected. The results of the study showed that, chloroform ($2.9\text{--}24.6 \mu\text{g m}^{-3}$) and carbon tetrachloride ($0.25\text{--}459 \mu\text{g m}^{-3}$) concentrations significantly increased during the use of bleach products.

In addition to all these potential sources, printers, computers and copiers can be sources of VOCs but related data are relatively limited. Berrios, et al. (2005) identified the VOCs emitted, from these sources. Mid and full-scale stainless steel chambers were used to characterize emission sources in a partitioned office environment, including personal computers (PCs), printers, copiers and office workstation components. The results showed that, emissions were 10 to 120 times higher when computers were “on” than “off”. All three computers emitted m-xylene, p-xylene, pentadecane, phenol, and toluene. Toluene was the only common VOC found in emissions from all three printers tested. Also styrene was found in two computer tests and one printer test. And all copiers emitted m-p-o xylenes, toluene, and benzaldehyde.

According to the summarized studies, the possible sources of VOCs include construction materials, furnishings, paints, carpets, adhesives, varnishes, polish, cleaning products, computers, printers, and copiers mostly exist in school buildings. These sources are generally found in school buildings. Therefore we may conclude that VOCs should be common indoors air pollutants in school buildings. Measured typical indoor air and school indoor air VOC concentrations from the literature will be presented in sections 2.5 and 2.6, respectively.

2.3.3. Health Effects

Over 900 different VOCs had been detected in the indoor environment before 1990 (EPA 2007). Exposure to VOCs can result in both acute and chronic health effects. Many VOCs found indoors have been determined to be human carcinogens and/or they affect the central nervous system. At high concentrations, many VOCs have been shown to result in kidney and liver damage. Acute symptoms of VOC exposure include (Maroni, et al. 1995, ECA 1997):

- eye irritation/watering
- nose and throat irritation
- headaches
- nausea/vomiting
- dizziness
- asthma exacerbation
- allergic skin reaction
- memory impairment

Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause cancer in humans. Benzene is known as a carcinogen VOC in humans. In animals, known carcinogen VOCs which have been measured indoors are carbon tetrachloride, chloroform, trichloroethene, tetrachloroethene, and 1,4-dichlorobenzene. VOCs such as 1,1,1-trichloroethane, styrene, and α -pinene are mutagens. Other VOCs such as octane, decane, and undecane are possible co-carcinogens. Although there are few risk assessments available for VOCs in indoor air, VOCs appear likely to pose a significant risk of cancer (Maroni, et al. 1995). People with respiratory problems such as asthma, young children, the elderly, and people with heightened sensitivity to chemicals may be more at risk due to indoor air VOCs.

VOCs are also thought to be related to “Sick Building Syndrome” (SBS). Sick Building Syndrome (SBS) is a term used to describe a collection of irritant and neurological effects that occur while occupants are in a building, that generally disappear when affected people are out of the building. Specific causes of SBS have not

yet been firmly identified. The most common symptoms include (Tenbrinke, et al. 1998):

- eye, nose and throat irritation;
- sensation of dry mucous membranes and skin;
- erythema;
- mental fatigue;
- headaches and elevated frequency of airway infections and cough;
- hoarseness, wheezing, and unspecific hypersensitivity; and
- nausea, dizziness.

Symptoms of high prevalence reported from various epidemiological investigations of SBS are those of sensory irritation. VOCs have been linked with sensory, pulmonary and neurologic responses. Thus, there is reason to suspect the VOCs. In the following part, the relation between SBS and VOCs is considered.

2.3.3.1. SBS and VOCs

The concentration of a pollutant indoors is very variable since several factors could affect the wide variety of potential emission sources. This could be one reason as to why there are divergent results concerning the associations between VOC and SBS. Some of the factors that affect the composition of indoor air are climate, activities, lifestyles, and different building techniques between regions (Jones 1999). In a review of the literature on VOC/TVOC and health, it was concluded that indoor air pollution most likely was a cause of health effects and comfort problems in indoor environments (Anderson, et al. 1997). It was also stated that the TVOC concept was not relevant from a health point of view. Brown, et al. (1994) summarized that no conclusions could be drawn about the VOC and TVOC concentrations in complaint buildings relative to those in established buildings (Brown, et al. 1994).

Over the years a lot of effort has been made to measure the concentrations of different organic compounds, and to identify the VOCs in indoor air. A common hypothesis was that the presence of SBS was coupled to the concentration of VOC, or the presence of specific compounds in the indoor environment. Several studies concerning the relation between SBS and levels of VOC have been made. However, up

to today no straightforward evidence of such an association has been found (Jones 1999, Brown, et al. 1994).

Mendell (1993) conducted a review of the epidemiological literature related to SBS. In reviewing 32 studies, he found consistent findings for an association of SBS symptoms with air conditioning, carpets, and more workers in a space, video display use, and ventilation rates at or below 10 liters/second /person. With specific causes unidentified, Mendell stressed the importance of using prudent design, operation, and maintenance practices to prevent sick building symptoms.

Investigators who study indoor reactive chemistry suggest that the degradation products of VOCs may be responsible for the reported SBS symptoms (Wolkoff, et al. 2000, Wolkoff and Nielsen 2001, Weschler 2004). These reactions include ozone/terpene reactions with propagation of hydroxyl radicals and reactions on indoor surfaces such as ozone interacting with carpet. The impact that the products of indoor chemistry can have on building occupants has also been studied on a physiological level (Weschler 2004).

Tenbrinke, et al. (1998) reported a new approach for using VOC exposure metrics as predictors of SBS. The authors were able to confirm a link between exposure to low level VOCs and SBS symptoms. Apte and Daisey (1999) used the methodology developed by Tenbrinke to identify an association between mucous membrane symptoms and photocopiers. Apte and Daisey also identified a relationship between sore throat symptoms and fresh paint.

Wolkoff, et al. (1997) addressed the question of whether the relevant indoor pollutants were measured. Often the more unreactive compounds were measured and relations to SBS were looked for. Maybe it is the more reactive compounds that are responsible for the health complaints and should be measured as well (Wolkoff, et al. 2001). These reactive compounds were shown to be more irritating than their precursors. Generally, these more reactive species are more difficult to sample. Furthermore, people might not even be aware of their existence, and those could be the compounds responsible for the health complaints reported.

2.3.4. Sampling Techniques

There are three basic approaches for analysis and determination of VOCs in indoor air. These differ with regard to the amount of work involved and the degree of information they provide. The first approach is *direct-reading instruments*. In this principle, chemical or biological detection system can be used and this system does not separate the mixture into its individual components. In the second approach, the components of a chemical mixture are separated, summed the instrumental responses for the individual compounds, although no identification is accomplished. Following the third approach, the constituents of the mixture are separated to permit an identification of individual compounds (ECA 1997).

Direct-reading instruments are easy to use. They are portable and provide a real-time signal which makes it possible to detect rapid concentration changes. Direct-reading instruments do not only respond to VOCs but also to other organic compounds, especially to VVOCs. As the instruments are calibrated with only one compound, the signal represents all compounds of the mixture as an equivalent of this compound. The output signal gives no information about the qualitative composition of the mixture (ECA 1997).

In many cases the information obtained from direct-reading instruments is insufficient because details are needed on individual organic compounds. To fulfill this need, the chemical mixture has to be separated into its constituents. Most VOC analyses of indoor air are carried out using sampling on a sorbent and subsequent separation by gas chromatography (GC). However, if special attention is paid to specific classes of VOCs, analytical techniques other than GC may be used. As an example, aldehydes are frequently determined using high-performance liquid chromatography.

In the following section, information is given on the general steps that are needed in separation procedure:

The complete procedure to analyze VOCs in indoor air generally includes the following steps: (a) sampling, (b) sample storage, (c) sample transfer to the analytical system, (d) separation, and (e) detection and quantification of individual VOCs.

Sampling: Air sampling can mainly be divided into two major categories: Active sampling and diffusive (passive) sampling. While active sampling is based on the pumping of air through/over the sampling medium, the transport of analyte molecules to

the surface of a passive sampling device relies only on diffusion. The sampling time is different for these two sampling methods, whereas active sampling generally extends over periods of minutes to hours; passive sampling is mostly covering hours or days. Typically, the sorbents used for sampling are identical for the two methods (Vogel, et al. 2005).

There are a lot of materials that can be used for adsorption of VOC. They can be divided in three categories - inorganic materials, carbon based adsorbents, and organic polymers. The inorganic materials often have high affinity to water and are therefore excluded in most cases.

The carbon-based adsorbents could be sub-classified into activated carbon, carbon molecular sieves (Carboxen), and graphitized carbon blacks (Carbotrap). Sampling with activated carbon can cause irreversible adsorption, degradation of analytes, and adsorption of water. High desorption temperatures were also required for some compounds. The carbon molecular sieves have affinity to water and in some cases low recovery of reactive analytes, and the graphitized carbon blacks have incomplete recovery of terpenes, which excluded them as suitable adsorbents (Pommer, et al. 2003, Dettmer, et al. 2002).

The porous organic polymers are a large group of adsorbents with different surface areas and polarities. These polymers are mostly very pure materials but have some drawbacks, e.g. limited temperature stability and artefact formation. The mostly used porous organic polymer is Tenax TA which is best evaluated sorbent for VOC sampling (Dettmer, et al. 2002). Tenax TA is also the adsorbent used in the present thesis.

Tenax is not suitable for sampling highly volatile organics. It was reported that, Tenax is suitable for sampling volatile compounds with 7-26 carbons or 6-14 carbons and Tenax TA can be used for quantitative sampling down to C5 (Pommer, et al. 2003).

Sample transfer: Once the VOCs are collected on the sorbent, the sample is transported to the laboratory for analysis. There are essentially two methods for the sample transfer: **(i)** solvent extraction of the trapped VOCs from the sorbent and injection of an aliquot of the extract into a gas chromatograph (GC) and **(ii)** thermal elution of adsorbed VOCs from the sorbent by means of a pure carrier gas, usually helium. In this latter case the desorbed compounds are re-concentrated in a cryotrap from which they are flash heated directly into a GC column. Using thermal elution all

compounds collected from an air sample are available for one analysis. Therefore, thermal elution is the most sensitive method and most often applied.

Separation: A GC column is used to separate the collected VOCs. The proper selection of the column as well as the temperature program is crucial as they influence the number of VOCs that can be identified by retention times or subsequent mass spectrometric analysis.

Detection and quantification: To detect the individual VOCs, different detectors may be used such as flame ionization detector (FID), an electron capture detector (ECD) or a mass spectrometer (MS). Most FID procedures that have been described in studies of VOCs in indoor air typically quantify only about 50 VOCs out of the many more present. The use of a combination of two GC columns of different polarity and/or the use of both an FID and an ECD permit a more reliable identification of a broader spectrum of individual VOCs. Although an MS has the advantage of providing more specific information on individual VOCs, even with a GC/MS combination not usually all compounds detected in a sample can be identified, and hence, quantified.

2.4. Formaldehyde

2.4.1. Definitions

A specific organic compound that is frequently found in indoor air is formaldehyde. It is unique because the carbonyl is attached directly to two hydrogen atoms. Formaldehyde can react with many other chemicals, and it will break down into methanol (wood alcohol) and carbon monoxide at very high temperatures. Formaldehyde is a colorless gas. At elevated concentrations it has a strong, pungent odor and can be irritating to the eyes, nose, and lungs. Although formaldehyde is a gas at room temperature, it is readily soluble in water, alcohols, and other polar solvents, but has a low degree of solubility in non-polar fluids. On condensing, it forms a liquid with a high vapor pressure (boiling at -19°C). Because of its high reactivity, it rapidly polymerizes with itself to form paraformaldehyde (Godish 2000).

Although formaldehyde is a volatile organic compound it is not detected by gas chromatographic methods applied to VOC analysis (Godish 2000). Chemical analysis for formaldehyde involves direct extraction from solid and liquid samples while absorption and/or concentration by active (filtration) or passive (diffusion)

sampling is necessary for air samples. A variety of absorbants is available. The most widely used methods of analysis are based on photometric determination. Low concentrations in air can be detected, after appropriate absorption, by means of high performance liquid chromatography (WHO 1989).

Because formaldehyde is one of the most dominant VOCs indoors and its special characteristics cited above, it is generally treated separately in the literature. Typical concentrations for formaldehyde are <10 ppbv for ambient air and 0.02-0.3 ppm for residential indoor air (Godish 2000). The most common human health effect of formaldehyde exposure is eye irritation, which occurs at concentrations of 0.01 to 2.0 ppm (Godish 2000). Other health effects include asthmatic and respiratory reactions, headache, and fatigue. Based on available evidence, the U.S. EPA, Occupational Safety and Health Administration (OSHA), and International Agency for Research on Cancer (IARC) have listed formaldehyde as a Class 2A (suspected human) carcinogen (Godish 2000).

2.4.2. Sources

Formaldehyde is naturally produced in very small amounts in our bodies as a part of our normal, everyday metabolism and causes us no harm. It can also be found in the air that we breathe at home and at work, in the food we eat, and in some products that we put on our skin. A major source of formaldehyde that we breathe every day is found in smog in the lower atmosphere. Automobile exhaust from cars without catalytic converters or those using oxygenated gasoline also contain formaldehyde. At home, formaldehyde is produced by cigarettes and other tobacco products, gas cookers, and open fireplaces.

Many materials and products emit formaldehyde. However, emissions studies have shown that building materials, particularly composite wood products, are likely the greatest contributors to formaldehyde in indoor air (Godish 2000). Sources that influence indoor levels of formaldehyde can be divided into two broad categories: combustion and off-gassing. Combustion sources include cigarettes and other tobacco products, and open fireplaces. Off-gassing sources include wood products such as particle board and other building materials made with adhesives containing formaldehyde as well as some varnishes, paints, carpeting, drapes and curtains.

Formaldehyde is also used in urea formaldehyde foam insulation (UFFI). The foam can emit formaldehyde, even after completion of work, depending on factors such as processing and installation, age of foam, temperature, and humidity (Maroni, et al. 1995, EPA Formaldehyde 2007).

Kelly, et al. (1999) reported the highest emission rates for numerous composite wood products manufactured with urea-formaldehyde resin. These products commonly used in home construction, cabinetry, and furniture, displayed formaldehyde emission rates ranging from 8.6 to 1.580 $\mu\text{g}/\text{m}^2/\text{hr}$. Over half of the urea-formaldehyde products tested had emission rates between 100 and 200 $\mu\text{g}/\text{m}^2/\text{hr}$. A covering over the wood such as a paper laminate, melamine laminate, or vinyl coating substantially reduced the emission rates to levels at or below 55 $\mu\text{g}/\text{m}^2/\text{hr}$ for all products tested. Composite wood products designed for outdoor use are made with phenol-formaldehyde resin. When tested, these products emitted 4.1 to 9.2 $\mu\text{g}/\text{m}^2/\text{hr}$ formaldehyde, a substantial reduction from the urea-formaldehyde resin products. Coated products and phenol-formaldehyde resin products are preferred alternatives to urea-resin products (Kelly, et al. 1999).

Laminate flooring is also a possible source of formaldehyde emission. Some laminate flooring may emit small quantities of formaldehyde at 23°C (Wiglusz, et al. 2002). Wiglusz, et al. studied the emission of formaldehyde concentrations at different temperatures from two different types of laminate flooring which are commonly available in the European market. One type of laminate flooring was with particleboard as substrate and the second one was with high density fiber (HDF). The laminate flooring tested did not show formaldehyde emission at the temperatures 23 and 29°C. Results were obtained when temperature increased at 50°C. Type 1 showed a high initial emission of formaldehyde at the rate of 0.410 $\text{mg m}^{-2}\text{h}^{-1}$ which rapidly decreased over the following days. The initial emission from Type B was about 14 times lower. Increase of the temperature to 50°C caused the emission of formaldehyde mainly from Type 1 laminate flooring. It was concluded as the source of the emission might be the particleboard substrate but also perhaps the laminate.

Formaldehyde emissions are greatest when building materials are new, and it takes years to complete the off-gassing. Investigators found statistically significant higher formaldehyde concentrations in newer homes than older homes (Air Resources Board 2005). Park, et al. (2006) studied monitoring organic compounds during three years (2000-2003) in new and older homes. In 2000 (July–October) the mean concentration for old homes was 88 $\mu\text{g}/\text{m}^3$, for new homes it was 134 $\mu\text{g}/\text{m}^3$. The

following three years, there was a definite tendency for levels of formaldehyde to decrease in the new homes, however the levels of the older homes showed that no significant decrease during the whole period.

The possible sources of formaldehyde include composite wood products, varnishes, paints, carpeting, curtains, furniture, and laminate flooring which are generally found in school buildings. Thus, formaldehyde should be common indoor air pollutants in school buildings.

2.4.3. Health Effects

Formaldehyde can cause effects that alter the health of persons exposed. It is possible to distinguish the appearance of different effects according to the duration and intensity of exposure. The nature of the effects will therefore be different depending whether the exposure was a single short-term exposure, also called acute exposure, or whether it was a repeated long-term exposure of a chronic nature (Carrier, et al. 2004).

The symptoms displayed after short-term exposure to formaldehyde are: irritation of the mucous membranes of the eye and upper respiratory tract (nose and throat). The related symptoms are tingling, redness or burns to the nose and throat, nasal discharge and watery eyes. These symptoms are generally negligible to slight for formaldehyde concentrations below 1 ppm. They can become bothersome and even intolerable at higher concentrations mainly when they exceed 2 to 3 ppm (Maroni, et al. 1995).

In the case of direct skin contact, formaldehyde may produce skin lesions such as irritation, irritant contact dermatitis and allergic contact dermatitis. The symptoms are itching, tingling and redness. Skin sensitization is likely to appear after contact with aqueous solutions of formaldehyde at concentrations equal to or greater than 2 %, (IPCS 1989). When someone is sensitized, skin allergy (erythema) symptoms may occur at every contact with solutions of increasingly lower concentration (starting at 0.5% formaldehyde) (IPCS 1989). These effects are easily avoidable by protecting exposed skin for example, by wearing gloves.

In rare cases, formaldehyde causes sensitizing or allergic type changes in lung function (Maroni, et al. 1995). These are manifested by a decrease in lung capacity and by asthma attacks likely to recur at decreasing concentrations. These effects were observed with asthmatic and non-asthmatic subjects exposed to more than 2 ppm

(Carrier, et al. 2004). Nevertheless, there is no consensus in scientific literature that asthmatics have a more severe reaction to formaldehyde exposure than non-asthmatics.

The allergenic effect of formaldehyde can be worsened by the presence of particles or dust (for example, wood dust), that trigger bronchial reactions even at concentrations below 2 ppm. Between 12 and 25 mg/m³ symptoms become severe and it becomes difficult to breathe normally (Maroni, et al. 1995). Pulmonary tissue and the lower airways are affected at concentrations of 6-40 mg/m³. A number of studies point to formaldehyde as a potential factor predisposing certain groups, particularly children, to respiratory tract infections (Maroni, et al. 1995).

In the case of occupational exposure over several years, formaldehyde has been related to causing cancer of the nasopharynx. Furthermore, the International Agency for Research on Cancer (IARC) has classified it as a human carcinogen since June 2004 (IARC 2006). As for other types of cancers (of the sinuses, oro- and hypopharynx, pancreas, larynx, lung, brain and leukemias), epidemiological studies have not established with certainty any cause-effect relationships with formaldehyde (IARC 2006).

As with many other chemical substances that affect human health, the extent of the effects of a given concentration varies from one person to the next and in a given individual over time. The effects attributed to exposure to formaldehyde are not specific. Many factors can induce the same ailments. Irritation of the eye and upper respiratory tract can also be caused by other chemical substances, particles and dusts, dry air, tobacco and a lack of sleep, to mention only a few examples (Carrier, et al. 2004).

2.4.4. Sampling Techniques

2,4-dinitrophenylhydrazine (2,4-DNPH)-coated silica gel cartridges have been used by numerous investigators since 1980 for sampling formaldehyde in ambient air (Levart, et al. 2001, Marchand, et al. 2006, Rivelino, et al. 2006, Hanoune, et al. 2006, Park, et al. 2006). The most commonly used technique is based on reacting airborne carbonyls with 2,4-DNPH coated on an adsorbent cartridge.

Organic carbonyl compounds (aldehydes and ketones) with DNPH-coated silica gel cartridges in the presence of a strong acid, as a catalyst, to form a stable color hydrazone derivative according to the reaction shown in Figure 2.1.

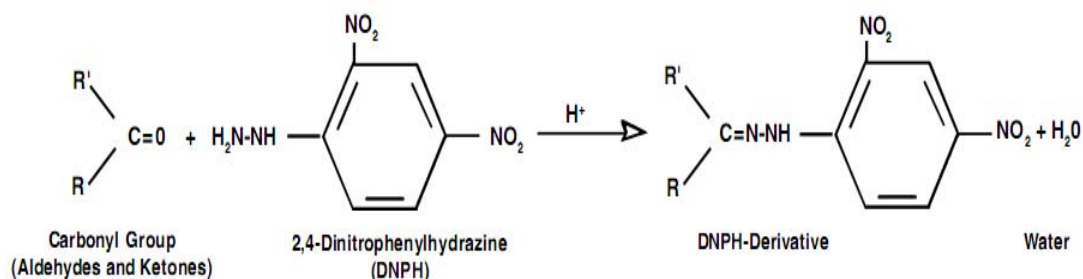


Figure 2.1. Reaction of 2,4-Dinitrophenylhydrazine with carbonyl group
(Source: USEPA 1999b)

In the reaction, R and R' are organic alkyl or aromatic group (ketones) or either substituent is a hydrogen (aldehydes). The reaction proceeds by nucleophilic addition to the carbonyl followed by 1,2-elimination of water to form the 2,4-diphenylhydrazone derivative followed by separation and analysis of the hydrazone derivative by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

2.5. Typical Indoor VOC and Formaldehyde Concentrations

Understanding the importance of the indoor air quality and VOCs as indoor air pollutants, studies have been carried out on registering the concentrations of selected pollutants. Most of the studies aimed at, investigating the ratio of the indoor/outdoor pollutant concentrations (Girman, et al. 1999, Khoder, et al. 2002, Rehwagen, et al. 2003, Serrano, et al. 2004, Petronella, et al. 2005, Srivastava, et al. 2006, Marchand, et al. 2006, Rivelino, et al. 2006). Obtaining a relation between seasonal variation and pollutant concentrations also was targeted (Rehwagen, et al. 2003, Adgate, et al. 2004, Posniak, et al. 2005). In addition, most of them focused on the relation between pollutant concentrations and the occupant symptoms (Anderson, et al. 1997, Jones 1999, Wargocki, et al. 1999, Wolkoff, et al. 2000). In this part, some of the studies that were

performed on VOC concentrations of indoor environments (also in outdoor environments) are summarized.

Indoor concentrations of pollutants generally exceed the outdoor burden, which might be responsible for many adverse health effects as people normally spend most time indoors. A study was performed in apartments in the city of Leipzig, Germany to find out the ratio of the indoor/outdoor air VOC concentrations and their seasonal variations (Rehwagen, et al. 2003). VOC measurements were carried out between 1994 and 2001. A total of 1499 indoor VOC measurements were carried out in apartments in the city of Leipzig, as well as 222 measurements of outdoor air. The indoor and outdoor VOC concentrations were compared. The annual median values of 30 VOC sum concentrations clearly indicated a lower pollution of the outdoor air. The median TVOC values were 138.12 and 14.55 $\mu\text{g}/\text{m}^3$ for indoor and outdoor environments, respectively. The ratio of indoor to outdoor for 30 VOC sum concentrations was found approximately as 10. This result openly supported that, indoor concentrations of VOC generally are higher than outdoor concentrations. The measurements were carried on during winter and summer. According to the results, median values of VOC concentrations were higher in winter and lower during summer. In the study, the maximum median TVOC value was obtained in January as approximately 300 $\mu\text{g}/\text{m}^3$, and minimum median TVOC value was obtained in August as approximately 150 $\mu\text{g}/\text{m}^3$ (Rehwagen, et al. 2003).

Environmental Protection Agency has performed a study under the Building Assessment Survey and Evaluation (BASE) title (Girman, et al. 1999). In the study, VOCs were measured in indoor and outdoor air in 56 randomly selected public and private office buildings across USA. between 1995 and 1998. The results showed that a broad range of VOCs present in the air inside office buildings. Forty-eight VOCs were measured indoors at quantifiable concentrations. All detectable VOCs had median indoor/outdoor concentration ratios greater than one. Eight VOCs (acetone, toluene, m- & p-xylenes, o-xylene, n-decane, n-undecane, n-dodecane and nonanal) were detected in all indoor samples (Girman, et al. 1999).

Righi, et al. (2001) measured formaldehyde and other VOCs including benzene, toluene and xylenes, in the libraries of the University of Modena and Reggio Emilia during the winter of 1998. Result of the study showed that formaldehyde levels ranged between 5-30.7 $\mu\text{g}/\text{m}^3$, and TVOC concentrations ranged from 203 to 749 $\mu\text{g}/\text{m}^3$. All

the individual VOCs were found in all libraries except for toluene, which was below the detection limit ($0.33 \mu\text{g}/\text{m}^3$) in one of the libraries. (Righi, et al. 2002).

Although there are some studies about exposures to VOC, information regarding indoor and ambient concentrations of VOCs is limited in terms of the number and types of compounds measured, the spatial and temporal variation of concentrations. Jia, et al. (2008) carried out the study to characterize the distribution and variability of VOCs across a gradient of suburban, urban and industrial communities in southeast Michigan, US. They randomly selected 159 residences (65 in suburban, 35 in urban and 59 in industrial communities). The sampling period was summer 2004 and winter 2005 for suburban and urban residences, and fall 2004 and spring 2005 for residences in industrialized city. Passive thermal desorption tube sampling was used for VOC sampling. Indoor sampling was conducted usually in living rooms. According to study results; 46 VOCs were detected outdoors, 29 of which were detected in the most of the samples. VOCs with the highest concentrations were benzene (median seasonal concentrations $0.7\text{-}1.4 \mu\text{g}/\text{m}^3$), toluene ($0.8\text{-}3.7 \mu\text{g}/\text{m}^3$), p,m-xylene ($0.7\text{-}2.7 \mu\text{g}/\text{m}^3$) and carbontetrachloride ($0.7\text{-}1.2 \mu\text{g}/\text{m}^3$). Spatial variations showed that, VOC levels in the three environments were generally ranked as Industrial>Urban>Suburban. For many compounds (chloroform, 1,1,1-trichloroethane, several aromatics and alkanes), ambient concentrations increased in winter. Indoors, 53 VOCs were detected, of which 38 were found in most residences. The most common VOCs included aromatics compounds, chloroform, carbon tetrachloride, alkanes and terpenes. Toluene, p,m-xylene and α -pinene had the highest concentrations based on medians, (6.8 , 3.3 and $3.2 \mu\text{g}/\text{m}^3$, respectively). It was reported that, seasonal variations in indoors were not consistent as consistent in outdoors. Based on this result, they suggested that, indoor emissions sources are the primary determinants of indoor concentrations. However, the VOCs levels ranking between three cities based on the spatial variations were the same as in outdoors. Residences in the industrial area had the highest indoor concentrations for the most of the VOCs.

2.6. Typical VOCs and Formaldehyde Concentrations in School Buildings

In schools the population density is high and poor ventilation, lack of maintenance and unsatisfactory cleaning are all thought to be common. Poor indoor air quality has been suggested as being related to the increase of allergic diseases that has occurred particularly among children and youths (Bayer, et al. 1999). As discussed in the section 2.4.3 and 2.4.4, VOCs and formaldehyde have adverse health effects and especially children are at more risk. In addition, VOCs are suspected as one of the causes of Building Related Symptoms (BRS). For these reasons, the most commonly measured pollutants in schools are VOCs and formaldehyde. In this part, the studies that were performed about VOCs and formaldehyde analysis in school buildings from different countries are summarized to take an idea about the concentrations in school buildings.

Norback, et al. (1990) studied VOCs and formaldehyde concentrations in classrooms in Sweden. They collected data between May 1982 and May 1986 in six classrooms. They collected VOCs using charcoal sorbent tubes and a tube desorbed with carbon disulfide. It was reported that, the concentration of formaldehyde was below the detection limit ($< 10 \mu\text{g}/\text{m}^3$) and the mean indoor VOC concentrations ranged from 70 to $180 \mu\text{g}/\text{m}^3$. Another study in Sweden was performed by Smedje, et al. (1997). They investigated the factors (humidity, temperature, VOCs, and formaldehyde) that affect the indoor environment. They randomly selected 38 public schools. Sampling was performed in 96 classrooms between March and June 1993. Formaldehyde was measured with glass fiber filters impregnated with 2,4-dinitro-phenylhydrazine. The filters were analyzed by liquid chromatography. VOCs were sampled on beaded charcoal sorbent tubes. The charcoal tubes were desorbed with 1 ml of carbon disulfide, and analyzed by GC/MS. Formaldehyde was below the detection limit of $5 \mu\text{g}/\text{m}^3$, mean of sum of 14 identified VOCs was $35 \mu\text{g}/\text{m}^3$. In addition, the highest concentrations of VOCs were of limonene, n-decane, toluene, and xylene.

Another study was performed in Hong Kong (Lee, et al. 1999). Five schools were selected and located residential, industrial and rural areas. In each school, the sampling was performed in one classroom. In the study, formaldehyde concentrations in classrooms were measured (November 97 to January 98). They used formaldehyde

monitoring kit for formaldehyde measurements. The Hong Kong Interim Indoor Air Quality Guidelines (HKIAQ) for formaldehyde relevant to the study was listed and the value was $100 \mu\text{g}/\text{m}^3$ (1-h average). They reported that the average formaldehyde at each school did not exceed the HKIAQ standard. The reason of this lower concentration was explained as there were no apparent sources indoors and classrooms furnishings. In addition, Lee, et al. (2002) studied indoor air quality in selected indoor environments in Hong Kong such as homes, offices, schools, and restaurants. Ten schools with air-conditioned classrooms were selected. The location of the schools was mixed as urban, industrial and residential areas. The indoor and outdoor VOC and formaldehyde concentrations were reported. Average indoor formaldehyde concentrations did not exceed HKIAQ standard of $100 \mu\text{g}/\text{m}^3$. Furthermore, these formaldehyde levels were found to be higher indoors than outdoors. The most abundant and frequently found VOCs were benzene, toluene, ethylbenzene, p/m-xylene and o-xylene among the different types of indoor environments. They reported the mean values of these compounds for air-conditioned classroom as 3.13, 17.74, 4.20, 3.30, and $1.66 \mu\text{g}/\text{m}^3$, respectively.

A review of the literature on indoor air quality examined VOCs and formaldehyde measurements in schools (Daisey, et al. 2003). According to the review, the average TVOC concentrations ranged from 0.1 to $1.6 \text{ mg}/\text{m}^3$ in different European and US schools under different conditions. The average formaldehyde concentrations in schools were ranged 0.01 to 0.35 ppm.

Adgate, et al. (2004) measured VOC concentrations in multiple locations in Minneapolis, Minnesota, USA. Fifteen common VOCs were measured at four locations: outdoors, indoors at school, indoors at home, and in personal samples. VOC measurements were obtained in winter (24 January-18 February) and spring (9 April- 12 May) 2000. VOCs were monitored using Organic Vapor Monitors (OVM) in nine randomly selected classrooms in each school. Maximum median values were reported as 4.6, 2.9, and $2.3 \mu\text{g}/\text{m}^3$ for d-limonene, toluene, and m-p-xylene, respectively. According to the results, all concentration values in winter term are higher than the values in spring term.

Indoor environmental quality in classroom was investigated in three standard primary schools in Western Australia (Zhang, et al. 2006). A year long sampling was performed. Six classrooms were selected randomly from each school. Passive sampling was used to collect formaldehyde that was analyzed by liquid chromatography. VOCs

were measured by active sampling using charcoal sorbent tubes and analyzed by a gas chromatography/flame ionization detector (GC/FID). Ten compounds were identified by comparing retention times: benzene, toluene, chlorobenzene, m,p-xylene, o-xylene, ethylbenzene, styrene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene. They reported that the VOC levels of the most of the samples were either very low or below the detectable limit. Detected VOCs had levels of TVOCs exceeding $10 \mu\text{g}/\text{m}^3$, with a maximum value of $94 \mu\text{g}/\text{m}^3$ in a visual art classroom.

Godvin, et al. (2007) performed a study on VOC concentrations in classrooms (March 31 to June 7, 2003). They randomly selected four elementary and five middle schools in a suburban school district in southeast Michigan. VOC samples were collected passively onto thermally desorbed adsorbents (Tenax GR). Collected samples were analyzed for over 80 compounds within several days of collection using automated short-path thermal desorption / cryofocusing system and a gas chromatograph/mass spectrometer (GC/MS) operating in scan mode. 64 rooms in five middle and four elemental schools were sampled. The most prevalent VOCs in schools were benzene, ethylbenzene, toluene, xylene, and limonene, and as expected, indoor concentrations usually exceeded outdoor levels. They reported that, total VOC value for indoor was $58 \mu\text{g}/\text{m}^3$ for outdoor $10.44 \mu\text{g}/\text{m}^3$. Also, they indicated that, these values were lower than levels previously reported in schools.

Some of the studies from the literature were summarized. These studies showed that, the most common VOCs which detected in school buildings were benzene, toluene, xylenes and ethylbenzenes. Also formaldehyde measurements were performed. The maximum median formaldehyde concentration was found as $38 \mu\text{g}/\text{m}^3$ (Zhang, et al. 2006). In addition, the TVOC values were reported in some studies. The maximum mean TVOC value was reported as $180 \mu\text{g}/\text{m}^3$ (Norback, et al. 1990). Furthermore, the outdoor VOC concentrations were measured and the results showed that the indoor concentrations were higher than the outdoor concentrations. Lastly, in some studies, the seasonal effects on VOC and formaldehyde concentrations were investigated. According to the results, the maximum concentrations were obtained in winter term. As a result, due to the objectives of this study, the obtained VOC and formaldehyde concentrations can be compared with these studies. By doing this, we can discuss our results based on the common results of these studies.

CHAPTER 3

MATERIALS AND METHODS

Sampling techniques and experimental procedures, quality control and assurance for the measurement of indoor air concentrations of VOCs and formaldehyde are described in this chapter. The Compendium Environmental Protection Agency (EPA) Method 17 and Method 11 were followed for determination of VOCs and formaldehyde concentrations in indoor air, respectively.

The study includes two main parts:

1. Sampling of the VOC and Formaldehyde in the schools (field study),
2. The analyses of the samples for the concentration determination (laboratory study),

The first part of the study includes the selection of certain primary schools, getting the required permissions, preparing the necessary equipments, placing the sample collection system in the schools, and the collection of the samples.

The second part of the study includes preparation of the standards for calibration of the instruments, the analysis of these samples by Gas Chromatography (GC) /Mass Spectrometer (MS)/Thermal Desorber (TD) and High Performance Liquid Chromatography (HPLC).

3.1. FIELD STUDY

3.1.1. Selection of the Schools

Three schools were selected based on their accessibility, availability, and willingness to participate, as well as their different geographic characteristics and building structure properties. The necessary official permissions for the sampling activities were obtained from the National Education Administration of İzmir. The schools are entitled as School 1, School 2, and School 3. The locations of first two schools are in the urban area and the last one is in a suburban area.

School 1: The school is located in an urban area. The street do not have a heavy traffic load, however, there are two main streets with a heavy traffic load parallel to

school street. The school is open between 07:30 and 17:30 in winter term, 08:00 and 18:00 in spring term. The school is consisted of four buildings. The main building which includes the offices and classrooms is Block-A. There is a kindergarten which is adjacent to Building-B. C- and D-buildings are adjacent buildings, but the entrances are separate. The sampling system was placed in a classroom on the second floor in Block-C. There are four classrooms on the floor. There is not a considerable air circulation on the corridor, because it is smelly probably due to the washrooms-toilets (WC) for the students on the corridor. The buildings are generally painted once a year; the last time of painting was in August 2007.

School 2: The school is also characterized as urban area. The main streets have heavy traffic load. The school is open between 07:30 and 17:30 in winter term, 08:00 and 18:00 in spring term. This school is consisted of three buildings. The sampling was performed in Block-B. The kindergarten is placed in this block at first floor. The sampling system was placed in a classroom on the second floor. There are five classrooms on the floor. At the end of the corridor there is WC for the students. It felt that there was not a considerable air circulation on the corridor. The buildings are painted once a year. The last date of painting was in summer, 2007.

School 3: This school is characterized as suburban area. The street did not have a heavy traffic load. The school is open between 07:30 and 15:00. This school is constructed of one building. The sampling system was placed on the first floor. There are three classrooms on that floor. The kindergarten classroom is on the first floor. There was a considerable air circulation on the corridor, and the classroom windows seemed to be main pathway for the air inlet. The buildings are painted once a year. The last date of painting was in summer, 2007.

General information about the schools was given in above part; in addition to these; the detailed information about the school buildings are given in Table 3.1.

Table 3.1. Building Properties

	School Name		
	School 1	School 2	School 3
Location	Urban	Urban	Suburban
Building construction year	1992	1988	2004
Occupied Floor Area(m ²)	1477	1410	1249
Exterior Wall Construction	Airbrick	Airbrick	Airbrick
Number of Occupants	1020	1760	370
Building Ventilation	Natural	Natural	Natural
Building Equipped with Cooling System	–	Air conditioner	Air conditioner
Building Equipped with Heating System	Central heating system	Central heating system	Central heating system
Type of Fuel Used	Coal	Fuel oil	Fuel oil
Past Occurrences of Water Damage	–	–	–
Current Water Leakage or Damage	–	–	–
Past Occurrences of Fire Damage	–	–	–
Frequency of painting	Once a year	Once a year	Once a year

In summary, there are common properties for School 1 and 2; selected as being located in the same region, built date and occupied floor area. School 3 is different in location area and building construction year. Also, number of occupants in this school is less than the others. The other properties listed in the table are common for three schools except the fuel type used School 1. In addition to building properties information, test space, the sampling site, properties should be considered. Table 3.2 gives the necessary properties of test spaces for the three schools.

Based on the properties of test spaces, it is clear that there are common properties for three test spaces. However, there are also distinct properties such as room area, air conditioning, and air freshener use.

Table 3.2. Test Space Properties

	School Name		
	School 1	School 2	School 3
Room type	Classroom	Classroom	Classroom
Windows area (m ²)	4.8	4.6	3.4
Percentage of openable windows	%50	%50	%50
Room area	62	56	52
No. of children	34	38	32
Area per person (m ² /person)	1.8	1.5	1.6
Floor material	Ceramic	Ceramic	Ceramic
Desk material	MDF	MDF	MDF
Shading elements material	Curtain	Curtain	Curtain
Board type	Black	Black	White
Ventilation type	Natural	Natural	Natural
Room AC unit	–	Yes	–
Last time of painting	August 2007	September 2007	August 2007
Type of painting used	Oil/Plastic paint	Oil/Plastic paint	Oil/Plastic paint
Air fresheners	No	Yes	No
Frequency of cleaning	Once a day	Once a day	Once a day
Furniture	Desks, cupboards	Desks, cupboards	Desks, cupboards
Electronic devices	TV	Computer, TV	Computer, TV

3.1.2 The Sampling Equipment

EPA TO-17 and TO-11 methods were followed to determine the concentrations of VOCs and formaldehyde, respectively. Sampling was performed actively in this study. The convenient equipments were selected based on the methods and described briefly below.

AirChek 2000 Pump: SKC AirChek 2000, a programmable personal pump, with Ni-Cd battery was used for collecting samples. The pump measures flow directly and acts as a secondary standard to maintain set flow constantly within $\pm 5\%$ accuracy. Flow range of this pump is between 5 to 3,250 ml/min. Also, sampling can be performed with flow from 5-500 ml/min with using a low flow adapter kit. In this study, one of the AirCheck 2000 pump was used for formaldehyde sampling at the high flow rate range, another one was used for VOCs sampling at the low flow rate range.

Tenax TA, Sorbent Sample Tube: Tenax TA is a porous polymer resin based on 2,6-diphenylene oxide. It has been specifically designed for the trapping of volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrices. Both the EPA and National Institute for Occupational safety and Health (NIOSH) specify the use of Tenax in their standard methods. Using thermal desorption techniques, detection of volatile organics in the ppb and ppt levels is feasible. Tenax TA, specially processed resin, is designed primarily as a trapping agent, and has very low levels of impurities. The features of Tenax TA includes high maximum operating temperature (350°C), short retention times, stable baseline after short conditioning time and relatively low temperature for effective separation. In this study, stainless steel thermal desorption tubes filled with Tenax TA (SKC 226-340) was used that contains 100 mg sorbent.

DNPH Coated Silica Gel Sorbent Sample Tube: Sorbent sample tube (SKC 226-120) is a three-section tube containing 300 and 150 mg of DNPH-coated silica gel, respectively (sample section and backup section to detect breakthrough) and a 1500 mg section of potassium iodide that acts as an ozone scrubber to eliminate atmospheric ozone interference.

Sorbent Tube Accessories: *Adjustable Low Flow Holder* allows higher flow pumps to sample in the 50 to 500 ml/min flow range, and provide for multiple tube sampling. Flow rate can be adjusted using the convenient flow adjust screw on the holder. When the pump was used for low flow application *Constant Pressure Controller* was connected to adjustable low flow holder. In addition to these, to protect the sample sorbent tubes from the external impacts *Protective tube cover* was used.

The sampling system is depicted in Figure 3.1.

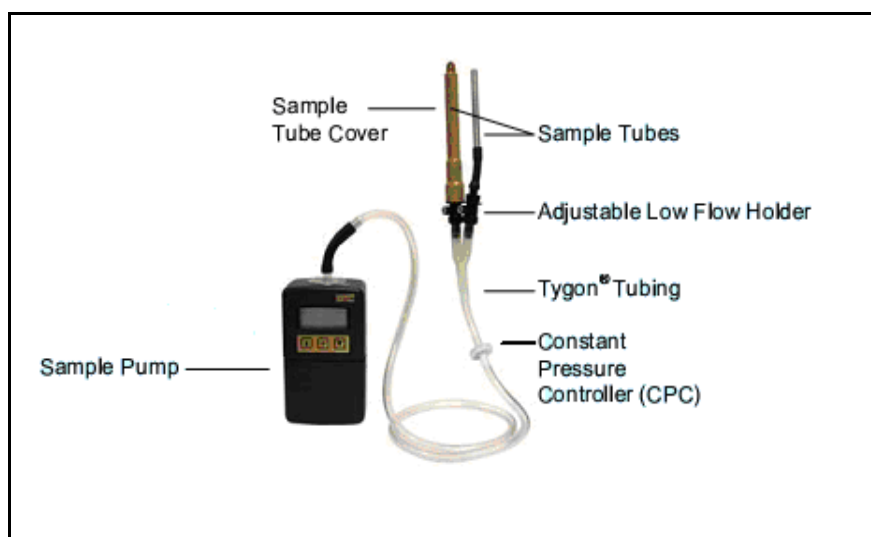


Figure 3.1. Schematic of the sampling system
(Source: USEPA 1999a)

3.1.3. Sample Collection

There were nine sampling days in each of the three schools in each season for the test spaces. Alternatively there were three sampling days for in outdoor air and other indoor spaces, i.e. kindergarten. In this investigation, collection of samples was performed in winter and spring seasons except for School 3. The winter sampling was planned for February 2008. The sampling campaign started as planned, however, as the ambient air temperature was increased over 15 C, the central heating systems in the city were stopped. Hence, the planned winter sampling was regarded as the spring sampling campaign in School 3. The winter term was from 7th to 28th of February for School 1, from 29th February to 18th March for School 2. The spring term was from 19th March to 7th April for School 3, 10th to 25th April for School 1 and from 28th April to 16th May for School 2. The schedule of the sampling program and temperature and relative humidity (RH) are given in Table 3.3 and 3.4 for winter and summer terms respectively. The indoor and outdoor temperature and relative humidity data were measured in each sampling day by an Indoor Air Quality Monitor (QUEST Technologies AQ 5001 pro). The average values of the temperature and relative humidity data for both winter and spring term were calculated (Table 3.3 and 3.4).

Based on the U.S. EPA methods, convenient sampling time and volume values are reported for determination of VOCs and formaldehyde concentrations. The appropriate sample volume is 1 and 4 liter for VOCs sampling in a period of 5-60 minutes. The flow rate can be set in the range of 10-200 ml/min. For formaldehyde sampling, short term sampling time is 5-60 minutes and the flow rates of 1,000-2,000 mL/min should be employed. The average flow rate in this study was set at 1300 ml/min for DNPH silica gel tubes and 66.7 ml/min for Tenax TA tubes. Based on these flow rates in 60 minutes sampling period, approximately 80 and 4 liters ($\pm 10\%$) air were collected in DNPH and Tenax TA tubes. These volumes were in the ranges that were reported in the U.S. EPA methods. All the sampling in weekdays was performed 11.⁰⁰ – 16.⁰⁰.

The appropriate location in the classroom was determined as 1.5 meters above the ground thinking that it would be representative for students' average height. The pumps were placed in a casing to prevent children to touch the sampler during the collection phase, and to prevent the pump noise.

Before starting the sampling, the pumps were calibrated using a flow controller (Defender 510, Bios International Corp.). The sampling system was prepared as shown in Figure 3.1 for calibration. One of the Tenax TA and DNHP silica gel sorbent tubes were designated as calibration tubes. The flow controller (Defender 510, Bios International Corp.) was connected to sampling system with tygon tubing as shown in Figure 3.2.

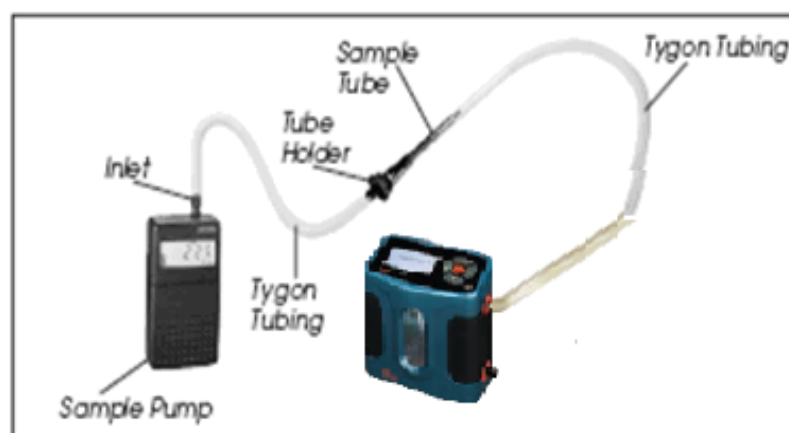


Figure 3.2. Sampling Train With a Tube Holder Connected to a Flowmeter
(Source: USEPA 1999a)

The pump for VOCs sampling was set to 66.7 ± 1.4 mL/min. The pump for formaldehyde sampling flow was adjusted to 1300 ± 34 mL/min. The sampling period was 1 hour and sample volumes calculated according to flow rates.

Table 3.3. Summary of Sampling Information for winter term

School	Date (2008)	Sample Number	Indoor Temperature (°C)	Outdoor Temperature (°C)	Relative Humidity (%)
School 1	07.02	B0702S	15.8	14.4	56.1
	08.02	B0802S	12.1	15.6	66.5
	11.02	B1102S	16.4	16.7	58.1
	14.02	B1402S	18.3	12.1	37.9
	15.02	B1502S	16.9	14.8	45.4
	20.02	B2002S	15.6	15.4	42.3
	21.02	B2102S	18.7	16.2	41.8
	22.02	B2202S	17.7	18.2	64.3
	26.02	B2602S	15.7	11.5	40.8
Average			16.4	14.9	50.3
School 2	27.02	G2702S	23.7	14.4	40.1
	28.02	G2802S	21.3	13.4	40
	29.02	G2902S	21.8	13.2	38.1
	04.03	G0403S	25.3	19.2	37.6
	05.03	G0503S	20.5	16.3	43.9
	07.03	G0703S	24.1	18	39
	11.03	G1103S	20.9	15.7	41.2
	12.03	G1203S	21.4	16.7	39.7
	13.03	G1303S	20.2	13.1	40.9
Average			22.1	15.6	40.1

Table 3.4. Summary of Sampling Information for Spring Term

School	Date (2008)	Sample Number	Indoor Temperature (°C)	Outdoor Temperature (°C)	Relative Humidity (%)
School 3	19.03	U1903S	21	19	66.4
	20.03	U2003S	21.9	19.6	64
	24.03	U2403S	21.2	18	66.2
	26.03	U2603S	25.1	19.2	64.1
	27.03	U2703S	22.2	15.1	59.7
	28.03	U2803S	22.4	15.3	60.1
	02.04	U0204S	23.1	17	59.3
	07.04	U0704S	23.2	18.7	61.1
	08.04	U0804S	20.3	24.1	47.9
Average			22.3	18.4	60.9
School 1	10.04	B1004S	22.2	21.6	54.3
	14.04	B1404S	22.1	23.4	56.6
	16.04	B1604S	24.2	18.8	39.4
	17.04	B1704S	21.7	16.6	41.3
	25.04	B2504S	25.6	18.7	39
	29.04	B2904S	22.9	20.9	44.6
	30.04	B3004S	22.5	27	52.8
	05.05	B0505S	21.4	27.3	41.5
	07.05	B0705S	20.9	31.7	58.5
Average			20.3	22.9	47.5
School 2	08.05	G0805S	20.2	27.9	40.3
	09.05	G0905S	22.6	26.3	45.4
	14.05	G1405S	24.2	31.4	50.8
	15.05	G1505S	22.4	29.4	48.3
	16.05	G1605S	22.2	30.4	47.1
	21.05	G2105S	30.3	24.4	48.7
	22.05	G2205S	26.5	18.6	36
	23.05	G2305S	26.1	23.6	33.2
	29.05	G2905S	29.6	27.3	43.6
Average			24.9	26.6	43.7

It is recommended that, Tenax TA tubes should be thermally conditioned with a high purity gas at elevated temperatures to remove any residual components using the following procedure before use. It is important that no oxygen is permitted to enter the Tenax TA material when it is at elevated temperatures. Tenax TA tubes were conditioned for at least 30 minutes at 350°C while passing at least 50 mL/min of pure helium carrier gas before first use. After then, purge time was 1 minute and desorb time was 3 minutes at 300 °C. DNPH silica gel tubes were for one-time-use only, therefore did not require any preconditioning. After conditioning, Tenax TA tubes were capped with Swagelok® fittings using PTFE ferrules. DNPH silica gel and conditioned Tenax TA tubes were wrapped with aluminum foil and placed in a storage container to protect from the light and maintain at 4°C during the transportation.

At the monitoring location, tubes were kept in their storage container during the calibration of the pumps. After calibration, the tubes were removed from the storage using clean gloves and waited some time to equilibrate the tubes temperature with ambient temperature. The sample tubes were capped off, and then attached to the sampling lines with non-outgassing flexible tubing. The sampling sorbent tubes are bidirectional, so the tubes should be placed in right direction. Air was pulled through the tube in the direction inscribed on the tube by an arrow.

Upon the completion of the sampling, the sampling tubes were immediately removed with clean gloves, recapped the Tenax TA tube with Swagelok® fittings using PTFE ferrules, then tubes were wrapped with aluminum foil and labeled the tubes for identification. The tubes were put into the storage container and transported to the laboratory. The tubes were stored in the refrigerator until analysis. Refrigeration period prior to analysis should not exceed two weeks. In this study, the Tenax TA tubes were analyzed in two days. The extraction of the DNPH silica gel tubes were performed in two weeks and analyzed in two weeks after extraction. Sample eluates are stable at 4°C for up to one month as stated in the EPA TO-11 method.

3.2. Laboratory Study

This phase of the study includes the preparation of the calibration solution standards for VOCs and formaldehyde, the condition parameters of the Gas Chromatography- Mass spectroscopy- Thermal Desorption and High Performance

Liquid Chromatography instruments for concentration determination of VOCs and formaldehyde analysis, and the extraction procedure for the DNPH silica gel tubes. In addition to these, quality assurance/quality control (QA/QC) measures such as field blanks concentrations, duplicate precisions, breakthrough volumes, and method detection limits were determined.

3.2.1. VOCs Analysis

Tenax TA sorbent sample tubes were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) instrument to determine the VOCs. Thermal desorption is a process that is used to extract the analytes (the sample to be analysed) from the sample media (i.e. the sorbent), using heat and a flow of inert gas (the carrier gas). Normally, the concentrations of VOC are low in indoor environment, and so thermal desorption tubes are often the best choice (Grote, et al. 2002).

Indoor air samples were analyzed using an automated short-path thermal desorption/cryofocusing system (Unity Markes International Limited) that sits injector/septum area of the gas chromatography/mass spectrometer. For analysis, a sorbent tube was removed from the refrigerated storage container, and then the caps were removed. In desorption, gas flow directions are reversed from sampling. The following procedures are carried out automatically before thermal desorption to ensure the integrity of this system:

Leak Test: All parts of the sample flow path should be stringently leak tested before each analysis without heat or gas flow applied to the sample tube. A leak in the system can cause loss of sample and incorrect flows through the tube trap and down the column, causing loss of sensitivity and reproducibility.

Purge air: Purge air from the tube and sample flow path at ambient temperature using carrier gas immediately before tube desorption. It helps to dry the sample and prevents analyte and sorbent oxidation thus minimizing artifact formation, ensuring data quality and extending tube lifetimes. Purge time for this study was 1 minute.

The sorbent tube assembly was then placed on the desorber carousel. The following steps are taken during desorption in the instrument. As the sample tube is heated, with carrier gas flowing through it, the sample is desorbed from the tube and flows through to the cold-trap. Tube desorption occurred in 3 minutes at 250 °C. With

the cold-trap at its lowest temperature (-10 °C hold at three minutes), the compounds will recondense onto the sorbent in the trap. This is the same amount as held originally on the sample tube, but is now much more concentrated. Typically, the cold trap sorbent is the same as in the sample tube, but it is a much smaller sorbent bed a maximum of 60 mm long and only 2 mm diameter. When desorption of the sample tube is complete, the trap is heated rapidly to 300 °C which, with the carrier gas flowing, providing a narrow injection band that enhances separation and resolution of the compounds. The automated desorption analysis for this investigation proceeded through the following steps that are summarized in Table 3.5. The GC program is then started.

The GC was equipped with a HP-VOC 60 m. 320 µm. 1.80 µm column. GC-MS parameters, optimized for the target compounds. The temperature program was summarized in Table 3.6. The run time for GC analysis, was 24.8 min. Compounds were identified using target ions (T.I.), qualifier ions (Q.I) and retention times (R.T), (Table 3.7.). The software Chemstation was used to acquire and quantify the data.

Table 3.5. Operating Conditioning for Automated Thermal Desorption System

Thermal Desorption	
Dry purge time	1 min
Inject time	1 min
Desorption temperature	250 °C
Desorption time	3 min
Cryo trap temperature	-10 °C
Cryo heat temperature	300 °C
Cryo heat time	3 min

Table 3.6. GC/ MS Operating Conditions

Temperature Program	
Column	HP-VOC 60 m. 320 μ m. 1.80 μ m
Carrier gas	Helium 1.1 ml/min. constant flow
Injection mode	Split
Initial oven temperature	40 °C
Initial oven hold	10 minutes
Oven ramp rate 1	25 °C / minute
Oven ramp final temperature 1	160 °C
Oven ramp rate 1 final time	0 minute
Oven ramp rate 2	10 °C / minute
Oven ramp final temperature 2	220 °C
Oven ramp rate 2 final time	4 minutes
Post temperature	250 °C
Post time	3 minutes
Run time	24.8 minutes

After analysis of the compounds, the VOCs concentrations were reported individually, also the Total VOCs (TVOCs) were calculated. As discussed in section 2.3.1, TVOCs is used because, interpretation of one individual parameter is simpler and faster than the interpretation of the concentrations of several dozens of VOCs typically detected indoors. However, different calculation methods used to determine the sum of VOCs. Therefore, there was a need for an agreement on the definition of TVOCs. In this study, the sum of the identified compounds were defined as the TVOCs concentration.

Table 3.7. Chemical properties of target compounds

NAME	M.W(g/mol)	R.T.(min)	T.I	Q.I
1.1.2-trichloroethane	115	17.07	97	83
1.1-dichloroethene	96.95	9.87	61	96
trans-1.2-dichloroethene	96.95	11.96	61	96
1.1-dichloroethane	98.96	12.51	63	27
cis-1.2-dichloroethene	96.95	13.44	61	96
2.2-dichloropropane	112.99	13.56	77	41
chloroform	119.38	13.74	83	85
1.1.1-trichloroethane	133.4	14.42	97	99
1.2-dichloroethane	98.96	14.63	62	27
1.1-dichloropropene	110.97	14.65	75	39
carbontetrachloride	153.82	14.8	119	117
benzene	78.11	14.84	78	77
trichloroethene	131.39	15.64	130	132
1.2-dichloropropane	112.99	15.69	63	62
dibromomethane	173.83	15.83	174	93
bromodichloromethane	163.83	15.88	83	85
cis-1.3-dichloropropene	110.97	16.44	75	39
trans-1.3-dichloropropene	110.97	16.44	75	39
toluene	92.14	16.93	91	92
1.3-dichloropropane	112.99	17.27	76	41
dibromochloromethane	208.28	17.58	127	129
tetrachloroethene	165.8	17.67	166	164
1.2-dibromoethane	187.86	17.79	107	109
chlorobenzene	112.56	18.33	112	77
1.1.1.2-tetrachloroethane	167.85	18.35	131	133
ethylbenzene	106.16	18.43	91	106
p-m-xylene	106.16	18.53	91	106
styrene	104.15	18.9	103	104
o-xylene	106.16	18.93	91	106
bromoform	252.73	19.09	173	171
1.1.2.2-tetrachloroethane	167.85	19.24	83	85
isopropylbenzene	120.19	19.31	105	120
1.2.3-trichloropropane	147.43	19.37	75	110

(cont. on next page)

Table 3.7. (cont.) Chemical properties of target compounds

NAME	M.W(g/mol)	R.T.(min)	T.I	Q.I
bromobenzene	157.01	19.67	77	156
n-propylbenzene	120.19	19.73	91	120
2-chlorotoluene	126.58	19.87	91	126
4-chlorotoluene	126.58	19.92	91	126
1.3.5-trimethylbenzene	120.19	19.89	105	120
tert-butylbenzene	134.22	20.28	119	91
1.2.4-trimethylbenzene	120.19	20.3	105	120
sec-butylbenzene	134.22	20.52	105	134
4-isopropyltoluene	134.21	20.65	119	134
1.4-dichlorobenzene	147	20.69	146	148
1.3-dichlorobenzene	147	20.78	146	148
n-butylbenzene	134.21	21.1	91	92
1.2-dichlorobenzene	147	21.18	146	148
dibromochloropropane	236.3	21.95	157	155
1.2.4-trichlorobenzene	181.45	23.49	180	182
naphthalene	128.16	23.8	128	127
hexachlorobutadiene	260.76	23.9	225	223
1.2.3-trichlorobenzene	181.45	24.27	180	182

3.2.2. Formaldehyde Analysis

For determination of formaldehyde, the DNPH-formaldehyde derivative was analyzed using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm. The HPLC system was operated in the linear gradient program mode. Acetonitrile was used as the solvent for the extraction of the sorbent tubes. The samples were returned to the laboratory in a shipping container and stored in a refrigerator at (<4°C) until analysis. The time between sampling and extraction should not exceed 2 weeks.

Extraction: Formaldehyde-free acetonitrile used to elute samples should be used only for this purpose, and stored in a carbonyl free environment. In this experiment, %

99.9 purity acetonitrile (Merck 1.00030) was used as a solvent. Sample cartridges were handled with polyethylene gloves. 5 and 10 stainless steel gas tight syringes (Agilent Gas Tight Luer Lock Valve 5183-4552 and 4451) was used to flow acetonitrile through the cartridge. Sample elution from the cartridge was collected in to 4 ml vials (National Scientific, Screw Caps with PTFE Septa, C4015-1). Contamination is most likely to occur during sample extraction. Before eluting derivatives, all glassware were cleaned by rinsing with acetonitrile, and then heated in a 60 °C vacuum oven for at least 30 minutes. The acetonitrile used to elute the DNPH derivatives is a typical source of contamination. The following steps were performed to extract the formaldehyde derivative from the cartridge.

- The sample cartridge removed from the refrigerator
- Attached the sample cartridge to stand in vertical direction (in the reverse direction of the arrow on the tube)
- Eluted the formaldehyde derivative from the cartridge sampler with 6-ml of acetonitrile.
- Collected effluent from the sampler in a 10-ml volumetric flask
- Transferred 3 ml of effluent into the 4-ml vial, and capped
- The vial was kept in the refrigerator until instrumental analysis by the instrument. Sample eluates are stable at 4 °C for up to one month.

HPLC analysis: The HPLC system (Agilent 1100 series, Japan) is assembled and calibrated as described in Section 3.2.3.1. The operating parameters are summarized in Table 3.8.

Table 3.8. Operation Conditions of HPLC

HPLC	
Column:	GL Sciences, Japan Zorbax ODS (4.6-mm ID x 25-cm, 5µm)
Mobile Phase:	60% acetonitrile/40% water, isocratic.
Detector:	Ultraviolet, operating at 360 nm.
Flow Rate:	1.0 mL/min.
Retention Time:	7.8-8.2 min (depending on temperature)
Sample Injection Volume	20 µL

3.2.3. Quality Assurance / Quality Control

3.2.3.1. Calibration Standards

Liquid standards were to be loaded onto Tenax TA sampling sorbent tubes for calibration purposes. The criteria of selecting a solvent is that; it should be pure (contaminants <10 % of minimum analyte levels) and, it should be more volatile than the target analytes. This then allows the solvent to be purged and eliminated from the tube during the standard preparation process. Methanol most commonly fills these criteria. In this investigation, methanol was selected as a solvent to prepare the calibration standards of VOC mixtures. The calibration standard solution contained 60 volatile organic compounds (LGC Promochem U-DWM-580-1). Five levels of calibration standards (0.2, 2, 10, 20, and 40 $\mu\text{g ml}^{-1}$ for VOCs) were used to prepare the calibration curves. For all compounds the linear fit was satisfactory ($R^2 > 0.99$).

DNPH – formaldehyde derivative liquid standards were purchased from the manufacturer (Formaldehyde-DNPH LGC Promochem CERE-004S). Calibration standards were prepared in acetonitrile with seven levels (0.05, 0.1, 0.2, 0.5, 1, 2, and 5 $\mu\text{g ml}^{-1}$). Each calibration standard was analyzed three times and area response was tabulated against to mass concentration injected. The results were used to prepare a calibration curve. The calibration curve was a good linear fit ($R^2 > 0.99$).

3.2.3.2. Blanks

Blank emission and artifact formation can affect method sensitivity and overall performance. Field blanks were analyzed to assess possible contamination through the sample collection and analysis process. The US EPA guidance was followed for blank emission investigation in this study. The field blank number was determined as % 10 of the total sampling number (72 sampling tubes total, Tenax TA and DNPH). The blank emissions were determined using a total eight freshly cleaned tubes half of them were Tenax TA and the rest of them were DNPH. The blank tubes were applied the same storage procedure and transportation condition. A blank tube was capped off at the sampling area, attached to the system, after a short while it was recapped, and the same transportation procedure for the sampling tubes as carried out. The analysis was performed to determine the VOC and formaldehyde concentrations in the blank tubes.

The VOC and formaldehyde amounts found in field blanks are presented in Table 3.9. Nineteen of the sixty VOCs were detected in the field blank samples. The rest of the VOCs were at below the detection limit, therefore when these VOCs were detected in the samples the FB/sample ratio was % 0. The US EPA guidance expresses that, the amount of the target compounds observed on the field blanks should not be exceed 10 % or more of the sampled tube amounts, otherwise the sampled tube data are invalidated.

The lowest concentration of analyte detectable with a stated degree of reliability is called the Limit of Detection (LOD). LOD is defined as the mean blank analyte mass plus three standard deviations. LODs for the VOCs and formaldehyde are given in Table 3.10. According to the LODs, VOC amounts in the samples were higher than LODs.

Table 3.9. VOC and Formaldehyde Amounts in Field Blanks

VOCs	Field Blank Amounts (ng)		Sampled tube amounts (ng)		%
	Mean	SD	Mean	SD	
chloroform	0.053	0.039	0.7	0.23	7.6
benzene	0.25	0.288	21.8	0.31	1.1
trichloroethene	0.002	0.003	0.31	0.23	0.6
toluene	1.304	0.588	21.9	19.6	6
chlorobenzene	0.005	0.008	0.08	0.01	5.6
ethylbenzene	0.024	0.016	0.8	0.4	3
p-m-xylene	0.039	0.028	1.04	0.57	3.8
styrene	0.118	0.075	1.1	0.6	11
o-xylene	0.044	0.071	0.63	0.34	7
n-propylbenzene	0.006	0.008	0.14	0.06	3.9
1.3.5-trimethylbenzene	0.006	0.005	0.35	0.12	3
1.2.4-trimethylbenzene	0.009	0.003	0.86	0.46	0.2
sec-butylbenzene	0.002	0.002	0.09	0.01	6.7
4-isopropyltoluene	0.016	0.011	0.6	0.2	1.4
1.4-dichlorobenzene	0.005	0.003	2.8	2.57	0.1
1.3-dichlorobenzene	0.037	0.019	1.82	0.63	0.9
n-butylbenzene	0.032	0.006	0.17	0.06	2.9
1.2.4-trichlorobenzene	0.005	0.004	0.6	0.1	2.8
naphthalene	0.052	0.013	4.4	1.5	5.3
1.2.3-trichlorobenzene	0.007	0.005	0.05	0.01	0.1
formaldehyde	0.04	0.0006	0.43	0.24	9.7

Table 3.10. Limits of Detection (LODs) for VOCs and Formaldehyde (n=5)

Components	LOD (ng)	LOD ($\mu\text{g}/\text{m}^3$)
chloroform	0.68	0.17
benzene	4.45	1.11
trichloroethene	0.05	0.01
toluene	12.3	3.07
chlorobenzene	0.11	0.03
ethylbenzene	0.29	0.07
p-m-xylene	0.5	0.12
styrene	1.37	0.34
o-xylene	1.03	0.26
n-propylbenzene	0.11	0.03
1.3.5-trimethylbenzene	0.08	0.02
1.2.4-trimethylbenzene	0.07	0.02
sec-butylbenzene	0.03	0.01
4-isopropyltoluene	0.2	0.05
1.4-dichlorobenzene	0.06	0.01
1.3-dichlorobenzene	0.37	0.09
n-butylbenzene	0.21	0.05
1.2.4-trichlorobenzene	0.07	0.02
naphthalene	0.36	0.09
1.2.3-trichlorobenzene	0.09	0.02
formaldehyde	0.04	0.007

3.2.3.3. Breakthrough Volume (BV)

One of the factors that must be considered in developing a sampling strategy is breakthrough volume for VOCs and formaldehyde. Breakthrough occurs when the absorptive capacity of the sampling media is exceeded. This term is expressed as the volume at which a significant amount of a constant atmosphere of an adsorbed compound drawn through a sorbent tube desorbs and appears in the tube effluent (MassDEP 2002).

Breakthrough volume analysis is performed to ensure that the sampling volume is adequate for the sorbent tube. The analysis was carried out based on the US EPA guidance. A second identical sampling tube was placed in series with a primary (front) tube. The pump was connected to the series tubes. Sampling was started. Sampling time was one hour for both Tenax TA and DNPH sorbent tubes and the flow rates were the same as indicated in the sampling procedures of VOCs and formaldehyde. The purpose of the backup tube is to capture compounds that pass through the primary tube because of breakthrough. Analysis of the backup tube may indicate unexpected

breakthrough or give evidence of channeling of sample through the tube because of loose packing.

If more than 5% of one or more of the target analytes is observed on any of the back-up tubes, breakthrough is shown to have occurred at that sample volume. This analysis was carried out for three times during sampling period. The amounts of VOCs and Formaldehyde on the back-up tubes were calculated and are given in Table 3.11. The results showed that target components amounts in the back-up tubes were not more than % 5 of the observed analytes in the first tubes as stated in the USEPA method

Table 3.11. Amounts of VOCs and Formaldehyde in Back-up Tubes (n=3)

Components	First tube (ng)	Back-up Tube (ng)	%
chloroform	3.5	0	0
1.1.1-trichloroethane	0.2	0	0
1.2-dichloroethane	0.6	0	0
carbontetrachloride	2.2	0	0
benzene	171	0.4	0.3
trichloroethene	1.1	0	0
dibromomethane	0.1	0	0
toluene	194.6	3.5	1.8
tetrachloroethene	2.7	0	0
1.2-dibromoethane	0.1	0	0
chlorobenzene	0.1	0	0
ethylbenzene	3.1	0.1	3.3
p-m-xylene	3.0	0.1	3.6
styrene	7.3	0.2	2.9
o-xylene	2	0	0
bromoform	0.1	0	0
isopropylbenzene	0.3	0	0
1.2.3-trichloropropane	0.03	0	0
n-propylbenzene	0.4	0	0
1.3.5-trimethylbenzene	0.5	0	0
tert-butylbenzene	0.2	0	0
1.2.4-trimethylbenzene	2	0	0
4-isopropyltoluene	0.9	0	0
1.3-dichlorobenzene	10.9	0.4	3.6
n-butylbenzene	0.8	0	0
1.2.4-trichlorobenzene	0.04	0	0
naphthalene	11.5	0.3	2.7
1.2.3-trichlorobenzene	0.04	0	0
formaldehyde	0.8	0	0

3.2.3.4. Performance Criteria for the Sampling Pump

The pumps were calibrated before each sampling. The flow rates of the calibrated pumps were recorded. At the end of the sampling, the pumps' flow rates were also recorded to observe the difference. In this study, the pumps flow rates were set at 66.7 and 1300 ml/min for VOCs and formaldehyde, respectively. USEPA TO-11 and TO-17 specify the limits for flow rate changes. The USEPA method states that, if a flow rate measured at the end of sample collection varies more than 10 % from that measured at the beginning of sample collection, then that sample is invalidated. According to our measurements, the pumps sampling flow rate differences between the beginning and at the end are valid based on the limitation with a mean \pm SD difference of $1300 \pm 5 \%$ and $66.7 \pm 4 \%$. No sample had to be invalidated due to this limit.

3.2.3.5. Method Detection Limit

Following the USEPA guidance, method detection limit (MDL) for each VOC was determined by making seven replicate measurements of a concentration near the expected detection limit (within a factor of five). The MDL was calculated as the standard deviation of the replicate determinations multiplied by 3.14, the 99 % confidence interval for $n = 7$ (from Student's *t* distribution). The criteria is defined as MDL value should be less than 0.5 ppb.

Based on a sampling volume of 4 and 80 liters for VOC and formaldehyde, respectively, MDLs for all target components were below 0.5 ppb and most were below 0.1 ppb (Table 3.12). Based on these results, it is clear that the analysis method easily met the USEPA methods MDL requirement for indoor air sampling.

3.2.3.6. Duplicate Precision

Duplicate precision measurement used in this study is the absolute value of the relative difference between two identical parallel samples (same flow rate over the same time period from with a common inlet to the sample volume). The analytical precision is expressed as a percentage as given in Equation 3.1. (USEPA 1999a):

$$\text{Analytical Precision} = \left[\frac{X_1 - X_2}{\bar{X}} \right] * 100 \quad (3.1)$$

where:

X_1 = A measurement value taken from the first of the two tubes used in precision measurement.

X_2 = A measurement value taken from the second of two tubes used in precision measurement.

\bar{X} = Average of X_1 and X_2 .

It is suggested that a replicate precision value of 25 percent can be achieved for each of the target compounds (USEPA 1999a). In this study, to calculate the replicate precision, two identical Tenax TA and DNPH tubes were used in parallel during sampling (n=3). The results show that, the agreement between the replicate precision values was within the 25 %. Table 3.13 shows the replicate values for each target compounds.

Table 3.12. Method Detection Limits (MDLs) for VOCs and Formaldehyde (n=7)

Components	MDL ($\mu\text{g}/\text{m}^3$)	ppb
chloroform	0.0157	0.0032
1.1.1-trichloroethane	0.0042	0.0008
1.2-dichloroethane	0.0221	0.0055
1.1-dichloropropene	0.062	0.0137
carbontetrachloride	0.106	0.0168
benzene	0.097	0.0304
trichloroethene	0.0496	0.0092
1.2-dichloropropane	0.0115	0.0025
dibromomethane	0.0414	0.0058
bromodichloromethane	0.0186	0.0028
cis-1.3-dichloropropene	0.0305	0.0067
trans-1.3-dichloropropene	0.0294	0.0065
toluene	0.0198	0.0052
1.3-dichloropropane	0.0141	0.0031
dibromochloromethane	0.0178	0.0021
tetrachloroethene	0.0379	0.0056
1.2-dibromoethane	0.0293	0.0038
chlorobenzene	0.0255	0.0055
1.1.1.2-tetrachloroethane	0.0117	0.0017
ethylbenzene	0.018	0.0042
p-m-xylene	0.0276	0.0063
styrene	0.0156	0.0037
o-xylene	0.0184	0.0042
bromoform	0.01	0.001
1.1.2.2-tetrachloroethane	0.0139	0.002
isopropylbenzene	0.0146	0.003
1.2.3-trichloropropane	0.0084	0.0014
bromobenzene	0.0221	0.0034
n-propylbenzene	0.0189	0.0038
2-chlorotoluene	0.0191	0.0037
4-chlorotoluene	0.0227	0.0044
1.3.5-trimethylbenzene	0.0186	0.0038
tert-butylbenzene	0.0119	0.0022
1.2.4-trimethylbenzene	0.0224	0.0046
sec-butylbenzene	0.0135	0.0025
4-isopropyltoluene	0.0156	0.0028
1.4-dichlorobenzene	0.0224	0.0037
1.3-dichlorobenzene	0.0143	0.0024
n-butylbenzene	0.0119	0.0022
1.2-dichlorobenzene	0.015	0.0025
dibromochloropropane	0.0089	0.0009
1.2.4-trichlorobenzene	0.0184	0.0025
naphthalene	0.0084	0.0016
hexachlorobutadiene	0.0124	0.0012
1.2.3-trichlorobenzene	0.0139	0.0019
formaldehyde	0.1172	0.095

Table 3.13. Duplicate Precisions for VOCs and Formaldehyde (n=3)

Components	Analytical Precision (%)
chloroform	20.6
1.1.1-trichloroethane	10.5
1.2-dichloroethane	3.3
1.1-dichloropropene	7.8
carbontetrachloride	5.5
benzene	13.3
trichloroethene	8.7
1.2-dichloropropane	12.6
dibromomethane	17.8
bromodichloromethane	8.3
cis-1.3-dichloropropene	4.9
trans-1.3-dichloropropene	5.3
toluene	16.4
1.3-dichloropropane	13.6
dibromochloromethane	9.8
tetrachloroethene	7.1
1.2-dibromoethane	6.8
chlorobenzene	10.5
1.1.1.2-tetrachloroethane	11.2
ethylbenzene	9.2
p-m-xylene	5.9
styrene	1.3
o-xylene	9.5
bromoform	1.3
1.1.2.2-tetrachloroethane	3.7
isopropylbenzene	6.5
1.2.3-trichloropropane	9.8
bromobenzene	9.5
n-propylbenzene	1.1
2-chlorotoluene	3.9
4-chlorotoluene	7.4
1.3.5-trimethylbenzene	1.3
tert-butylbenzene	1.2
1.2.4-trimethylbenzene	10.5
sec-butylbenzene	4.8
4-isopropyltoluene	15.4
1.4-dichlorobenzene	1.4
1.3-dichlorobenzene	1.2
n-butylbenzene	1.9
dibromochloropropane	8.7
1.2.4-trichlorobenzene	7.5
naphthalene	2.9
hexachlorobutadiene	12.2
1.2.3-trichlorobenzene	20.4
formaldehyde	6.8

3.3. Statistical Methods

Statistical analysis and tests were performed with SigmaPlot for Windows version 11 software. Descriptive statistics i.e., mean, maximum, minimum, standard deviation, 95th percentiles, were calculated, and the normality of the data was tested. The Shapiro-Wilk test was used to test the normality.

The Kolmogorov-Smirnov test can be applied to test whether data follow any specified distribution, not just the normal distribution. The Kolmogorov-Smirnov Test is a non-parametric test based on the maximum absolute difference between the theoretical and sample Cumulative Distribution Functions (CDFs). The Kolmogorov-Smirnov test is most sensitive around the median and less sensitive in the tails and is best at detecting shifts in the empirical CDF relative to the known CDF. As a general test, it may not be as powerful as a test specifically designed to test for normality

The Shapiro-Wilk test is specifically designed to detect departures from normality, without requiring that the mean or variance of the hypothesized normal distribution be specified in advance. This test tends to be more powerful than the Kolmogorov-Smirnov test, it will not indicate the type of nonnormality, say whether the distribution appears to be skewed as opposed to heavy-tailed (or both). The null hypothesis for this test is that the data are normally distributed. The statistic W is calculated, and the null hypothesis of a normal distribution was rejected if the calculated W statistic was less than $W_{0.05}$. The Shapiro-Wilk test provides evidence for certain types of "non-normality" it does not guarantee "normality".

Depending on the results of the normality testing, parametric or non parametric tests were applied to see whether there is a statistical difference between two groups. Two sample t-test is a parametric test which is used to determine whether the two population means are equal. The non-parametric Mann-Whitney U test (at the significance level of $p < 0.05$) was used to test whether two non-normally distributed independent samples are from the same population. (Montgomery 2007).

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents and discusses the results of VOC and formaldehyde measurements in classrooms, outdoors (school playground) and alternatively in kindergarten classrooms for each school. Descriptive statistics of the indoor and outdoor VOCs and formaldehyde concentrations are presented. TVOC indoor/outdoor ratios, and seasonal variation were also investigated.

4.1. VOC Concentrations in Classroom and Playground at School 1

The samples were collected in winter and spring terms. The sampling period was from 7th to 28th of February in winter and was from 10th to 25th April in spring term for School 1. Nine sampling days in a classroom, and three sampling days in the outdoor playground were performed.

Thirty two and 27 compounds were measured at quantifiable concentrations in indoor air sampling from School 1 in winter and spring terms, respectively. Indoor and outdoor VOC concentrations are given in Table 4.1 and Table 4.2 in winter term and in Table 4.3 and Table 4.4 in spring term for School 1.

Seventeen VOCs (benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, n-propylbenzene, 1,3,5-trimethylbenzene, tertbutylbenzene, 1,2,4-trimethylbenzene, 4-isopropyltoluene, 1,4-dichlorobenzene, n-butylbenzene, naphthalene, 1,2,3-trichlorobenzene) were detected in all indoor samples of School 1 in winter term. Eight VOCs were detected in 76 to 99 % of the samples of indoor air in this classroom, two VOCs were found in 51 to 75 %, five VOCs were found in 31 to 50 %. Seventeen VOCs were not detected in any of the samples from the classroom: 1,1,2-trichloroethane, 1,1-dichloroethene; trans-1,2-dichloroethene, 1,1-dichloroethane, cis-1,2-dichloroethene, 2,2-dichloropropane, 1,2-dichloroethane, 1,1-dichloropropene, bromodichloromethane, cis-1,3-dichloropropene, trans-1,3-dichloropropene, dibromo- chloromethane, 1,1,1,2-tetrachloroethane, bromobenzene, 2-chlorotoluene, 4-chloro- toluene, 1,2-dichlorobenzene.

Table 4.1. Summary statistics of winter term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the classroom, School 1 (n=9)

Compound Name	% Freq	Mean	Median	SD	CIM*	Min	Max
chloroform	89	0.46	0.41	0.16	0.14	0.30	0.75
1.1.1-trichloroethane	89	0.08	0.08	0.01	0.01	0.06	0.10
carbontetrachloride	89	0.64	0.67	0.24	0.22	0.36	1.02
benzene	100	16.41	16.50	6.37	5.32	7.48	29.07
trichloroethene	100	1.49	0.81	1.52	1.27	0.19	4.23
1.2-dichloropropane	33	0.10	0.10	0.05	0.44	0.07	0.14
dibromomethane	89	0.03	0.03	0.02	0.02	0.01	0.06
toluene	100	25.70	22.07	12.14	10.15	4.69	40.11
1.3-dichloropropane	56	0.26	0.26	0.09	0.15	0.14	0.36
tetrachloroethene	100	0.96	0.67	1.00	0.84	0.12	3.24
1.2-dibromoethane	56	0.04	0.03	0.03	0.04	0.02	0.08
ethylbenzene	100	2.60	2.38	1.57	1.65	0.95	5.26
p-m-xylene	100	2.05	1.81	0.78	1.24	1.42	3.17
styrene	100	0.80	0.77	0.32	0.26	0.48	1.18
o-xylene	100	1.25	1.15	0.40	0.50	0.81	1.88
bromoform	89	0.06	0.04	0.05	0.04	0.02	0.14
1.1.2.2-tetrachloroethane	44	0.17	0.15	0.12	0.29	0.07	0.30
isopropylbenzene	89	0.44	0.08	0.66	0.61	0.04	1.66
1.2.3-trichloropropane	33	0.12	0.12	0.13	1.07	0.03	0.21
n-propylbenzene	100	0.17	0.18	0.06	0.05	0.09	0.24
1.3.5-trimethylbenzene	100	0.25	0.27	0.11	0.09	0.11	0.41
tert-butylbenzene	100	0.14	0.15	0.06	0.05	0.06	0.22
1.2.4-trimethylbenzene	100	1.09	1.15	0.47	0.39	0.43	1.71
sec-butylbenzene	44	0.19	0.13	0.14	0.34	0.10	0.35
4-isopropyltoluene	100	0.31	0.31	0.17	0.15	0.11	0.52
1.4-dichlorobenzene	100	50.86	39.32	57.37	47.97	0.63	141.70
n-butylbenzene	100	0.24	0.25	0.06	0.05	0.16	0.32
dibromochloropropane	33	0.01	0.01	0.00	0.02	0.01	0.01
1.2.4-trichlorobenzene	78	0.02	0.01	0.01	0.01	0.01	0.04
naphthalene	100	3.88	2.78	2.41	2.02	1.20	7.81
hexachlorobutadiene	78	0.02	0.02	0.00	0.01	0.01	0.02
1.2.3-trichlorobenzene	100	0.01	0.01	0.01	0.01	0.01	0.04
TVOC		104.00	86.79	86.54	75.43	20.20	246.40

CIM*: % 95 confidence interval

The box plots of the indoor concentrations of eleven VOCs with the highest mean concentrations are shown in Figure 4.1. Chloroform, carbontetrachloride, trichloroethene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, isoprpylbenzene, 1.2.4-trimethylbenzene and naphthalene had the highest mean indoor concentrations as 0.46, 0.64, 1.49, 0.96, 2.6, 2.1, 0.8, 1.3, 0.5, 1.1, 3.9 $\mu\text{g}/\text{m}^3$

respectively. Also, benzene, toluene and 1,4 dichlorobenzene detected in all indoor samples and had the highest mean values as 16.4, 25.7, and 50.9 $\mu\text{g}/\text{m}^3$, respectively.

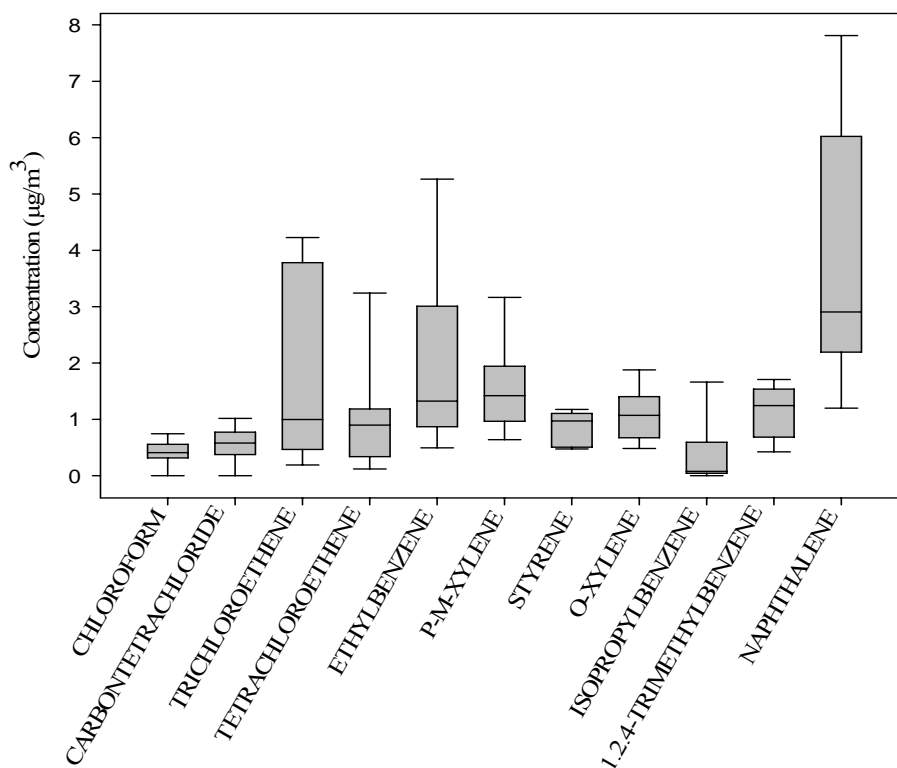


Figure 4.1. Box plots of winter term indoor VOC concentrations in School 1

The outdoor VOC concentration results for winter term are given in Table 4.2. The results showed that, compounds detected above 71% of the outdoor samples were similar to compounds detected in indoor samples. Figure 4.2 presents the comparison of indoor and outdoor mean values of twenty one VOCs with the common detected compounds ($\geq 70\%$) and the highest mean concentrations. The indoor/outdoor VOC concentration ratio gives an idea about the sources of the components. Indoor/outdoor ratios near unity (1 ± 0.5) indicate compounds that arise primarily from outdoor sources; ratios from about 1.5 to 10 indicate both indoor and outdoor sources. Ratios exceeding about 10 reveal primarily or exclusively indoor sources (Jia, et al. 2008). According to median values of twenty one VOCs, the indoor to outdoor ratios were obtained. The median indoor/outdoor concentration ratios for seven VOCs (chloroform, dibromomethane, chlorobenzene, ethylbenzene, p-m xylene, isopropylbenzene, 1,2,3 trichlorobenzene) were near or lower than one. Nine VOCs (1,1,1 trichloroethene, carbontetrachloride, trichloroethene, styrene, o-xylene, n-propylbenzene, 1,3,5

trimethylbenzene, tert-butylbenzene, 1,2,4-trimethylbenzene) had median indoor/outdoor concentration ratios between 1 and 1.5.

Table 4.2. Summary statistics of winter term VOC concentrations ($\mu\text{g}/\text{m}^3$) in outdoor, School 1 (n=3)

Compound Name	Mean	Median	SD	Min	Max
chloroform	0.37	0.40	0.03	0.28	0.42
1,1,1-trichloroethane	0.06	0.06	0.01	0.04	0.07
carbontetrachloride	0.41	0.40	0.02	0.38	0.41
benzene	12.05	13.03	1.39	11.09	14.02
trichloroethene	0.65	0.61	0.06	0.57	0.95
dibromomethane	0.03	0.02	0.01	0.02	0.03
toluene	18.73	16.10	12.14	4.69	40.11
tetrachloroethene	0.32	0.28	0.05	0.25	0.51
1,2-dibromoethane	0.03	0.03	0.01	0.02	0.04
chlorobenzene	0.04	0.03	0.01	BDL	0.05
ethylbenzene	1.75	2.46	1.00	1.09	3.16
p-m-xylene	1.78	1.78	0.18	1.65	1.90
styrene	0.45	0.39	0.08	0.34	0.62
o-xylene	1.15	1.09	0.08	1.04	1.28
bromoform	0.03	0.02	0.01	0.01	0.04
isopropylbenzene	0.08	0.07	0.01	0.07	0.10
n-propylbenzene	0.17	0.16	0.02	0.15	0.17
1,3,5-trimethylbenzene	0.21	0.21	0.00	0.18	0.21
tert-butylbenzene	0.13	0.12	0.01	0.11	0.20
1,2,4-trimethylbenzene	0.83	0.80	0.04	0.77	0.98
sec-butylbenzene	0.05	0.05	0.02	0.03	0.06
4-isopropyltoluene	0.15	0.14	0.02	0.12	0.19
1,4-dichlorobenzene	0.02	0.02	0.00	0.02	0.03
1,3-dichlorobenzene	0.80	0.74	0.09	0.68	0.98
n-butylbenzene	0.09	0.13	0.05	0.07	0.17
1,2-dichlorobenzene	0.04	0.04	0.02	0.03	0.05
dibromochloropropane	0.03	0.03	0.01	0.02	0.04
1,2,4-trichlorobenzene	0.04	0.04	0.01	0.03	0.05
naphthalene	0.54	0.53	0.03	0.52	0.56
hexachlorobutadiene	0.01	0.01	0.00	0.01	0.02
TVOC	41.00	39.83	15.45	24.28	67.49

BDL : Below Detection Limit

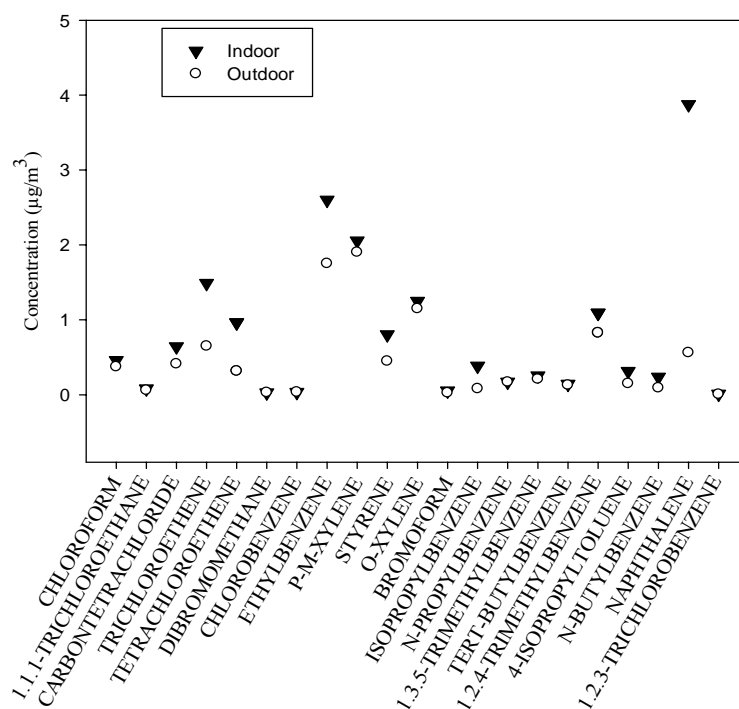


Figure 4.2. Winter term VOC Concentrations profile of indoor and outdoor in School 1

Five VOCs (tetrachloroethene, bromoform, 4-isopropyltoluene, n-butylbenzene, and naphthalene) had a median indoor/outdoor concentration ratio greater than 1.5. Another most prevalent detected compound was 1,4-dichlorobenzene which was measured at high concentrations indoors; however, this compound was detected at very low concentration in outdoor air. That result indicates primarily indoor sources. The cleaning chemicals and air fresheners could contain 1,4-dichlorobenzene. In School 1, the classroom was near the toilet where the cleaning materials were stored. During the day the toilet door is generally open and the classroom door is also frequently open, therefore, this could be the reason of detecting very high concentrations in the classroom.

The benzene and toluene concentrations detected in the classroom were higher than all other detected VOCs. Because of this reason, indoor/outdoor concentration comparisons of benzene and toluene were investigated individually. The benzene and toluene concentration distributions of classroom and outdoor are given in Figure 4.3. The indoor concentration of benzene and toluene are higher than the outdoor concentrations. The indoor/outdoor ratio for both compounds is higher than 1 but less than 1.5 which suggest both indoor and outdoor sources.

Total Volatile Organic Compound (TVOC) concentration was determined by the sum of the identified compounds. The median TVOC concentrations were $86.79 \mu\text{g}/\text{m}^3$ in indoor, $39.82 \mu\text{g}/\text{m}^3$ in outdoor for School 1 in winter term.

Mann-Whitney Rank Sum test was applied to compare the indoor and outdoor air TVOC concentrations. As a result of this test, in winter term there was a significant difference between indoor and outdoor TVOC concentrations in School 1.

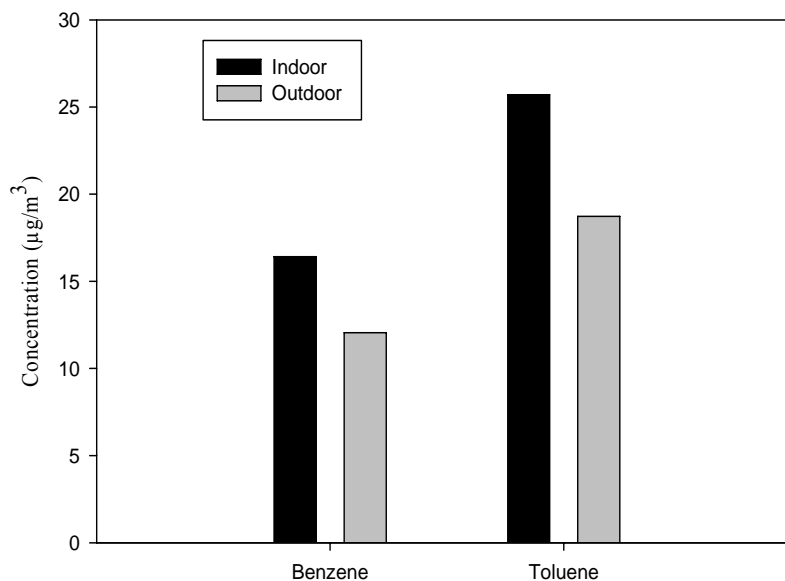


Figure 4.3. Winter term indoor and outdoor benzene and toluene concentrations in School 1

Table 4.3 presents the frequency and the descriptive statistics with detected VOCs in indoor air of School 1 in spring term. In spring term, twenty five VOCs were measured indoors at quantifiable concentrations. Nineteen VOCs (chloroform, carbontetrachloride, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, iso-propylbenzene, n-propylbenzene, 1.3.5-trimethylbenzene, tertbutylbenzene, 1.2.4-trimethylbenzene, 4-isopropyltoluene, 1.4-dichlorobenzene, n-butylbenzene, and naphthalene) were detected in all indoor samples. 1.1.1- trichloroethene was found in 88.9 % of the indoor air samples. Three VOCs were found in 55 to 75 % of the air samples: dibromomethane, bromoform, and sec-butylbenzene. Twenty four VOCs (1.1.2-trichloroethane, 1.1-dichloroethene; trans-1.2-dichloroethene, 1.1-dichloroethane, cis-1.2-dichloroethene, 2.2-dichloropropane, 1.2-dichloroethane, 1.1-dichloropropene, 1.2-dichloropropane, bromodichloromethane, cis-1.3-dichloropropene, trans-1.3-dichloropropene, 1.3-dichloropropane,

dibromochloromethane, 1.1.1.2-tetrachloroethane, 1.1.2.2-tetrachloroethane, 1.2.3-trichloropropane, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, 1.3-dichlorobenzene, 1.2-dichlorobenzene, dibromochloropropane, and hexachlorobutadiene) were not detected in any of the indoor air samples in spring term.

Table 4.3. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the classroom, School 1(n=9)

Compound Name	% Freq	Mean	Median	SD	CIM*	Min	Max
chloroform	100	0.93	0.47	0.91	0.70	0.28	2.69
1.1.1-trichloroethane	88.9	0.05	0.06	0.01	0.01	0.03	0.08
carbontetrachloride	100	0.47	0.38	0.23	0.18	0.19	0.94
benzene	100	8.29	4.42	12.46	9.58	BDL	40.08
trichloroethene	100	2.29	0.23	5.36	4.48	0.15	15.53
dibromomethane	66.7	0.02	0.02	0.01	0.01	0.01	0.02
toluene	100	16.50	13.80	12.30	10.30	4.91	45.35
tetrachloroethene	100	0.28	0.22	0.15	0.11	0.11	0.58
1.2-dibromoethane	22.2	0.07	0.07	0.07	0.59	0.02	0.12
ethylbenzene	100	1.36	0.65	1.63	1.25	0.27	5.26
p-m-xylene	100	1.83	1.01	2.57	1.98	0.35	8.59
styrene	100	0.36	0.37	0.08	0.06	BDL	0.47
o-xylene	100	0.81	0.66	0.52	0.40	BDL	1.93
bromoform	66.7	0.02	0.02	0.00	0.00	0.01	0.02
isopropylbenzene	100	0.07	0.05	0.06	0.05	0.02	0.21
n-propylbenzene	100	0.20	0.11	0.24	0.19	0.05	0.83
1.3.5-trimethylbenzene	100	0.32	0.16	0.38	0.30	0.08	1.30
tert-butylbenzene	100	0.16	0.09	0.17	0.13	0.04	0.58
1.2.4-trimethylbenzene	100	1.24	0.70	1.34	1.03	0.29	4.56
sec-butylbenzene	66.7	0.04	0.04	0.03	0.03	0.01	0.09
4-isopropyltoluene	100	0.19	0.18	0.10	0.08	0.06	0.33
1.4-dichlorobenzene	100	28.78	31.91	17.23	13.24	9.84	63.59
n-butylbenzene	100	0.18	0.16	0.07	0.06	0.12	0.36
naphthalene	100	1.93	2.18	0.78	0.60	0.81	3.18
1.2.3-trichlorobenzene	22.2	0.00	0.00	0.00	0.02	0.00	0.01
TVOC		66.42	57.95	56.70	45.36	18.60	196.70

CIM* : % 95 confidence interval, BDL : Below detection Limit

The most prevalent compounds that were measured in indoor air in spring term were similar to these measured in winter term. The number of compounds that were detected in winter term was higher than the detected in spring term. The compounds that

were not at quantifiable concentrations in spring term were found in less than 50 % of the indoor air samples in winter term

These compounds were mostly chlorinated hydrocarbons (1.2 dichloropropane, 1.3 dichlorobenzene, 1.1.1.2 tetrachlorethene) and the sources of these compounds can be paints, cleaning agent, deodorant and moth balls (Maroni et al., 1997). In winter term, the door and the windows were not opened as much as in spring term, so this could be a reason for this difference.

Figure 4.4 presents the distribution of the indoor concentrations of the seven VOCs with the highest indoor mean concentrations. Chloroform, carbontetrachloride, ethylbenzene, p-m-xylene, o-xylene, 1.2.4-trimethylbenzene and naphthalene had the highest mean indoor concentrations at 0.93, 0.47, 1.36, 1.84, 1.24, and 1.93 $\mu\text{g}/\text{m}^3$. Benzene, toluene, and 1.4 dichlorobenzene compounds were measured at high concentration values similar to the winter term.

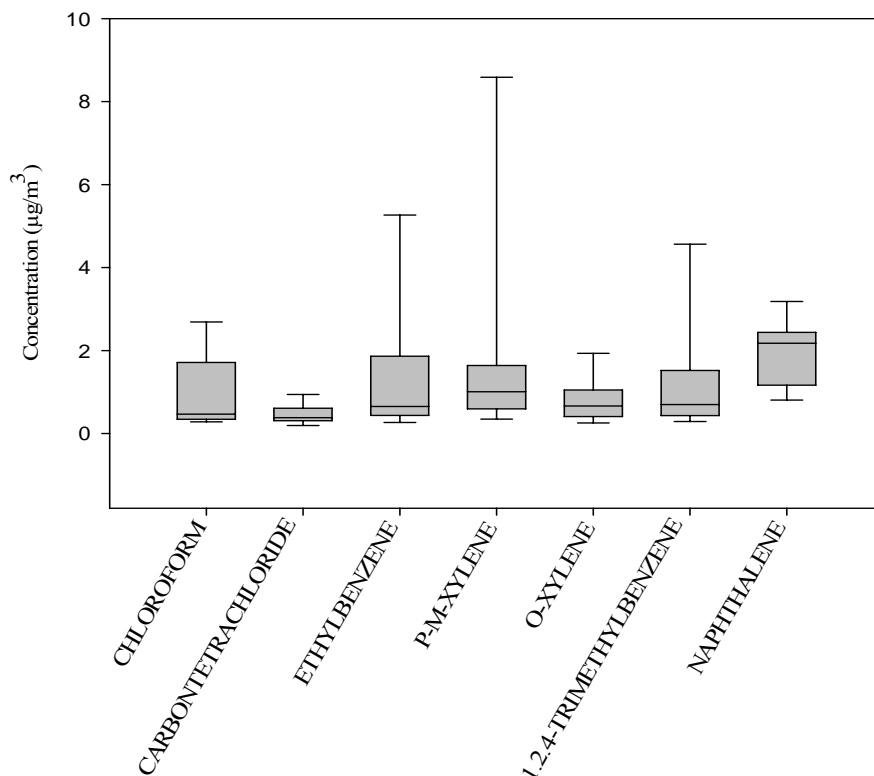


Figure 4.4. Box plots of spring term indoor VOC concentrations in School 1

The results of outdoor VOC concentration for School 1 in spring term are presented in Table 4.4. The results indicated that, the common detected compounds in indoor air samples were also measured in outdoor air samples. Seventeen common

detected compounds in both indoor and outdoor air samples were compared with their mean concentration values and presented in Figure 4.5. 1,1,1-trichloroethene, carbontetrachloride, ethylbenzene, o-xylene, isopropylbenzene and n-propylbenzene had median indoor/outdoor concentration ratios below one.

Table 4.4. Summary statistics of VOC spring term concentrations ($\mu\text{g}/\text{m}^3$) in outdoor, School 1 (n=3)

Compound Name	Mean	Median	SD	Min	Max
chloroform	0.15	0.16	0.02	0.12	0.17
1,1,1-trichloroethane	0.06	0.07	0.02	0.04	0.07
carbontetrachloride	0.59	0.52	0.21	0.43	0.82
benzene	5.71	1.61	7.56	1.13	14.36
trichloroethene	0.31	0.19	0.23	0.16	0.58
toluene	6.02	6.02	2.15	4.50	7.55
tetrachloroethene	0.16	0.16	0.12	0.08	0.24
chlorobenzene	0.03	0.03	0.00	BDL	0.03
ethylbenzene	0.75	0.71	0.44	0.33	1.21
p-m-xylene	1.04	0.96	0.66	0.44	1.74
o-xylene	0.64	0.67	0.28	0.34	0.90
bromoform	0.02	0.02	0.01	0.02	0.03
isopropylbenzene	0.05	0.06	0.01	0.04	0.06
bromobenzene	0.01	0.02	0.01	0.01	0.02
n-propylbenzene	0.10	0.11	0.03	0.07	0.12
1,3,5-trimethylbenzene	0.13	0.14	0.04	0.08	0.16
tert-butylbenzene	0.07	0.08	0.02	0.05	0.08
1,2,4-trimethylbenzene	0.50	0.58	0.17	0.31	0.61
sec-butylbenzene	0.01	0.02	0.01	0.01	0.02
4-isopropyltoluene	0.23	0.16	0.24	BDL	0.50
1,4-dichlorobenzene	2.08	0.60	2.57	0.60	5.05
n-butylbenzene	0.11	0.09	0.04	0.08	0.15
naphthalene	0.24	0.23	0.02	0.23	0.27
1,2,3-trichlorobenzene	0.02	0.00	0.02	0.01	0.04
TVOC	19.40	13.50	15.20	9.20	35.40

BDL : Below Detection Limit

The indoor/outdoor ratios for eight compounds (trichloroethene, tetrachloroethene, p-m-xylene, styrene, 1,3,5-trimethylbenzene, and 4-isopropyltoluene) were between 1 and 1.5. The median indoor/outdoor concentration ratios of chloroform, n-butylbenzene and naphthalene were higher than 1.5 but less than two. In addition, the median indoor/outdoor concentrations of benzene and toluene were higher than two, which means that; these compounds come primarily from indoor. The concentration

profiles of benzene and toluene in indoor and outdoor air in spring term are shown in Figure 4.6. As indicated in the figure, the indoor mean concentrations are higher than the outdoor mean concentrations with a sharper difference for toluene.

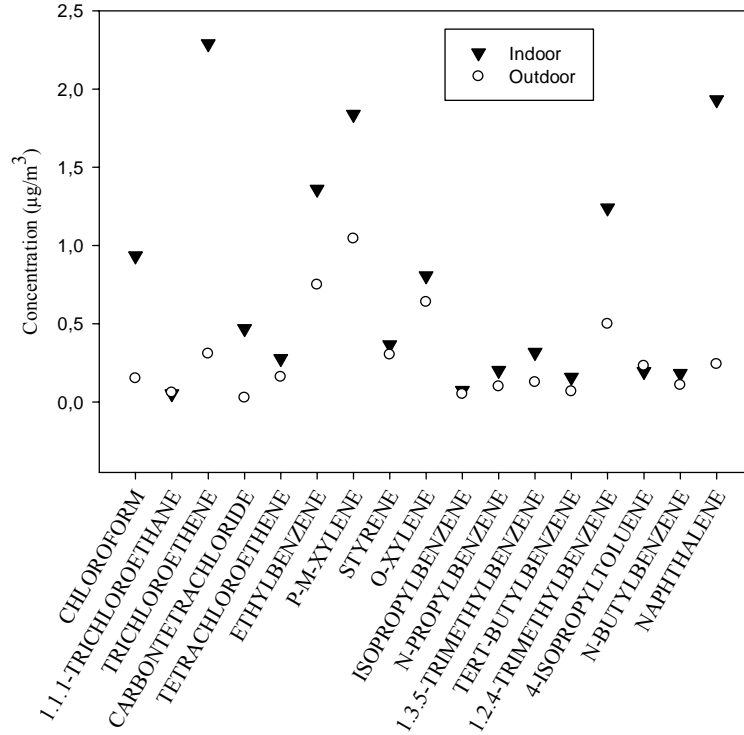


Figure 4.5. Spring term VOC Concentrations profile of indoor and outdoor in School 1

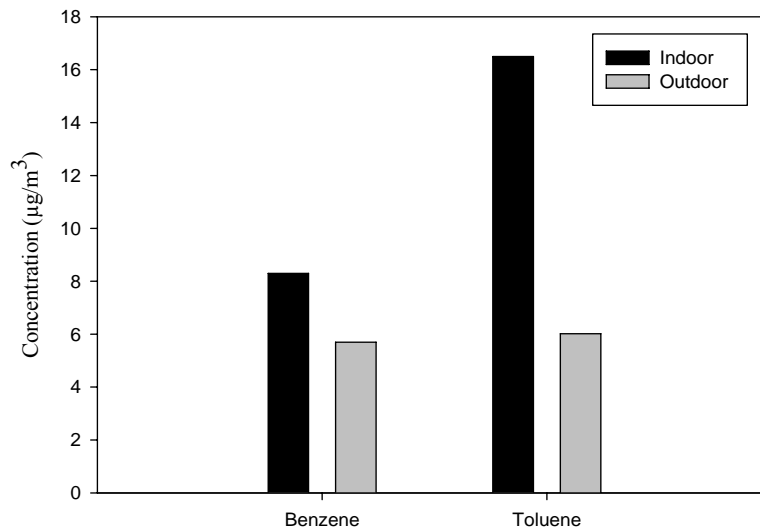


Figure 4.6. Spring term indoor and outdoor benzene and toluene concentrations in School 1

The median TVOC concentrations of indoor and outdoor air were 57.95 and 13.5 $\mu\text{g}/\text{m}^3$, respectively. The difference is statistically significant.

4.2. VOC Concentrations in Classroom and Playground at School 2

Air sampling for School 2 was performed both in winter and spring term. The sampling period was from 29th February to 18th March in winter, and from 28th April to 16th May in spring term for School 2. As the same in School 1, nine sampling days in a classroom, and three sampling days in outdoor play ground were performed in School 2. The results for the two microenvironments are presented one by one, starting with classroom.

In spring term, twenty four VOCs were detected at quantifiable concentrations in indoor air, which is two VOCs less in School 2. The concentrations of detected VOCs in indoor and outdoor air samples are presented in Table 4.5 and Table 4.6 for winter term, and in Table 4.7 and Table 4.8 for spring term at School 2 as descriptive statistics.

Eighteen VOCs were measured in all indoor air samples in winter term, which were carbontetrachloride, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, 1.3.5-trimethylbenzene, 1.2.4-trimethylbenzene, 4-isopropyltoluene, 1.3-dichlorobenzene, n-butylbenzene, naphthalene, chlorobenzene, isopropylbenzene, and n-propylbenzene. Five VOCs (chloroform, 1.1.1 trichloroethane, dibromomethane, bromoform, and tert-butylbenzene) were found in 76 to 99 %, and dibromochloromethane and hexachlorobutadiene were found in 44 % of the indoor air samples. Twenty five VOCs (1.1.2-trichloroethane, 1.1-dichloroethene; trans-1.2-dichloroethene, 1.1-dichloroethane, cis-1.2-dichloroethene, 2.2-dichloropropane, 1.2-dichloroethane, 1.1-dichloropropene, 1.2-dichloropropane, bromodichloromethane, cis-1.3-dichloropropene, trans-1.3-dichloropropene, 1.3-dichloropropane, 1.2-dibromo ethane, 1.1.1.2-tetrachloroethane, 1.1.2.2-tetrachloroethane, 1.2.3-trichloropropane, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, sec-butylbenzene, 1.4-dichloro benzene, 1.2-dichlorobenzene, dibromochloropropane and 1.2.3-trichlorobenzene) were not detected in any of the samples from the classroom in winter term.

Similar to School 1, the highest mean concentrations of the most common VOCs were benzene, toluene, xylenes, and naphthalene with the exception of 1.3-

dichlorobenzene. The mean concentrations of these compounds were 10.6 $\mu\text{g}/\text{m}^3$, 26.5 $\mu\text{g}/\text{m}^3$, 1.7 $\mu\text{g}/\text{m}^3$, 4.1 $\mu\text{g}/\text{m}^3$ and 1.8 $\mu\text{g}/\text{m}^3$, respectively. Figure 4.7 presents the distribution of these compounds with the exception of benzene and toluene.

The analysis of outdoor air samples showed that the detected VOCs were mostly similar to the detected VOCs in indoor air samples.

Table 4.5. Summary statistics of VOC winter term concentrations ($\mu\text{g}/\text{m}^3$) in the classroom, School 2 (n=9)

Compound Name	% Freq	Mean	Median	SD	CIM*	Min	Max
chloroform	88.90	0.66	0.60	0.28	0.26	0.29	1.12
1.1.1-trichloroethane	88.90	0.06	0.06	0.01	0.01	0.06	0.08
carbontetrachloride	100.00	0.45	0.48	0.12	0.10	0.19	0.56
benzene	100.00	10.60	3.02	22.20	18.50	0.37	65.20
trichloroethene	100.00	0.64	0.47	0.63	0.53	0.16	2.14
dibromomethane	77.80	0.03	0.03	0.01	0.01	0.02	0.04
toluene	100.00	26.54	8.87	29.46	22.65	6.29	88.41
dibromochloromethane	44.40	0.03	0.02	0.01	0.03	0.02	0.04
tetrachloroethene	100.00	0.70	0.63	0.44	0.37	0.21	1.68
chlorobenzene	100.00	0.03	0.03	0.01	0.01	0.02	0.05
ethylbenzene	100.00	0.79	0.68	0.40	0.33	0.40	1.44
p-m-xylene	100.00	1.04	0.82	0.57	0.48	0.51	1.90
styrene	100.00	0.60	0.55	0.26	0.21	BDL	1.16
o-xylene	100.00	0.69	0.58	0.34	0.28	0.34	1.32
bromoform	88.90	0.04	0.03	0.04	0.04	0.01	0.12
isopropylbenzene	100.00	0.07	0.05	0.04	0.03	0.04	0.14
n-propylbenzene	100.00	0.14	0.12	0.06	0.05	0.08	0.23
1.3.5-trimethylbenzene	100.00	0.21	0.15	0.12	0.10	0.09	0.39
tert-butylbenzene	88.90	0.12	0.08	0.06	0.06	0.06	0.20
1.2.4-trimethylbenzene	100.00	0.86	0.62	0.47	0.39	0.42	1.55
4-isopropyltoluene	100.00	0.40	0.40	0.20	0.17	0.15	0.68
1.3-dichlorobenzene	100.00	1.82	1.66	0.63	0.52	0.90	2.73
n-butylbenzene	100.00	0.17	0.17	0.06	0.05	0.11	0.27
naphthalene	100.00	4.14	4.21	1.47	1.23	2.66	6.99
hexachlorobutadiene	44.40	0.01	0.01	0.00	0.01	0.01	0.02
TVOC	50.86	24.35	57.90	46.43	13.72	178.50	50.86

CIM*: % 95 confidence interval

The outdoor VOC concentration results of School 2 for winter term are presented in Table 4.6. The indoor and outdoor mean concentrations of twenty one VOCs which were detected above 70 % of the indoor air samples and also detected in outdoor air samples were shown in Figure 4.8. It was seen that the indoor mean concentrations of eleven compounds were higher than the outdoor mean concentrations. The rest of the VOCs, the indoor and outdoor mean concentrations were similar. But, the indoor/outdoor VOC concentration ratios help understanding the difference between them to interpret their sources. Seven VOCs (benzene, toluene, 1,1,1-trichloroethane, carbontetrachloride, bromoform, isopropylbenzene and n-butylbenzene) had indoor/outdoor median concentration ratios 1 ± 0.5 .

The median indoor /outdoor concentration ratios for thirteen compounds (chloroform, trichloroethene, tetrachloroethene, chlorobenzene, ethylbenzene, p-m-xylene, styrene, o-xylene, n-propylebenzene, 1,3,5-trimethylbenzene, tert-butylbenzene, 1,2,4-trimethylbenzene, 4-isopropyltoluene, and 1,3-dichlorobenzene) were between 1.5 and 10. The indoor air median concentration value of naphthalene was 17.5 times higher than the median outdoor concentration.

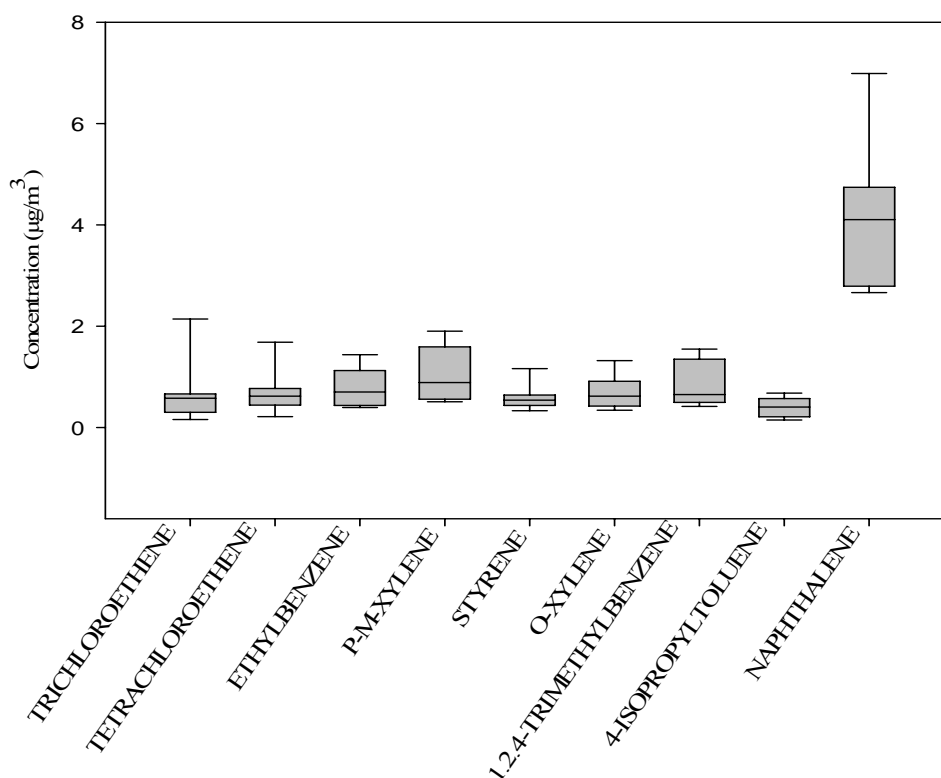


Figure 4.7. Box plots of winter term indoor VOC concentrations in School 2

The comparison of benzene - toluene indoor and outdoor concentrations are presented separately because of their relatively high concentrations. Figure 4.9 shows that indoor concentration of benzene and toluene are higher than the outdoor concentrations. The indoor/outdoor concentration ratios for both compounds were between 1 and 1.5.

TVOC concentrations for both indoor and outdoor air were calculated and presented in Table 4.5 and Table 4.6. The median TVOC concentrations were 57.9 $\mu\text{g}/\text{m}^3$ in indoor, 13.3 $\mu\text{g}/\text{m}^3$ in outdoor air for School 2 in winter term. Statistical comparison revealed that the difference was significant.

Table 4.6. Summary statistics of winter term VOC concentrations ($\mu\text{g}/\text{m}^3$) in outdoor, School 2 (n=3)

Compound Name	Mean	Median	SD	Min	Max
chloroform	0.19	0.20	0.05	0.14	0.24
1.1.1-trichloroethane	0.07	0.07	0.01	0.05	0.08
carbontetrachloride	0.72	0.67	0.11	0.64	0.84
benzene	6.34	3.33	5.33	1.93	15.00
trichloroethene	0.04	0.04	0.01	0.02	0.04
dibromomethane	0.03	0.03	0.01	0.02	0.03
toluene	6.32	5.97	0.61	5.96	7.03
tetrachloroethene	0.11	0.11	0.04	0.07	0.15
chlorobenzene	0.02	0.02	0.01	BDL	0.03
ethylbenzene	0.36	0.36	0.21	0.15	0.56
p-m-xylene	0.51	0.49	0.32	0.20	0.84
o-xylene	0.33	0.30	0.20	BDL	0.54
bromoform	0.05	0.02	0.06	0.02	0.12
isopropylbenzene	0.03	0.04	0.01	0.02	0.04
n-propylbenzene	0.05	0.07	0.05	0.00	0.09
1.3.5-trimethylbenzene	0.08	0.09	0.05	0.04	0.13
tert-butylbenzene	0.04	0.04	0.02	0.02	0.07
1.2.4-trimethylbenzene	0.32	0.32	0.19	0.14	0.51
4-isopropyltoluene	0.04	0.05	0.02	BDL	0.06
1.3-dichlorobenzene	0.41	0.39	0.26	0.16	0.68
n-butylbenzene	0.12	0.12	0.02	0.10	0.14
naphthalene	0.33	0.24	0.19	0.21	0.55
TVOC	16.78	13.27	7.88	10.20	28.12

BDL : Below Detection Limit

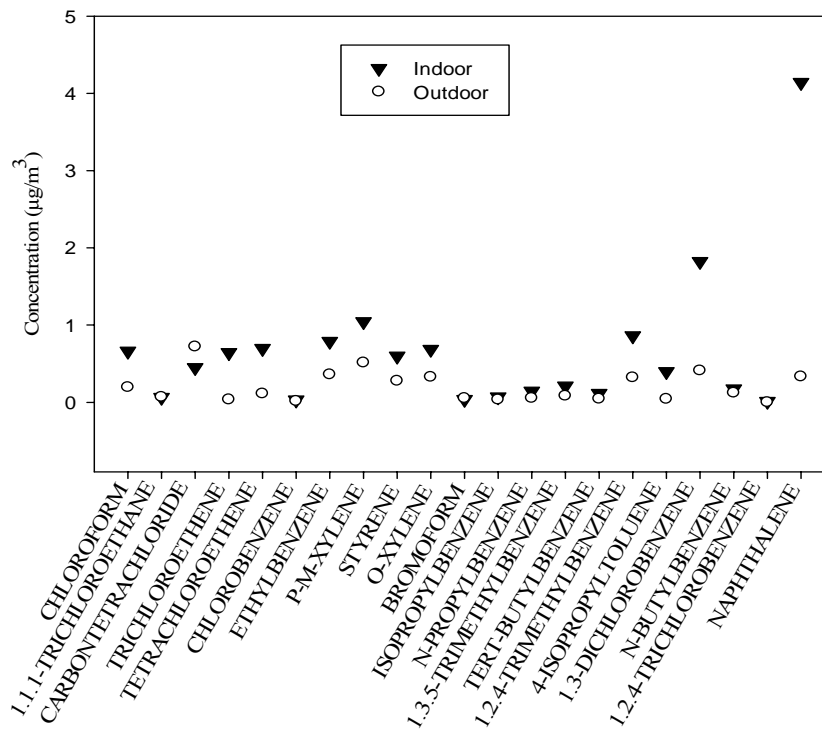


Figure 4.8. Winter term VOC concentrations profile of indoor and outdoor in School 2

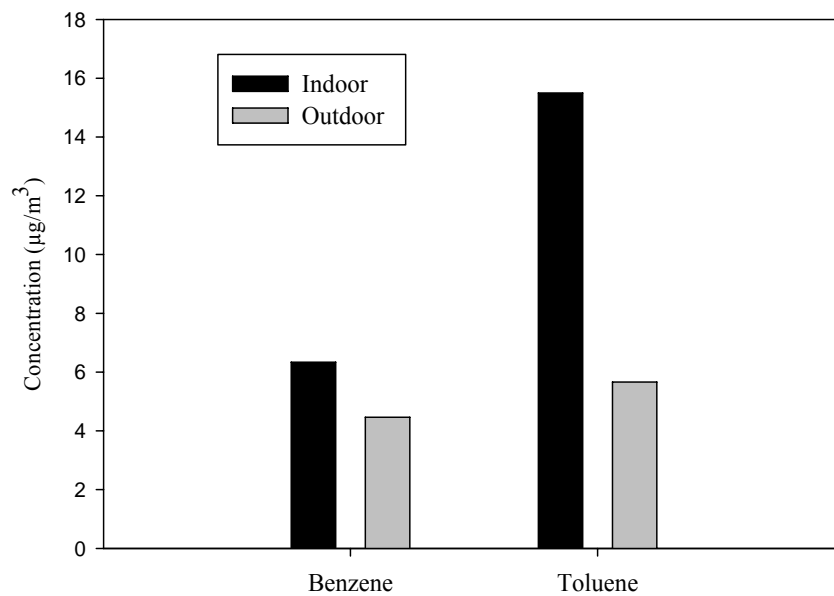


Figure 4.9. Winter term indoor and outdoor benzene and toluene concentrations in School 2

The results of the indoor and outdoor air samples of School 2 in spring term are presented in Table 4.7 and Table 4.8 respectively. Descriptive statistics for the detected VOCs in indoor air samples are in Table 4.7. In spring term, twenty four VOCs were measured in indoor air samples at quantifiable concentrations.

Table 4.7. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the classroom, School 2 (n=9)

Compound Name	% Freq	Mean	Median	SD	CIM*	Min	Max
chloroform	89.00	0.35	0.32	0.13	0.11	0.20	0.59
1.1.1-trichloroethane	78.00	0.05	0.05	0.01	0.01	0.04	0.07
carbontetrachloride	89.00	0.37	0.32	0.13	0.10	0.28	0.64
benzene	89.00	6.34	3.33	5.33	4.46	1.93	15.00
trichloroethene	100.00	0.18	0.18	0.10	0.08	0.06	0.32
toluene	100.00	15.50	13.43	7.14	5.97	7.43	26.95
tetrachloroethene	100.00	0.26	0.20	0.13	0.10	0.10	0.43
ethylbenzene	100.00	0.84	0.55	0.70	0.54	0.37	2.60
p-m-xylene	100.00	1.12	0.74	1.14	0.87	0.34	4.00
styrene	100.00	0.53	0.55	0.17	0.13	BDL	0.92
o-xylene	100.00	0.55	0.47	0.32	0.24	0.31	1.35
bromoform	89.00	0.02	0.01	0.02	0.02	0.01	0.07
1.1.2.2-tetrachloroethane	67.00	0.02	0.01	0.00	0.00	0.01	0.02
isopropylbenzene	100.00	0.03	0.03	0.00	0.00	0.03	0.04
n-propylbenzene	100.00	0.07	0.06	0.01	0.01	0.06	0.10
1.3.5-trimethylbenzene	100.00	0.10	0.10	0.01	0.01	0.08	0.12
tert-butylbenzene	100.00	0.04	0.04	0.01	0.01	0.03	0.06
1.2.4-trimethylbenzene	100.00	0.34	0.38	0.12	0.09	0.04	0.44
sec-butylbenzene	100.00	0.06	0.03	0.09	0.07	0.02	0.28
4-isopropyltoluene	100.00	0.28	0.26	0.10	0.08	0.15	0.45
1.3-dichlorobenzene	100.00	2.98	2.19	1.35	1.04	1.58	5.26
n-butylbenzene	100.00	0.12	0.13	0.02	0.01	0.11	0.15
naphthalene	100.00	1.97	1.87	0.59	0.45	1.22	2.92
TVOC		32.10	25.25	17.60	14.39	14.70	62.77

CIM*: % 95 confidence interval

Seventeen VOCs (trichloroethene, toluene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, iso-propylbenzene, n-propylbenzene, 1.3.5-trimethylbenzene, tertbutylbenzene, 1.2.4-trimethylbenzene, sec-butylbenzene, 4-isopropyltoluene, 1.3-dichlorobenzene, n-butylbenzene, and naphthalene) were detected in all indoor air samples. Six VOCs (chloroform, 1.1.1-trichloroethane, carbontetrachloride, benzene, chlorobenzene and bromoform) were found in 70 to 99 % of the indoor air samples. 1.1.2.2-tetrachlorethane was detected in 66.7 % of the indoor air samples. In spring

term, there were twenty seven compounds (1.1.2-trichloroethane, 1.1-dichloroethene; trans-1.2-dichloroethene, 1.1-dichloroethane, cis-1.2-dichloroethene, 2.2-dichloropropane, 1.2-dichloroethane, 1.1-dichloropropene, 1.2-dichloropropane, dibromomethane, bromodichloromethane, cis-1.3-dichloropropene, trans-1.3-dichloropropene, 1.3-dichloropropane, dibromochloromethane, 1.2-dibromoethane, 1.1.2.2-tetrachlorethane, 1.2.3-trichloropropane, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, 1.4-dichlorobenzene, 1.2-dichlorobenzene, dibromochloropropane, 1.2.4-trichlorobenzene, hexachlorobutadiene and 1.2.3-trichlorobenzene) that were not found in any of the indoor air samples. In spring term only two more VOCs were not detected than in winter term. 1.2.4-trimethylbenzene was not detected in spring term but in winter term these compounds was found above 70% of the indoor air samples.

The sources of 1.2.4-trichlorobenzene are defined as pesticide and dye carrier (Maroni, et. al. 1995). This compound was not detected in outdoor air samples in School 2 in winter term only, found in indoor air samples with lower median concentration. So, that information suggests for 1.2.4-trichlorobenzene indoor sources. The reason of finding that compound in winter term in contrast not finding in spring term could be the increased ventilation due to opened windows and doors. In winter term, generally only a window of the test space (classroom) was opened but in spring term generally both the door and more than one or all windows were opened. So, more natural ventilation occurred in spring term resulting in a decrease in pollutant concentrations.

Chloroform, carbontetrachloride, trichloroethene, ethylbenzene, p,m-xylene, styrene, o-xylene, naphthalene, 1.3-dichlorobenzene, toluene, and benzene that were detected > 80 % of indoor air samples of School 2 in spring term with the highest mean concentrations. Figure 4.10 presents the box plot diagram of these compounds. The mean concentrations of the compounds shown in the figure were 0.35, 0.37, 0.18, 0.84, 1.12, 0.53, 0.55 and $1.97\mu\text{g}/\text{m}^3$ respectively.

Table 4.8 presents the results of the outdoor VOC sampling as the descriptive statistics for spring term in School 2. Twenty two VOCs were identified in outdoor air samples. All detected compounds were the same as indoor air samples; only one more compound, 1.1.2.2-tetrachlorethane, was quantified in indoor air. Moreover, the compound was found in 66.7 % of the indoor air samples at low concentrations. Possible indoor sources could be varnishes and solvents (Maroni, et al. 1995).

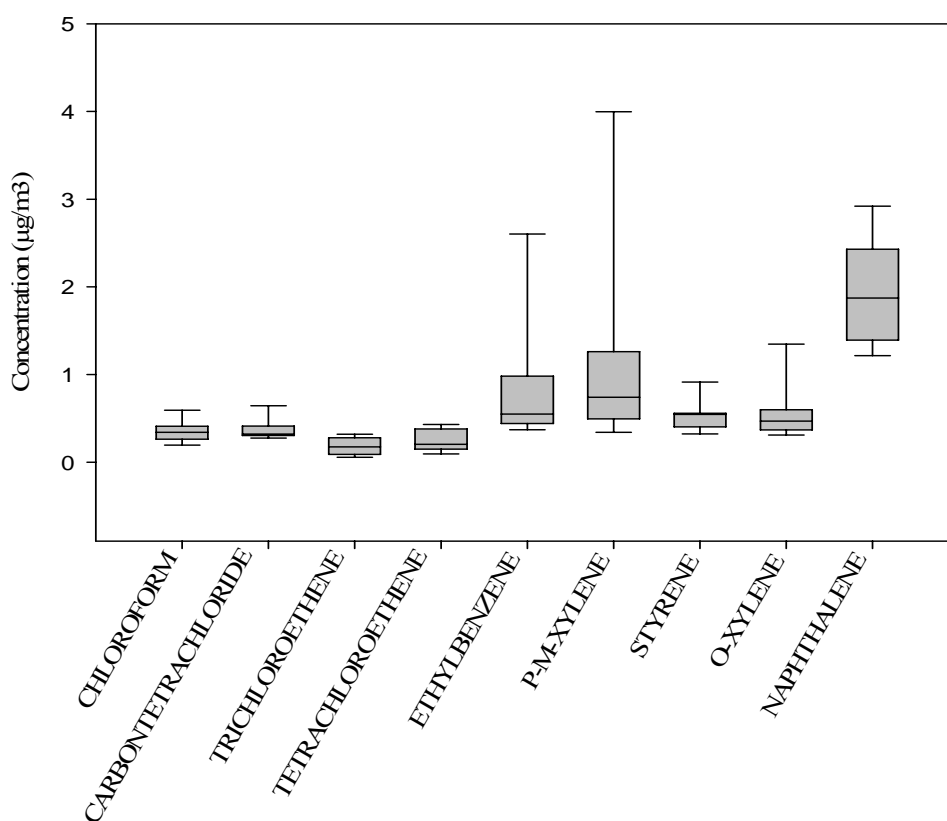


Figure 4.10. Box plots of spring term indoor VOC concentrations in School 2

The mean indoor and outdoor concentrations of fifteen common detected VOCs (chloroform, carbontetrachloride, trichloroethene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, bromoform, 1.3.5-trimethylbenzene, tertbutylbenzene, 1.2.4-trimethylbenzene, sec-butylbenzene, 4-isopropyltoluene, and naphthalene) were compared in Figure 4.11. The figure shows that, nine of these VOCs (chloroform, trichloroethene, tetrachloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, 4-isopropyltoluene, and naphthalene) had higher concentrations in indoor air than outdoor air. Furthermore, the indoor/outdoor ratios of these VOCs were obtained to put forward an idea about the sources of these compounds. The indoor/outdoor median ratios for ($I/O > 2.5$) chloroform, trichloroethene, toluene, tetrachloroethene, ethylbenzene, styrene, 1.3.5-trimethylbenzene, sec-butylbenzene, 4-isopropyltoluene, and 1.3-dichlorobenzene, and I/O ratio (> 10) for naphthalene suggest indoor sources for these VOCs. In contrast, the indoor/outdoor median ratios ($I/O = 1 \pm 0.5$) for carbontetrachloride, benzene, tertbutylbenzene, p,m-xylene, o-xylene, bromoform, and 1.2.4-trimethylbenzene

indicates both indoor and outdoor sources. Indoor and outdoor concentrations of benzene and toluene were relatively high so, these were plotted in a separate graph (Figure 4.12).

Table 4.8. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in outdoor, School 2 (n=9)

Compound Name	Mean	Median	SD	Min	Max
chloroform	0.06	0.06	0.01	BDL	0.06
1,1,1-trichloroethane	0.03	0.03	0.01	0.03	0.04
carbontetrachloride	0.41	0.35	0.15	0.31	0.58
benzene	4.46	2.17	5.28	0.71	10.50
trichloroethene	0.05	0.03	0.04	0.02	0.10
toluene	5.66	4.80	4.77	BDL	10.80
tetrachloroethene	0.11	0.08	0.10	0.04	0.23
ethylbenzene	0.29	0.34	0.22	BDL	0.48
p-m-xylene	0.45	0.50	0.34	BDL	0.75
styrene	0.34	0.18	0.36	BDL	0.76
o-xylene	0.31	0.34	0.23	BDL	0.52
bromoform	0.01	0.01	0.01	BDL	0.02
isopropylbenzene	0.02	0.03	0.02	0.01	0.03
n-propylbenzene	0.05	0.05	0.04	0.02	0.09
1,3,5-trimethylbenzene	0.06	0.06	0.05	BDL	0.10
tert-butylbenzene	0.03	0.03	0.03	0.01	0.06
1,2,4-trimethylbenzene	0.27	0.27	0.21	0.06	0.48
sec-butylbenzene	0.01	0.01	0.01	0.00	0.02
4-isopropyltoluene	0.07	0.06	0.08	BDL	0.16
1,3-dichlorobenzene	0.22	0.25	0.10	0.11	0.29
n-butylbenzene	0.07	0.08	0.03	BDL	0.10
naphthalene	0.21	0.18	0.14	BDL	0.37
TVOC	13.19	9.89	12.19	3.17	26.52

BDL : Below Detection Limit

Benzene and toluene indoor concentrations were higher than outdoor concentrations, but according to indoor/outdoor median ratios, benzene has both indoor and outdoor sources whereas toluene has primarily indoor sources.

The median TVOC concentrations of indoor and outdoor air were 25.5 and 9.9 $\mu\text{g}/\text{m}^3$ respectively. The results revealed that, there was a significant difference between indoor and outdoor air TVOC concentrations statistically.

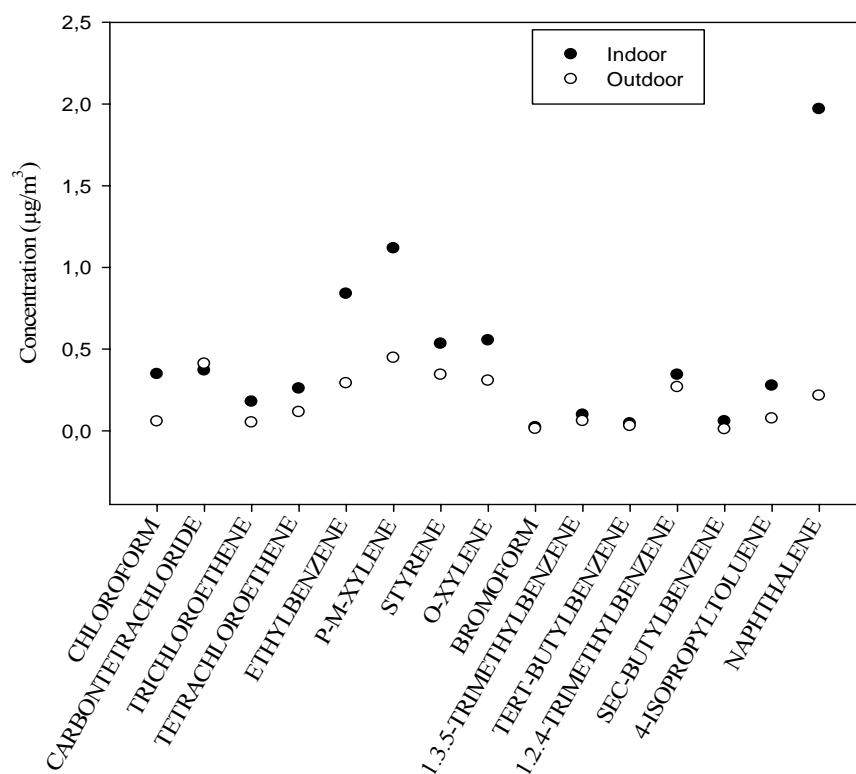


Figure 4.11. Spring term VOC Concentrations profile of indoor and outdoor in School 2

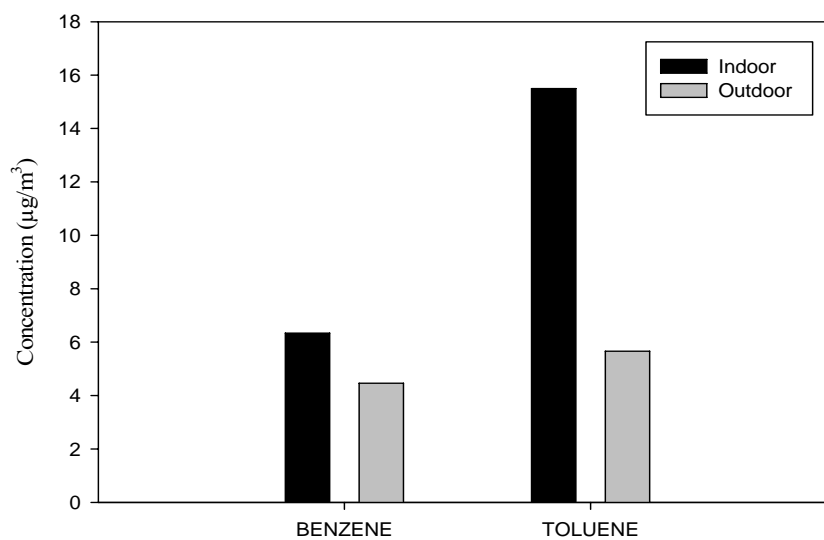


Figure 4.12. Spring term indoor and outdoor benzene and toluene concentrations in School 2

4.3. VOC Concentrations in Classroom and Playground at School 3

The spring term sampling at School 3 was performed from 19th March to 8th April. Nine sampling days in a classroom and, three sampling days in the outdoor playground were performed similar to the other two primary schools.

Twenty six VOCs were detected in spring term. The descriptive statistics of the concentrations are presented in Table 4.9.

Table 4.9. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in classroom, School 3(n=9)

Compound Name	% Freq	Mean	Median	SD	CIM*	Min	Max
chloroform	77.8	0.75	0.19	1.33	1.23	BDL	3.73
1.1.1-trichloroethane	66.7	0.12	0.08	0.13	0.13	0.05	0.38
carbontetrachloride	66.7	0.55	0.56	0.10	0.11	0.42	0.69
benzene	88.9	8.92	2.66	12.56	11.62	BDL	28.67
trichloroethene	100	0.14	0.08	0.17	0.13	BDL	0.54
dibromomethane	55.6	0.04	0.03	0.03	0.04	0.02	0.10
toluene	100	19.70	10.17	25.30	21.61	BDL	80.64
tetrachloroethene	100	0.17	0.15	0.06	0.05	0.11	0.29
ethylbenzene	100	0.42	0.41	0.18	0.14	0.15	0.74
p-m-xylene	100	0.54	0.57	0.24	0.18	0.17	0.86
styrene	100	0.65	0.53	0.46	0.35	BDL	1.80
o-xylene	100	0.47	0.45	0.19	0.15	BDL	0.68
bromoform	77.8	0.12	0.04	0.22	0.20	0.03	0.62
isopropylbenzene	100	0.06	0.06	0.03	0.02	0.01	0.10
1.2.3-trichloropropane	44.4	0.04	0.01	0.06	0.09	0.01	0.13
n-propylbenzene	100	0.09	0.09	0.04	0.03	0.03	0.17
1.3.5-trimethylbenzene	100	0.12	0.13	0.05	0.04	0.03	0.19
tert-butylbenzene	100	0.06	0.06	0.02	0.02	0.02	0.10
1.2.4-trimethylbenzene	100	0.45	0.45	0.19	0.15	0.13	0.74
sec-butylbenzene	77.8	0.03	0.03	0.01	0.01	0.02	0.04
4-isopropyltoluene	100	0.21	0.20	0.07	0.05	0.08	0.31
1.3-dichlorobenzene	100	16.15	5.58	16.92	13.00	3.40	51.60
n-butylbenzene	100	0.16	0.15	0.04	0.03	0.09	0.20
1.2.4-trichlorobenzene	77.8	0.01	0.01	0.00	0.00	0.01	0.02
naphthalene	100	1.09	1.07	0.52	0.40	0.34	2.23
TVOC		51.09	23.77	58.93	49.79	8.29	175.6

CIM*: % 95 confidence interval, BDL : Below Detection Limit

Seventeen VOCs (trichloroethene, toluene, tetrachloroethene, chlorobenzene, ethylbenzene, p-m-xylene, styrene, o-xylene, isopropylbenzene, n-propylbenzene, 1.3.5-trimethylbenzene, tertbutylbenzene, 1.2.4-trimethylbenzene, 4-isopropyltoluene, 1.3-

dichlorobenzene, n-butylbenzene, and naphthalene) were found in all indoor air samples from the classroom. Five VOCs were detected in 76 to 99 %, four VOCs were found in 51 to 75 % of the indoor air samples. Twenty five VOCs were not detected at quantifiable concentrations in any of the air samples from the classroom in School 3: 1.1.2-trichloroethane, 1.1-dichloroethene; trans-1.2-dichloroethene, 1.1-dichloroethane, cis-1.2-dichloroethene, 2.2-dichloropropane, 1.2-dichloroethane, 1.1-dichloropropene, 1.2-dichloropropane, bromodichloromethane, cis-1.3-dichloropropene, trans-1.3-dichloropropene, 1.3-dichloropropane, 1.2-dibromoethane, 1.1.1.2-tetrachloroethane, 1.1.2.2-tetrachloroethane, 1.2.3-trichloropropane, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, 1.4-dichlorobenzene, 1.2-dichlorobenzene, dibromochloropropane, 1.2.3-trichlorobenzene and hexachlorobutadiene.

The VOCs that were detected in all samples with the highest mean concentrations are shown in Figure 4.13.

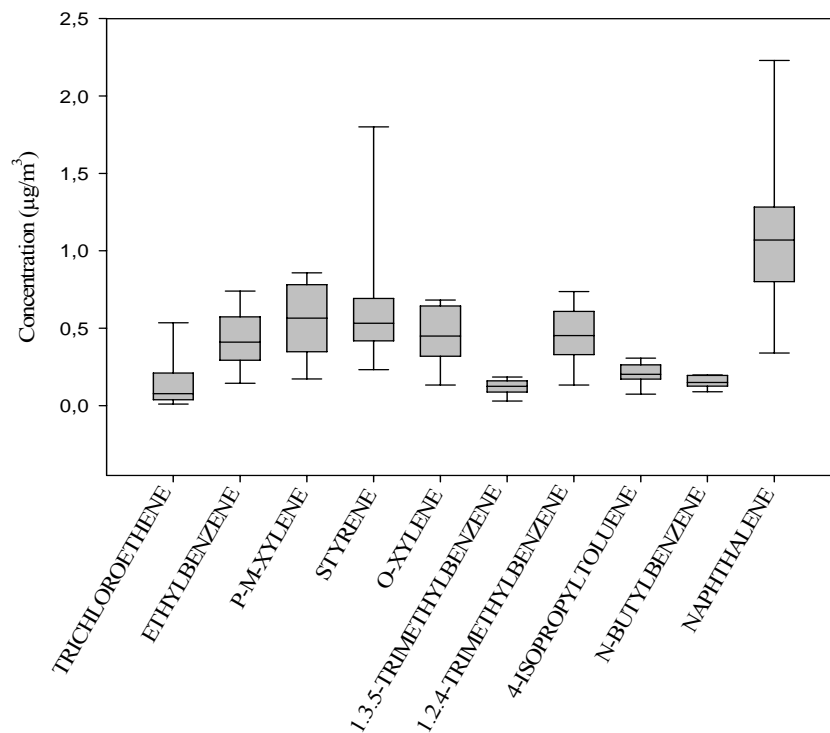


Figure 4.13. Box plots of spring term indoor VOC concentrations in School 3

Trichloroethene, ethylbenzene, p-m-xylene, styrene, o-xylene, 1.3.5-trimethylbenzene, 1.2.4-trimethylbenzene, 4-isoprpyltoluene, n-butylbenznen, and naphthalene had the highest mean concentrations as 0.14, 0.42, 0.54, 0.65, 0.47, 0.12, 0.45, 0.21, 0.16 and

1.1 $\mu\text{g}/\text{m}^3$, respectively, except for three VOCs which were at an order of magnitude higher concentration levels. Benzene, toluene, and 1,3-dichlorobenzene were found in all indoor air samples with mean values of 8.92, 19.7 and 16.2 $\mu\text{g}/\text{m}^3$, respectively.

VOC concentrations at the outdoor playground of School 3 in spring term are given in Table 4.10. Twenty five VOCs were detected at quantifiable concentrations in outdoor air samples. The results showed that, these common compounds with high mean concentrations in indoor air samples were similar to these measured in outdoor air samples.

Table 4.10. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in outdoor, School 3(n=9)

Compound Name	Mean	Median	SD	Min	Max
chloroform	0.47	0.58	0.36	BDL	0.76
1,1,1-trichloroethane	0.24	0.24	0.26	0.06	0.42
carbontetrachloride	2.07	1.77	1.93	0.31	4.12
benzene	8.09	8.23	6.13	1.90	14.15
trichloroethene	0.03	0.03	0.02	0.02	0.05
toluene	6.05	5.96	0.16	5.95	6.23
tetrachloroethene	0.16	0.20	0.11	0.04	0.25
chlorobenzene	0.04	0.06	0.04	BDL	0.07
ethylbenzene	0.77	0.71	0.27	0.53	1.06
p-m-xylene	1.04	0.89	0.29	0.85	1.37
styrene	0.83	0.88	0.12	0.69	0.92
o-xylene	0.79	0.71	0.24	0.60	1.06
bromoform	0.04	0.04	0.02	0.03	0.05
isopropylbenzene	0.09	0.09	0.04	0.06	0.11
n-propylbenzene	0.15	0.16	0.06	0.09	0.20
1,3,5-trimethylbenzene	0.18	0.16	0.04	0.15	0.23
tert-butylbenzene	0.13	0.11	0.04	0.10	0.18
1,2,4-trimethylbenzene	0.53	0.61	0.49	BDL	0.98
4-isopropyltoluene	0.08	0.07	0.03	0.06	0.11
1,3-dichlorobenzene	2.81	2.50	1.95	1.03	4.90
n-butylbenzene	0.39	0.41	0.09	0.30	0.47
naphthalene	0.76	0.71	0.12	0.67	0.89
TVOC	25.72	25.11	12.80	13.48	38.58

BDL : Below Detection Limit

Eight common measured compounds in both indoor and outdoor air samples were compared using their mean concentration values (Figure 4.14). The figure showed that most of the compounds had higher mean concentrations in outdoor air than in indoor air. Ethylbenzene, xylenes, styrene and 1,2,4-trimethylbenzene had indoor/outdoor

ratios smaller than one, which indicated that outdoor sources were dominant during the sampling period. This result was opposite to the results in the other two schools. 4-isopropyltoluene and naphthalene, however, had I/O ratios > 1 as in the other two schools. Indoor/outdoor ratios of these two compounds were higher than 1.5 which suggests indoor sources.

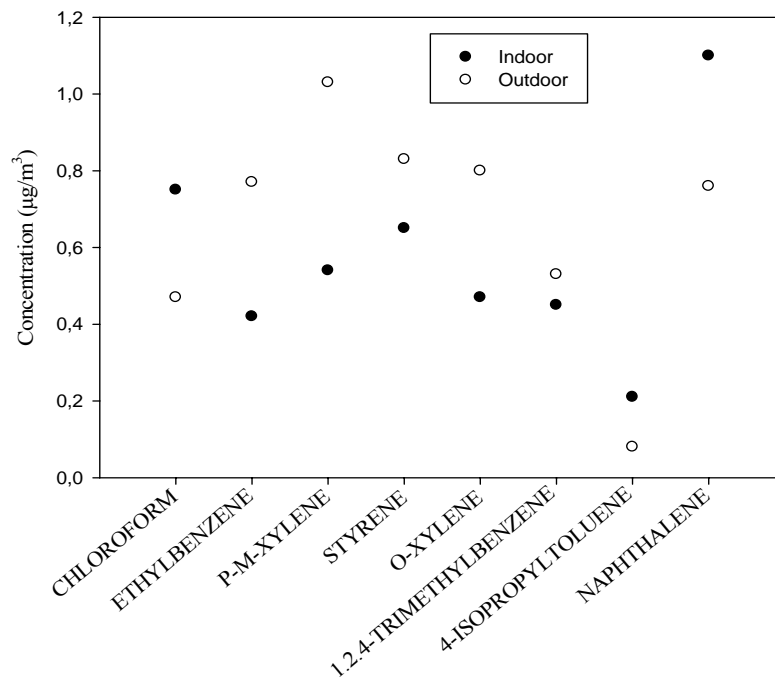


Figure 4.14. Spring term VOC concentrations profile of indoor and outdoor in School 3

The concentration profiles of benzene and toluene in indoor and outdoor air in spring term are shown in Figure 4.15. The mean indoor concentration of toluene is higher than the mean outdoor concentration, but the trend was not similar for benzene; the indoor and outdoor benzene concentrations being nearly the same. The median TVOC concentrations of indoor and outdoor air were 23.8 and 25.1 µg/m³ respectively. These results were investigated statistically and there was no significant difference between indoor and outdoor air TVOC concentrations. Because the school is located in a suburban area, there was no heavy traffic except for parents dropping off and picking up their children and about 5-6 minivans serving as school busses. There may be two possible explanations for this situation. Classrooms in this building are located on the southwest side with a lot of sunshine exposure from noon until the end of the school day. Average temperature during the nine sampling days was 20.3°C. Therefore almost 100 % of the windows were open through afternoons, resulting in high exchange rates.

The second possible reason may be related to meteorological conditions. Negative pressure may have occurred during the spring sampling period. The average CO₂ concentration during the sampling period was 1380 ppm almost equal to the atmospheric CO₂ concentration.

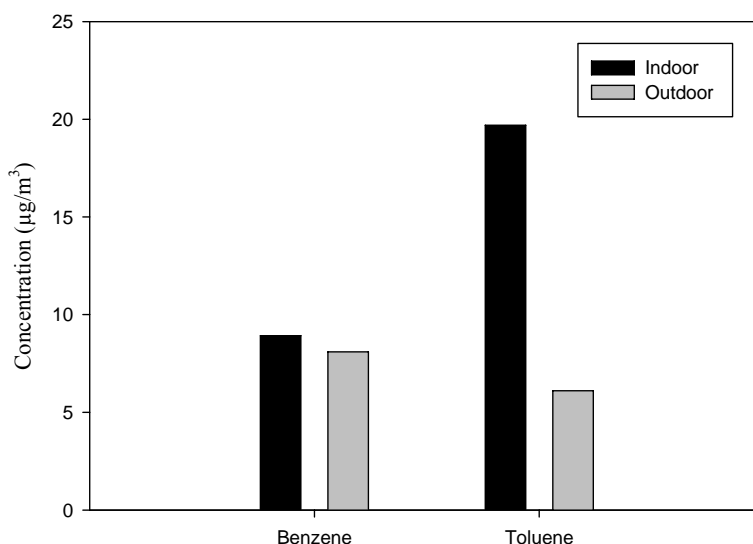


Figure 4.15. Spring term indoor and outdoor benzene and toluene concentrations in School 3

4.4. VOC Concentrations in Kindergarten Classrooms

In all three schools, in addition to the classroom and outdoor, air sampling was performed in a kindergarten classroom. Three air samples were collected in each kindergarten. In this part, the concentration results of VOCs in kindergarten classrooms at School 1 in spring term, at School 2 in winter and spring term and, in School 3 in spring term are investigated.

In School 1, twenty six VOCs were detected at quantifiable concentrations in the kindergarten classroom in spring term. Nineteen VOCs were measured in all air samples of kindergarten classroom. Descriptive statistics for the 19 compounds are presented in Table 4.11. The highest mean concentrations were for toluene, benzene, 1.2.4-trimethylbenzene, 1.3-dichlorobenzene, p-m-xylene, o-xylene, ethylbenzene, naphthalene, and 1.3.5-trimethylbenzene.

These compounds were also measured at high concentrations in classroom air samples but, the concentrations of these compounds in kindergarten classroom were higher than the concentrations measured in classroom air samples with the only exception for benzene and naphthalene. The highest median concentrations were as 91.6, 4.3, 3.8, 2.6, 1.6 and 1.5 $\mu\text{g}/\text{m}^3$ for toluene, benzene, 1,2,4-trimethylbenzene, p-m-xylene, ethylbenzene, and naphthalene, respectively. The concentrations of these compounds were detected as 13.8, 4.4, 0.7, 1, 0.7 and 2.2 $\mu\text{g}/\text{m}^3$, respectively, in the classroom.

Table 4.11. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the kindergarden, School 1 (n=3)

Compound Name	Mean	Median	SD	Min	Max
benzene	4.57	4.26	1.90	2.85	6.61
trichloroethene	0.19	0.17	0.10	0.10	0.30
toluene	97.30	91.60	17.70	83.10	117.0
tetrachloroethene	0.28	0.28	0.01	0.27	0.29
ethylbenzene	3.95	1.58	4.16	1.52	8.75
p-m-xylene	5.27	2.63	5.08	2.06	11.10
styrene	0.68	0.72	0.22	0.44	0.88
o-xylene	1.95	2.09	0.49	1.41	2.36
isopropylbenzene	0.33	0.22	0.31	0.08	0.68
n-propylbenzene	0.86	0.55	0.84	0.21	1.81
1,3,5-trimethylbenzene	1.41	0.79	1.50	0.33	3.13
tert-butylbenzene	0.84	0.51	0.92	0.13	1.88
1,2,4-trimethylbenzene	6.19	3.76	6.14	1.64	13.20
sec-butylbenzene	0.50	0.27	0.54	0.12	1.11
4-isopropyltoluene	0.87	0.47	0.89	0.26	1.89
1,3-dichlorobenzene	2.38	2.98	1.36	0.83	3.34
n-butylbenzene	1.17	0.86	1.01	0.35	2.30
naphthalene	1.30	1.46	0.28	0.98	1.47
TVOC	130.0	115.0	43.50	96.70	178.0

The results showed that benzene concentrations were similar in classroom and kindergarten classroom but, naphthalene concentration in classroom was higher than kindergarten classroom. The indoor (classroom) and outdoor benzene concentration comparison was done and, the I/O ratio showed that benzene had both indoor and outdoor sources. The reason could be having high traffic load around the school. Because of the same reason, similar concentration of benzene was measured in the

kindergarten classroom. Although naphthalene concentration was not much low in kindergarten classroom according to the concentration in classroom (indoor), the possible explanation for this difference could be the location of the toilets. In the toilets, the small balls which contain naphthalene were used as cleaning products in the washstands and these could be the main sources for the naphthalene which caused high naphthalene concentration. The reason of obtaining higher naphthalene concentration in classroom than kindergarten classroom could be the distance of the toilets to classrooms. The distance between the toilet and kindergarten classroom is longer than the distance between the toilet and the classroom. In contrast, the other widespread compounds (toluene, 1,2,4-trimethylbenzene, p,m-xylene, and ethylbenzene) had higher concentrations in kindergarten classroom than in classroom (indoor). In classroom, the cleaning was done at the end of the school day, however, in kindergarten classroom it was more than twice times during the school day due to the children activities. The cleaning products could contain these compounds. This could be the reason of obtained higher concentrations of these compounds in kindergarten classroom. The median TVOC concentration was $115 \mu\text{g}/\text{m}^3$ in kindergarten classroom in spring term. This result was compared statistically with the result of median TVOC concentration in classroom in spring term ($57.95 \mu\text{g}/\text{m}^3$) at School 1. The comparison showed TVOC concentration was higher in kindergarten classroom than in classroom in spring term at School 1.

In School 2, air sampling in kindergarten classroom was performed both in spring and winter term. Twenty four compounds were detected at quantifiable concentrations in air samples of kindergarten classroom in winter term. Eighteen VOCs were measured in all air samples of kindergarten classroom in School 2. These compounds were similar with the measured compounds in kindergarten classroom at School 1. Distinctly, styrene and sec-butylbenzene were detected in kindergarten classroom at School 2. The concentration results of these eighteen VOCs are presented in Table 4.12.

The highest mean concentrations of VOCs, the same as in School 1, were benzene, toluene, ethylbenzene, p-m-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3-dichlorobenzene and naphthalene. The median TVOC concentration was $72.6 \mu\text{g}/\text{m}^3$ in kindergarten classroom at School 2. This value is lower than the TVOC concentration in kindergarten classroom at School 1 ($115 \mu\text{g}/\text{m}^3$). Furthermore, the median TVOC concentration in kindergarten classroom ($72.6 \mu\text{g}/\text{m}^3$)

is higher than the median TVOC concentration in classroom at School 2 in winter term (57.9 $\mu\text{g}/\text{m}^3$). All differences are statistically significant.

In spring term, twenty four VOCs were detected, but 21 compounds of these were measured in all air samples of kindergarten classroom at School 2. The statistics for the VOC concentrations are presented in Table 4.13. The highest mean concentrations of VOCs were benzene, toluene, ethylbenzene, p-m-xylene, o-xylene, 1.2.4-trimethylbenzene, 1.3-dichlorobenzene and naphthalene in spring term, similarly determined in winter term. The median TVOC concentration was 50.4 $\mu\text{g}/\text{m}^3$ in kindergarten classroom at School 2 in spring term. In winter term the median value was determined as 70.8 $\mu\text{g}/\text{m}^3$, which indicates that TVOC concentration in winter term was higher than in spring term. This result is similar with the TVOC results in the classroom in winter and spring terms. In addition, median TVOC concentration in classroom at School 2 in spring term was 25.25 $\mu\text{g}/\text{m}^3$ which showed that TVOC concentration in the kindergarten was higher than TVOC concentration in the classroom.

Table 4.12. Summary statistics of winter term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the kindergarden, School 2 (n=3)

Compound Name	Mean	Median	SD	Min	Max
carbontetrachloride	0.76	0.55	0.73	0.15	1.57
benzene	13.54	19.70	178.0	2.41	319.0
trichloroethene	1.56	0.91	1.84	0.14	3.64
toluene	32.85	37.20	63.60	19.20	137.0
tetrachloroethene	0.27	0.29	0.09	0.17	0.34
chlorobenzene	0.10	0.02	0.13	BDL	0.25
ethylbenzene	2.25	2.24	1.38	0.88	3.64
p-m-xylene	3.14	2.63	2.16	1.28	5.51
o-xylene	2.36	1.34	2.27	0.78	4.96
isopropylbenzene	0.43	0.17	0.52	0.10	1.03
n-propylbenzene	0.80	0.24	0.99	0.22	1.95
1.3.5-trimethylbenzene	1.23	0.45	1.52	0.25	2.98
tert-butylbenzene	0.64	0.28	0.74	0.15	1.49
1.2.4-trimethylbenzene	4.45	1.99	5.04	1.11	10.30
4-isopropyltoluene	0.47	0.35	0.30	0.25	0.82
1.3-dichlorobenzene	1.08	1.15	0.21	0.84	1.24
n-butylbenzene	0.70	0.41	0.66	0.24	1.46
naphthalene	2.72	2.70	0.35	2.38	3.09
TVOC	70.80	72.60	260.0	30.60	500.0

BDL : Below Detection Limit

Table 4.13. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the kindergarden, School 2 (n=3)

Compound Name	Mean	Median	SD	Min	Max
1,1,2-trichloroethane	0.49	0.49	0.14	0.35	0.63
chloroform	0.21	0.21	0.07	0.14	0.29
carbontetrachloride	0.70	0.38	0.76	0.15	1.57
benzene	8.21	3.52	10.00	1.41	19.70
trichloroethene	0.44	0.35	0.43	0.06	0.91
toluene	36.30	37.20	3.03	32.90	38.80
tetrachloroethene	0.61	0.74	0.23	0.34	0.76
ethylbenzene	1.19	0.82	0.92	0.53	2.24
p-m-xylene	1.56	1.29	0.97	0.76	2.63
styrene	0.54	0.34	0.36	BDL	0.95
o-xylene	0.90	0.86	0.42	0.51	1.34
bromoform	0.02	0.02	0.01	0.01	0.03
isopropylbenzene	0.12	0.14	0.06	0.06	0.17
n-propylbenzene	0.23	0.22	0.09	0.15	0.32
1,3,5-trimethylbenzene	0.34	0.25	0.16	0.24	0.52
tert-butylbenzene	0.19	0.15	0.08	0.13	0.29
1,2,4-trimethylbenzene	1.38	1.11	0.55	1.02	2.02
4-isopropyltoluene	0.23	0.24	0.03	0.19	0.25
1,3-dichlorobenzene	0.97	0.84	0.31	0.75	1.33
n-butylbenzene	0.27	0.24	0.08	0.22	0.37
naphthalene	1.47	1.07	0.80	0.95	2.38
TVOC	56.40	50.40	19.50	41.20	77.50

BDL : Below Detection Limit

The air sampling in kindergarten classroom was also carried out in School 3. Twenty eight VOCs were detected at quantifiable concentrations in kindergarten classroom air samples. Sixteen of them were measured in all air samples. The statistics for the VOC concentrations are presented in Table 4.14. As in the other kindergartens, the similar compounds were determined at the highest mean concentrations (benzene, toluene, ethylbenzene, p-m-xylene, 1,3-dichlorobenzene and naphthalene). The median TVOC concentration was $53.6 \mu\text{g}/\text{m}^3$ which was similar with the median TVOC concentration in kindergarten classroom at School 2 in spring term.

In all three kindergarten classrooms, similar VOCs were detected at high concentrations (benzene, toluene, ethylbenzene, p-m-xylene, 1,3-dichlorobenzene and naphthalene). These compounds were also measured at high concentrations in classrooms and school playgrounds. Benzene, toluene, ethylbenzene and xylenes were

reported as the most common VOCs detected at high concentrations in indoors at school buildings (Godwin, et al. 2007, Adgate, et al. 2004, Lee, et al. 2002).

The TVOC concentrations in kindergartens were higher than the concentrations in classrooms. This may be expected because there were lots of extra materials in the kindergarten for activities that could be sources of VOCs. In kindergartens, there were lots of plastic toys, adhesives were used in play and learning activities, and variety of coloring material were used. Also, children used paints during the play activities.

The results showed that, the highest TVOC concentration was measured at School 1. In fact, numbers of students, floor area are similar for three kindergarten classrooms. However, there were lots of materials, which are potential sources for VOCs in kindergarten classroom of School 1, such as plastic toys, painted pasteboards, cupboards. During one sampling, in School 1 kindergarten classroom, the children were doing an activity using adhesives. In addition, type fuel used in School 1 was different. Fuel type was coal in this school and the furnace room was near the kindergarten classroom. These could be the reasons of high TVOC concentration in School 1 kindergarten classroom.

Table 4.14. Summary statistics of spring term VOC concentrations ($\mu\text{g}/\text{m}^3$) in the kindergarten, School 3(n=3)

Compound Name	Mean	Median	SD	Min	Max
benzene	4.95	5.22	0.60	4.25	5.37
toluene	20.20	27.80	13.30	4.83	27.9
tetrachloroethene	0.35	0.33	0.20	0.16	0.55
ethylbenzene	0.93	1.19	0.59	0.26	1.34
p-m-xylene	1.17	1.53	0.73	0.33	1.66
styrene	0.65	0.78	0.29	BDL	0.84
o-xylene	0.83	1.09	0.51	BDL	1.17
bromoform	0.09	0.11	0.04	0.05	0.12
isopropylbenzene	0.06	0.09	0.04	0.02	0.09
n-propylbenzene	0.12	0.13	0.06	0.06	0.17
1.3.5-trimethylbenzene	0.15	0.18	0.08	0.05	0.21
1.2.4-trimethylbenzene	0.55	0.70	0.29	0.22	0.74
4-isopropyltoluene	0.23	0.30	0.14	0.07	0.31
1.3-dichlorobenzene	11.40	12.20	7.55	3.51	18.6
n-butylbenzene	0.14	0.16	0.03	0.11	0.17
naphthalene	1.55	1.77	0.94	0.52	2.35
TVOC	43.4	53.6	25.4	14.98	61.6

BDL : Below Detection Limit

4.5. Discussions on Concentrations of VOC in Three Schools

The samples were analyzed for total of 51 VOCs of which about > 50 % of these VOCs were detected both indoors and outdoors. The most common VOCs included benzene, toluene, trichloroethene, ethylbenzene, xylenes, styrene, 1,3,5-trimethylbenzene, naphthalene, 1,4-dichlorobenzene, 1,3 dichlorobenzene, chloroform and carbon tetrachloride. Most of these compounds were reported in some studies as most common VOCs detected in indoor air samples, indoor concentrations usually exceeding outdoor levels (Girman, et al. 1999, Lee, et al. 2002, Adgate, et al. 2004, Godwin, et al. 2007). Bozkurt et al. (2007) measured some of these most common VOCs (benzene, toluene, ethylbenzene and xylene) in three schools in Kocaeli, Turkey. Concentrations of these compounds in our study were lower than the concentrations reported by Bozkurt et al. (2007). Furthermore, the VOC concentrations in outdoor air measured in this study were compared to the levels reported by Odabasi et al. (2001). They measured benzene, toluene, and xylene in outdoor air from different locations in İzmir. The average concentrations of these compounds were presented in his study as 45, 116.8 and 105.3 $\mu\text{g}/\text{m}^3$ for benzene, toluene and xylene respectively. The average outdoor concentrations of these compounds in this study were significantly lower than the study of Odabasi et al. (2001). Odabasi et al. (2001) sampled on streets with heavy traffic. The relationship between VOC concentrations in indoor and outdoor air was investigated in the present study; the results show that most of the VOCs had higher median concentrations in indoor air than outdoor air. As indicated in chapter three, generally, adequate ventilation was not available in classrooms in all three schools. Classrooms were cleaned everyday at the end of the school day. Chemicals contained in cleaning products might affect the indoor air quality of schools. However, no definite information about the chemicals contained in the cleaning products was available. Moreover, the indoor sources could be the materials in the classrooms as desks, chairs, computers etc. The studies that were carried on the varnishes, paints, and computers, wood based products to determine the emissions of VOCs were discussed in chapter three.

The median indoor/outdoor VOC concentration ratios were calculated in each season for each school. The results of the VOCs median indoor/outdoor ratios give an idea about the sources of the compounds. For all three schools, the common compounds

that had ratios higher than 1.5 were 4-isopropyltoluene, 1,3-dichlorobenzene and naphthalene. This result suggests dominant indoor sources for these compounds. That result showed similar trend with the studies performed in different microenvironments, apartments (Rehwagen, et al. 2003), outdoor, home (Adgate, et al. 2004), schools (Adgate, et al. 2004, Godwin, et al. 2007). In fact, there was a similarity with the detected VOCs in indoor and outdoor air of three schools but, there was no similar trend in the indoor/outdoor ratios for each of detected VOCs. In School 1 and 3, toluene had indoor/outdoor ratios higher than 1.5 suggesting dominant indoor sources for toluene, which was supported with by studies performed in different microenvironments, office buildings (Khoder, et al. 2006), apartments (Rehwagen, et al. 2003), schools (Godwin, et al. 2007). However, in School 2 toluene had a median indoor/outdoor ratio of 1.4 which was similar with the study of Adgate et al. (2004). In their study they indicated that there could be indoor and outdoor sources for toluene. Furthermore, ethylbenzene, xylenes, and chloroform showed different indoor/outdoor ratios in three schools. For these compounds, the results suggested outdoor sources in School 1 and 3. In contrast, the indoor/outdoor ratios for these compounds indicate that indoor sources were the primary contributors in School 2. In addition, carbon tetrachloride had indoor/outdoor ratio less than one which suggested outdoor sources in School 2 and 3. Adgate et al. (2004) also reported that, carbon tetrachloride had mainly outdoor sources. But this ratio was greater than 1.5 in School 1 which meant that carbon tetrachloride had both indoor and outdoor sources. Another widespread compound detected at high concentrations was benzene. The indoor/outdoor ratios for benzene in three schools for both seasons were in the range of 1 ± 0.5 but only in spring term that value was 2.7 in School 1. Due to that information, benzene had both outdoor and indoor sources as indicated in the studies performed in school environments (Lee, et al. 2002, Adgate, et al. 2004, Godwin, et al. 2007). Furthermore, the studies carried out in offices and homes results showed that indoor/outdoor median ratios for benzene were < 2 and indicating primarily outdoor sources (Girman, et al. 1999, Lee, et al. 2002, Rehwagen, et al. 2003, Khoder 2006).

TVOC concentrations of indoor and outdoor air were also investigated statistically with using Mann-Whitney Rank Sum test. The median indoor/outdoor TVOC concentrations are presented in Table 4.15. These results were compared the literature studies which are summarize in Table 4.16. Indoor TVOC concentrations were significantly higher than outdoor TVOC concentrations in each season for School 1 and

2. This result was similar to literature (Khoder, et al. 2002, Rehwagen, et al. 2003, Bozkurt, et al. 2007, Godwin, et al. 2007). The minimum and maximum TVOC median concentrations for indoor air were 32.1 and 104 $\mu\text{g}/\text{m}^3$, for outdoor air were 9.9 and 49.1 $\mu\text{g}/\text{m}^3$. These concentrations were generally higher than the studies performed in schools in other countries, in Sweden (mean TVOC 6 $\mu\text{g}/\text{m}^3$, Smedje, et al. 1997), Minnesota (median TVOC 14.4 $\mu\text{g}/\text{m}^3$ Adgate, et al. 2004), Australia (max TVOC 94 $\mu\text{g}/\text{m}^3$, Zhang, et al. 2006), and Michigan (mean TVOC 58 $\mu\text{g}/\text{m}^3$, Godwin, et al. 2007). In addition, the seasonal variations of TVOC concentrations in indoor air were investigated for each school. The indoor air median TVOC concentrations for winter and spring terms were 86.8 and 57.9 respectively in School 1. TVOC concentrations in winter term was higher than spring term, statistically there was a significant difference between winter and spring seasons ($p=0.047$). It was obtained the same result for the School 2. The indoor air median concentrations were 57.9 and 25.3 for winter and spring terms respectively. The difference was statistically significant ($p=0.017$).

The indoor and outdoor TVOC concentrations of three schools were compared in each term. The highest TVOC median concentration was obtained from indoor air samples of School 1 in winter and spring terms. Also, outdoor TVOC concentrations in School 1 were significantly higher than School 2 both in winter and spring terms. Only spring term sampling was performed in School 3, the comparisons were carried out for spring term between the three primary schools. As a result of statistical analysis, there was a significant difference between indoor and outdoor air concentrations in School 2 and 3. The indoor TVOC concentration of School 2 was significantly higher than School 3. In contrast, the outdoor TVOC concentration of School 3 was significantly higher than School 2 also than School 1 in spring term. It was expected that, the TVOC concentrations in outdoor air of School 3 were lowest because it is located in the suburban region. Due to measured concentrations in indoor and outdoor air of School 3, it was determined that most of the VOCs had outdoor sources with the exception of toluene, 4-isopropyltoluene, 1,3-dichlorobenzene and naphthalene which mostly expected to come from indoor sources like cleaning products (Maroni, et al. 1995). Especially 1,3-dichlorobenzene and naphthalene had high concentrations indoors in all three schools in both seasons. In all three schools, the test spaces (classrooms) were near the student toilets where mostly used toilet air fresheners contain naphthalene and 1,3-dichlorobenzene compounds. This could be the reason of measured these compounds in indoors at high concentrations.

Total and individual VOC values were in line with those found in other studies. The TVOC levels should be compared with the guideline value. An important study reported by Molhave, he suggested according to a classification into four groups for TVOC: $< 200 \mu\text{g}/\text{m}^3$ = comfort; $200\text{-}3000 \mu\text{g}/\text{m}^3$ = irritation and discomfort if other factors exist; $> 3000\text{-}25000 \mu\text{g}/\text{m}^3$ = discomfort range; $> 25000 \mu\text{g}/\text{m}^3$ toxic range. The TVOC values in this study (Table 4.15) were in the first group (Molhave, et al. 1997). Furthermore, benzene concentrations should be considered, because being human carcinogen. Benzene concentration range was between 6.3 and $16.4 \mu\text{g}/\text{m}^3$ in indoor air measurements. EPA uses mathematical models, based on human and animal studies, to estimate the probability of a person developing cancer from breathing air containing a specified concentration of a chemical. EPA estimates that, if an individual were to breathe air containing benzene at $0.1 \text{ mg}/\text{m}^3$ over his or her entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical. Similarly, EPA estimates that breathing air containing $1.0 \text{ mg}/\text{m}^3$ would result in not greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing $10.0 \text{ mg}/\text{m}^3$ would result in not greater than a one-in-ten thousand increased chance of developing cancer (EPA-IRIS 2003). Due to this information, the benzene concentrations in our study are very smaller than the stated concentrations. However, these risk calculations were performed according to the adults. The effects from exposure to benzene can be quite different among children. Children may have a higher unit body weight exposure because of their heightened activity patterns which can increase their exposures. This could entail a greater risk of leukemia and other toxic effects to children if they are exposed to benzene at similar levels as adults.

Table 4. 15. TVOC concentrations in the schools

	Winter term TVOC ($\mu\text{g}/\text{m}^3$)		<i>p</i> -value	Spring term TVOC ($\mu\text{g}/\text{m}^3$)		<i>p</i> -value
	Indoor	Outdoor		Indoor	Outdoor	
School 1	86.8	39.8	0.027	57.9	13.5	≤ 0.001
School 2	57.9	13.3	≤ 0.001	25.3	9.9	≤ 0.001
School 3	-	-		23.8	25.1	0.58

Table 4. 16. Summary of the studies

Subjects	Researchers	Compounds	Results
64 classes Michigan	Godwin, et al. (2007)	VOC	Mean concentrations($\mu\text{g}/\text{m}^3$) Benzene 0.09 Toluene 2.81 α – pinene 1.35 Limonene 4.41
3 schools West Australia	Zhang, et al. (2006)	VOC Formaldehyde	10 VOCs were detected and maximum TVOC concentration was $94 \mu\text{g}/\text{m}^3$ Maximum formaldehyde median value $38 \mu\text{g}/\text{m}^3$
5 classes Minnesota	Adgate, et al. (2004)	VOC	Benzene 0.6 Ethylbenzene 0.6 Toluene 2.9 p-m xylene 2.3
Different schools in Europe	Daisey, et al. (2003)	TVOC Formaldehyde	0.1 – 1.6 mg/m^3 0.01 – 0.35 ppm
10 schools Hong Kong	Lee, et al. (2002)	VOC Formaldehyde	Benzene 3.13 Toluene 17.74 Etyl benzene 4.20 p/m-xylene 3.30 O-xylene 1.66 < $20 \mu\text{g}/\text{m}^3$
96 classes Switzerland	Smedje, et al. (1997)	VOC Formaldehyde	Prevalant VOCs; benzene, toluene, xylenes Mean TVOC concentration was $35.5 \mu\text{g}/\text{m}^3$ < $5 \mu\text{g}/\text{m}^3$
6 classes Switzerland	Norback, et al. (1990)	VOC Formaldehyde	Mean TVOC concentration range, 70-180 $\mu\text{g}/\text{m}^3$ < $10 \mu\text{g}/\text{m}^3$
3 schools Kocaeli/ Turkey	Bozkurt, et al. (2007)	VOC	Benzene 7.5 Toluene 55.05 Etyl benzene 11.11 Xylenes 15.44

4.6. Formaldehyde Concentrations

In this part, results of the formaldehyde sampling are presented for the three schools. Formaldehyde sampling and analytical techniques are different from the VOCs. The detailed information about the techniques is given in chapter three. Furthermore, the important adverse health effects of this compound, which were mentioned in chapter two, makes formaldehyde a special case. Finally, formaldehyde is one of the most abundant VOCs indoors in terms of frequency of detection and concentration levels as there are many indoor sources. Because of these reasons, formaldehyde results are investigated separately.

In winter term, the sampling was performed only in two schools and the descriptive statistics for formaldehyde concentrations are presented in Table 4.17. The median formaldehyde concentrations in indoor air were 32.2 and 42.6 $\mu\text{g}/\text{m}^3$ in School 2 and 1. Formaldehyde concentrations were higher in classroom of School 1 than School 2 (Figure 4.16) but, the difference was not statistically significant ($p=0.16$).

Table 4.17. Summary statistics of winter term formaldehyde concentrations ($\mu\text{g}/\text{m}^3$) in indoors of Primary Schools (n= 9)

	School 1		School 2	
	Indoor (n=9)	Outdoor (n=3)	Indoor (n=9)	Outdoor (n=3)
Mean	44.36	7.64	30.78	7.15
Median	42.58	7.75	32.20	6.43
SD	22.92	0.38	15.57	1.60
CIM*	17.62	-	11.97	-
Max	80.39	7.95	51.29	6.05
Min	8.86	7.23	10.73	8.99

CIM* : % 95 confidence interval

In spring term, air sampling was performed in all three schools. The formaldehyde concentrations are given in Table 4.18. The median indoor formaldehyde concentrations were 36.6, 46.4 and 33.9 $\mu\text{g}/\text{m}^3$ in the classrooms of School 2, School 1 and School 3.

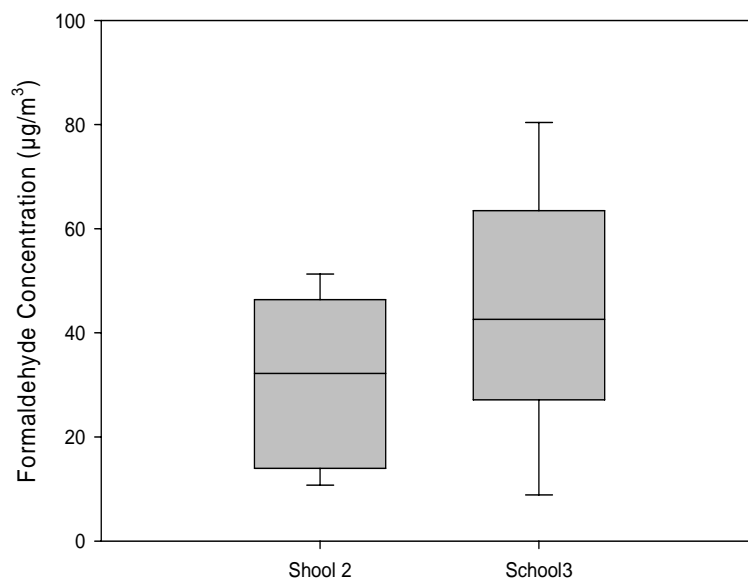


Figure 4.16. Box plots of indoor formaldehyde concentrations in winter term

Table 4.18. Summary statistics of spring term formaldehyde concentrations ($\mu\text{g}/\text{m}^3$) in indoors of Primary Schools ($n=9$)

	School 1		School 2		School 3	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Mean	43.73	7.64	35.82	7.21	36.53	0.61
Median	46.42	7.73	36.56	3.96	33.95	0.60
SD	16.13	1.33	12.52	6.54	9.86	0.04
CIM*	12.40	-	9.60	-	7.58	-
Max	61.95	8.93	62.17	14.7	56.60	0.65
Min	15.75	6.28	18.50	2.90	26.40	0.57

CIM*: % 95 confidence interval

Figure 4.17 presents the box plot of formaldehyde concentrations for the three schools. As shown in the figure, formaldehyde concentration was highest in School 1 similar to the winter term. The lowest concentration was in School 3. Although the mean and median formaldehyde concentrations of School 1 was higher than two schools, the difference was not statistically significant between School 1 and 2 ($p=0.26$) and between School 2 and 3 ($p=0.89$) also between School 1 and 3 ($p=0.27$).

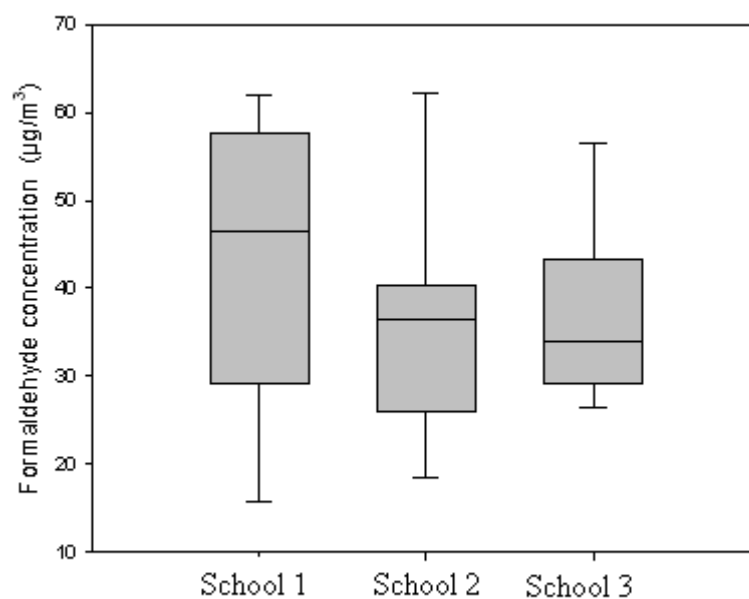


Figure 4.17. Box plots of indoor formaldehyde concentrations in spring term

As discussed in chapter two, the indoor sources of formaldehyde could be varnishes that are used on the desk or cabinets, cigarette smoke, adhesives, wood products and plastics. The indoor/outdoor median formaldehyde concentration ratios for three schools and both season higher than five which indicates that formaldehyde comes from primarily indoor sources.

The results showed that, median indoor formaldehyde concentration in the three schools was ranged from $32.2 \mu\text{g}/\text{m}^3$ (0.026ppm) to $46.2 \mu\text{g}/\text{m}^3$ (0.038 ppm). The formaldehyde concentration results of the studies performed in the schools in other countries (Sweden, Norback, et al. 1990 and Smedje, et al. 1997, Hong Kong, Lee, et al. 2002, Australia, Zhang, et al. 2006) were lower than the concentrations in this study. However, the indoor concentrations of formaldehyde in the studies performed in homes and offices were higher than the concentrations in this study (Khoder 2006, Park, et al. 2006). The possible reasons of high concentrations in offices and homes could be smoking in offices and homes, photocopy and printers used in offices, combustion processes (heating or cooking) in homes. In addition to these, the indoor formaldehyde concentrations in this study are much lower than a study performed in a coffeehouse in Ankara, Turkey (Evcı, et al. 2005). There was no ventilation system, and smoking was allowed in the coffeehouse. It was reported that, the mean formaldehyde concentrations

in the coffeehouses were 0.2 ppm which is much higher than the concentrations determined in this study. This is a reasonable result because of the cigarette smoke factor. One of the major sources of the formaldehyde is known as cigarette smoke. Furthermore, the results in this study were similar to concentration results in the study of Hanoune, et al. (2006), and Righi, et al. (2002). They measured formaldehyde concentrations in the libraries. The libraries and the classrooms have similar features; the libraries had natural ventilation as in this study. As mentioned in chapter two, US Consumer Product Safety commission (1997) reported that, formaldehyde is normally present at low levels, usually less than 0.03 ppm, in both outdoor and indoor air. According to this information, the comparison of the indoor formaldehyde concentrations in this study were at this value in contrast outdoor formaldehyde concentrations were lower than the this value (0.03 ppm).

According to the World Health Organization, the lowest formaldehyde concentration that has been associated with nose and throat irritation after short-term exposure is $100 \mu\text{g}/\text{m}^3$ (WHO 2000). In our study, the formaldehyde concentrations were lower than the recommended ($100 \mu\text{g}/\text{m}^3$) value. Furthermore, it was reported that, symptoms are rare below than 0.5 ppm, and become increasingly prevalent in studies as concentrations increase (IARC 2006). In addition, formaldehyde levels in our study were low on the whole international regulations and guidelines related to emissions of and exposures to formaldehyde have been set in several countries and range from 0.1 to 2 ppm (IARC 2006).

CHAPTER 5

CONCLUSIONS

Volatile Organic Compound (VOC) and formaldehyde concentrations were measured in classrooms (indoors), outdoors (school play ground), and in kindergarten classrooms for three schools. The sampling was performed in spring and winter terms. The most common indoor VOCs were determined. The indoor and outdoor concentrations were statistically compared. Total VOCs (TVOCs) concentrations were investigated. In addition, seasonal effects on VOCs and formaldehyde concentrations were examined.

The indoor concentrations of VOCs and formaldehyde were higher than the outdoor concentrations. The indoor/outdoor (I/O) ratios of VOCs were determined. The I/O ratios were >2 for chloroform, ethylbenzene, xylenes, styrene, naphthalene, and formaldehyde which could have indoor sources. Carbontetrachloride, chlorobenzene, bromoform, isopropylbenzene, n-propylbenzene, n-butylbenzene, and 1,2,4-trichlorobenzene had $I/O \leq 1$ which suggested the outdoor sources.

The common VOCs detected indoors were benzene, toluene, xylenes, ethylbenzene, and naphthalene. The maximum median concentrations were obtained for benzene and toluene as $26.5 \mu\text{g}/\text{m}^3$ and $16.4 \mu\text{g}/\text{m}^3$, respectively. The I/O ratios for benzene and toluene were between 1 and 2 which indicated the both indoor and outdoor sources.

Median TVOCs and formaldehyde indoor concentrations were calculated for three schools in winter and spring terms. TVOCs and formaldehyde concentrations were $86.8 \mu\text{g}/\text{m}^3$ and $42.6 \mu\text{g}/\text{m}^3$ in winter, and $57.9 \mu\text{g}/\text{m}^3$ and $46.4 \mu\text{g}/\text{m}^3$ in spring terms for School 1; and $57.9 \mu\text{g}/\text{m}^3$ and $32.2 \mu\text{g}/\text{m}^3$ in winter, and $25.3 \mu\text{g}/\text{m}^3$ and $36.6 \mu\text{g}/\text{m}^3$ in spring term for School 2, and $23.8 \mu\text{g}/\text{m}^3$ and $33.9 \mu\text{g}/\text{m}^3$ in spring term for School 3, respectively. The indoor median TVOCs concentrations in winter term were higher than in spring term statistically, however, indoor formaldehyde concentrations were similar in both seasons and there were no statistically significant difference.

VOCs have both indoor and outdoor sources. The TVOCs concentrations were $< 200 \mu\text{g}/\text{m}^3$ which suggested the comfort range. However, diclorobenzenes and naphthalene were measured at very high levels indoors and the possible sources of these

compounds could be the cleaning products. To reduce levels it will be necessary to eliminate the sources of the chemicals through a better choice of construction and furnishing materials. Also, greater care must be taken with respect to and necessary use of chemical substances. A classroom near the toilets where cleaning products were stored was identified with relatively high level of VOCs. Therefore, we recommend that the cleaning products should be kept in a proper storage area away from the classrooms. Ventilation and air-conditioning can have a considerable influence on the level of chemical substances in indoor air. They should be operated to provide hygienic conditions that have positive effects on human health. Therefore, their efficiency and service reliability must be maintained.

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