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Volatile Organic Compounds in Urban and Industrial Areas in the Philippines

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"In everyone's life, at some time, our inner fire goes out. It is then burst into flame by an encounter with another human being. We should all be thankful for those people who rekindle the inner spirit..."

Albert Schweitzer

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ABSTRACT

Volatile organic compounds (VOCs) have been known as major precursors in the formation of photochemical smog and ground level ozone as well as primary health risk factor in both indoor and ambient air. Despite this fact, few studies on the ambient and indoor air levels of VOCs have been done for developing countries like the Philippines, where the VOC levels are expected to be high due to rapid industrialization and lenient regulations. At present, VOCs remains unregulated and are rarely monitored in the Philippines.

In this study, presence and concentration levels of VOCs were investigated for urban (Manila) and industrial areas (Calamba and Binan) in the Philippines. Ambient and indoor samples from both areas were obtained by means of active sampling using Tenax TA tubes as sorbent material. Analysis and quantification were done by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) and internal standard calibration. A total set of 37 VOCs consisting of alkanes, aromatic hydrocarbons, halogenated compounds, oxygen containing hydrocarbons and terpenes were identified from the six sampling sites representing the urban and industrial environments. Aromatic compounds were observed to be the dominant VOCs in all the sampling sites. TVOCs was highest at 248 µg/m^3, in one of the industrial areas where a nearby roof painting plant was situated, while roadside mean TVOC at urban area was 129 µg/m^3. Diagnostic ratios and correlation analysis were utilized for source identification and based on the results, urban ambient area was seen to be influenced primarily by traffic emissions while industrial ambient area showed poor correlation which is indicative of multiple sources. Indoor samples was shown to be influenced both by outdoor and indoor sources. Ozone formation potentials were also estimated based on MIR-2010 (Maximum Incremental Reactivity) scale. Estimated values showed that 3 of the 4 outdoor sites exceeded the WHO recommended level of 100 µg/m^3 for ozone. Based on this study, traffic and industries emit significant amount of VOCs that could cause immense health risks to population residing near the emission sources.

LIST OF ABBREVIATIONS

ADB	Asian Development Bank
APCS	Absolute Principal Component Scores
B/T	Benzene-to-toluene concentration ratio
BTEX	Benzene, toluene, ethylbenzene and meta-, para-, and ortho-xylene
BTV	Breakthrough volume
$BVOC_S$	Biogenic volatile organic compounds
CMB	Chemical Mass Balance
CTS	Closed two-phase system
EB/B	Ethylbenzene-to-benzene ratio
ECD	Electron Capture Detection
EMB	Environment Management Bureau
EPA	Environmental Protection Agency
EU	European Union
FID	Flame ionization detector
GC	Gas chromatography
GWP	Global warming Potential
HSBD	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IS	Internal standard
IPCC	Intergovernmental Panel on Climate Change
LIIP	Laguna International Industrial Park
LOD	Limit of detection
LOQ	Limit of quantification
LTO	Land Transportation Office
MIR	Maximum incremental reactivity
MOIR	Maximum ozone incremental reactivity
MS	Mass spectrometry
MW	Molecular weight
ND	Not detected
NMVOCs	Non-methane volatile organic compounds
NO_x	Nitrogen oxides
ODS	Ozone-depleting substance
OFP	Ozone formation potential
OH	Hydroxyl radical
(m,p-)X /EB	m-/p-xylene-to-ethylbenzene ratio
PAN	Peroxy acetyl nitrate
PCA	Principal Component Analysis
PCBs	Polychlorinated biphenyls
PM	Particulate Matter
PMF	Positive Matrix Factorization
PTR-MS	Proton Transfer Reaction Mass Spectrometry
POCP	Photochemical ozone creation potential
ppbv	Parts per billion (volumetric)
pptv	Parts per trillion (volumetric)
RF	Response factor
RSRF	Relative sample response factor
S/N	Signal-to-noise ratio

SBS	Sick Building Syndrome
SIM	Selective ion monitoring
SIS	Scientific Instrument Services
SRF	Sample response factor
SSV	Safe sampling volume
TD	Thermal desorption
TIC	Total ion current
TSP	Totals Suspended Particles
TVOCs	Total volatile organic compounds
US EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
VOC/Bz	Volatile organic compounds-to-benzene concentration ratio
WB	World Bank
WHO	World Health Organization

Table of Contents

GENERAL INTRODUCTION

Air quality has become a major issue specially in developing nations where the regulations to protect ambient as well as indoor air conditions is not yet well placed primarily because of the priority in improving industrial strength and national wealth over environmental conditions.

Among the different anthropogenic pollutants emitted into the troposphere, volatile organic compounds (VOCs) are particularly important because they contribute to two of the most serious air quality problems. They have been known as major precursors for the formation of photochemical smog and ground level ozone. In addition several VOCs directly affect the health conditions of humans as some VOCs found in urban air such as 1,3-butadiene, benzene, formaldehyde and acetaldehyde are classified as carcinogens (Gee and Sollars, 1998; Barletta et al., 2008).

Like many developing countries, rapid industrialization and increasing number of transport vehicles have caused detrimental effects on the air quality of the Philippines especially in the urban areas of the country. The number of transport vehicles in the country for instance has been increasing at the rate of 5 to 6 percent per year (ADB, 2006). Emissions from motor vehicles largely affect the urban air quality in addition to the emissions from rising number of industries. Having realized the implications of the deteriorating air quality in the country, the government started to take initiatives in regulating pollutant emissions. Laws, such as the Philippine Clean Air Act of 1999, were promulgated but they cover mostly criteria pollutants (e.g. Totals Suspended Particles (TSP), Particulate matter (PM), SO_2, NO_2) while VOCs remained unregulated and are rarely monitored in the Philippines (Balanay and Lungu, 2009).

Several studies on the ambient and indoor air levels of VOCs in different environments such as industrial and urban areas have been done in many developed countries. However very few researches have been made for the developing ones although VOCs are expected to be an important environmental and health risk factor for the rapidly industrializing countries (Han and Naeher, 2006). From the open literature, there are only two studies that deal with the ambient levels of VOC in the Philippines which were limited to roadside environments. On the other hand, there is no known published data yet to assess the indoor VOCs of residential houses in the Philippines. Beyond this, proper information on VOC levels for urban and industrial areas in the Philippines is still lacking.

Knowledge of ambient and indoor levels of VOCs, their source profile identification and effect on health due to exposure are necessary in creating development programs, planning and implementing regulations and pollution reduction strategies. This study therefore aimed to investigate the levels and nature of VOCs in urban and industrial areas in the Philippines as well to provide information that would be useful in environmental and health policy making process in the Philippines.

CHAPTER ONE: LITERATURE REVIEW

1.1 Volatile organic compounds

Interest in volatile organic compounds (VOCs) in the atmosphere begun since Haagen–Smit recognized the importance of anthropogenic organic compounds in atmospheric chemistry in his pioneering studies of Los Angeles smog in the 1950s. In that study, it was shown that VOCs and nitrogen oxides (NO_x) combine photochemically to produce tropospheric ozone (Derwent, 1995; Goldstein and Galbally, 2007). With the growing concern for quality life in safe and clean environment, attention to ambient and indoor VOCs has been increased ever since (Kumar and Víden, 2007).

VOCs stands for a very large and heterogeneous group of organic chemicals that includes aliphatic and aromatic hydrocarbons, alcohols, aldehydes, ketones, esters and halogenated compounds that share a common characteristic of high volatility in the ambient environment (Demeestere et al., 2007; Van Langenhove, 2010; Talapatra A., 2011). Methane is an organic gas that is much less reactive than other hydrocarbons in the troposphere, so it is often considered separately (Demeestere et al., 2007; U.S.EPA, 2010).

1.2.1 Definitions and classifications

A wide range of definitions can be found for VOCs. Generally definition can be categorized as either effect oriented or based on the compound's physical property.

According to EU Directive 1999/13/ EC or Solvent Emissions Directive (EU, 1999), VOCs are functionally defined as organic compounds having at 293.15 K (i.e., 20°C) a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under particular conditions of use. The EU Paint Directive, 2004/42/EC (EU, 2004) on the other hand, uses the boiling point, rather than its volatility in its definition of VOCs and defines VOC as an organic compound having an initial boiling point lower than or equal to 250 °C at an atmospheric pressure of 101.3 kPa. Similarly, the European Eco-labelling scheme, 2002/739/EC (EU, 2002) for paints and varnishes defines VOCs as any organic compounds having a boiling point (or initial boiling point) lower than or equal to 250°C.

United States Environmental Protection Agency (US EPA) in their regulations for outdoor air, uses an effect oriented definition and defines VOCs as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (U.S.EPA, 2009). EU National Emissions Ceilings Directive 2001/81/EC (EU, 2001) also uses an effect oriented definition, where a VOC is any organic compound of anthropogenic nature, other than methane, that is capable of producing photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight.

The effect oriented definition however is rather limitative. For instance, chloromethane and tetrachloroethylene are exempted compounds for outdoor regulation on the basis of their relative non-reactivity, but they could pose serious health risks to exposed individuals if present indoors (IARC, 2012; U.S.EPA, 2012). Therefore, this study used the more broad definition of VOCs to include such toxic VOCs in the discussion.

1.2.2 Major Sources

Emission sources for VOCs include both anthropogenic and biogenic sources (Mintz and McWhinney, 2008; Kansal, 2009; Van Langenhove, 2010). On the global scale however, biogenic emissions far exceeds anthropogenic emissions by approximately a factor of 10. Biogenic emission rates are estimated to be about 1150 Tg C/yr while anthropogenic sources emit approximately 142 Tg C/yr (Guenther et al., 1995; Goldstein and Galbally, 2007; Talapatra A., 2011; Sahu, 2012).

Global budget for atmospheric VOCs was estimated and proposed by Goldstein and Galbally (2007). Formation of secondary organic aerosols, which are eventually removed either by deposition or oxidation to CO was suggested to account for the loss of approximately half of non-methane volatile organic compounds (NMVOCs) entering the atmosphere. This is shown in Figure 1.1.

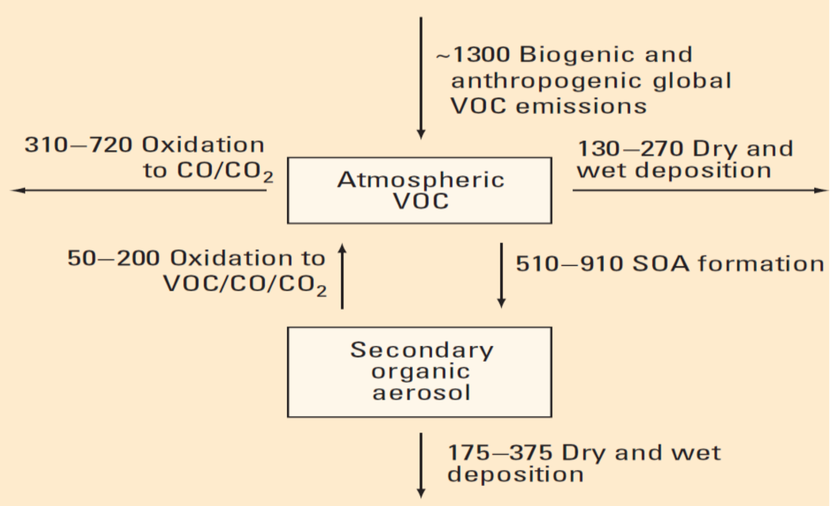

Figure 1.1 Proposed mass-balanced based estimate of the global budget for atmospheric VOCs; Units in Tg C/yr (Goldstein and Galbally, 2007)

1.2.2.1 Natural sources

Natural sources of atmospheric VOCs include emissions from vegetation, specifically rural forested areas, oceans, marine phytoplanktons, soil microbiota and geological hydrocarbon reservoirs (Guenther et al., 1995; Stavrakou et al., 2009; Van Langenhove, 2010; Sahu, 2012). Among these, the major natural source of NMVOCs is terrestrial vegetation. Predominant NMVOCs emitted from vegetation include isoprene (2-methyl-buta-1,3-diene), monoterpenes and oxygenated terpenes. Annual global (VOCs) flux from plants was estimated to consist of 44% isoprene, 11% monoterpenes, 22.5% other reactive hydrocarbons and 22.5% other non-reactive hydrocarbons (Guenther et al., 2000; Kansal, 2009; Van Langenhove, 2010).

Biogenic VOCs (BVOCs) are important in atmospheric chemistry because of their large impact on both regional and global air quality. They have high reactivity in the atmosphere and thus have shorter atmospheric lifetimes than anthropogenic VOCs due to faster reaction rates with hydroxyl (•OH) radicals. BVOCs have been reported to have disproportionately large impact In tropical photochemistry, compared to higher latitudes (Sahu, 2012). BVOCs can be a major influence in ozone chemistry in a variety of ways. It can act as a source through oxidation products like ketones, aldehydes and carbon monoxide, or as a direct sink of oxidants by competing with ozone as a sink for NO (Guenther et al., 2000). In some urban environments, BVOCs emissions were shown to have the same degree of importance as anthropogenic VOCs emissions in terms of regional photochemical ozone production (Goldstein and Galbally, 2007).

1.2.2.2 Anthropogenic Sources

Anthropogenic sources of ambient VOCs primarily include mobile sources emissions (transport sector), and stationary sources (industrial solvent use, production and storage processes, combustion processes). Vehicle emissions is often the main source of VOCs in urban areas (Barletta et al., 2005; Theloke and Friedrich, 2007; Van Langenhove, 2010; Huang et al., 2011).

Anthropogenic emissions are important in urban areas because of the higher potential for tropospheric ozone formation. Unlike the rural areas where there are also significant BVOC production, industrial and vehicular pollution in urban atmosphere also contribute to increased NOx level that promotes production of tropospheric ozone even in small concentration of VOCs (Talapatra A., 2011).

(a) Mobile Sources

At present, traffic is the predominant source of ambient VOCs in many urban areas in industrialized countries. Among the exhaust VOCs, approximately half of the mass emitted is unburned fuel (Caplain et al., 2006). Traffic related VOCs include alkanes, alkenes, alkynes and aromatic hydrocarbons. Among traffic related VOCs, aromatic compounds, including benzene, toluene, ethyl benzene, and isomers of xylene (BTEX), have public health importance and are of great concern because of their relative abundance (Han and Naeher, 2006; Buczynska et al., 2009).

Vehicular VOC emission depends on a variety of factors. Rubin et al. (2006) reported that exhaust contribution to VOC levels varies depending on time of day and day of week and that there is positive association between the headspace vapor contribution and ambient air temperature for afternoon hours. Composition of exhaust was also found to be dependent on the type of vehicle and use of catalytic converters (Verma and des Tombe, 2002). For instance, light alkanes and alkenes were reported to constitute the highest proportions of VOCs from catalyst-equipped, gasoline-driven passenger cars (Stemmler et al., 2005; Lai and Peng, 2012). Vehicles using unleaded fuels without catalytic converters on the other hand were observed to generate more VOCs (Wang and Zhao, 2008). The influence of the type of fuel and fuel composition was also reported. Chemical composition and magnitude of vehicle exhaust emissions was shown to be directly related to the gasoline composition used (Schuetzle et al., 1994). Decrease of aromatic compounds in vehicle exhaust was reported by shifting from Euro 1 to Euro 3 fuel standards (Caplain et al., 2006). BTEX level in exhaust was also reported to decrease for all vehicles fueled with methanol/gasoline blends but increase in formaldehyde levels was also noted (Zhao et al., 2011).

(b) Stationary sources

Stationary anthropogenic sources of VOCs are grouped into several categories which include energy production, industries, solvent evaporation, waste treatment and disposal and agriculture and food industries. Among the anthropogenic stationary emission sources, use of organic solvents is the most important. Solvents can belong to any of these classes: aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ketones, esters, amides (Van Langenhove, 2010).

Industrial zones can thus be a significant source of stationary VOCs as it involves emissions from all these categories. Industrial power plants, combustion and a broad range of industrial processes are extensive in industrial zones. Use of solvents in metal surface coating, degreasing, printing and fabric coating and flatwood-panelling are common in many manufacturing activities (Van Langenhove, 2010). Indeed industries can be a significant source of VOCs. For instance high concentrations of BTEX were observed at many industrial locations (Tiwari et al., 2010). Emission of VOCs from dye industry (Jo et al., 2004), printing industry (Leung et al., 2005), and petroleum refinery (Lin et al., 2004) have been published. Polymer industry, rendering industry and pulp and paper industry were also cited as important industrial sources of VOCs (Van Langenhove, 2010).

1.2.2.3 Indoor sources of VOCs

The main sources of VOCs in the indoor environment are building materials, furnishings, cleaning products, dry cleaning agents, paints, varnishes, waxes, solvents, glues, aerosol propellants, refrigerants, fungicides, germicides, cosmetics and textiles, appliances, air fresheners and clothing (Weschler, 2009; Sarigiannis et al., 2011; Talapatra A., 2011). Human activities such as cooking and smoking also contribute to indoor VOCs (Talapatra A., 2011). Other contributors had been cited which includes, solid fuel combustion (Duricova et al., 2010), emissions following house renovations (Herbarth and Matysik, 2010), poor ventilation (Dimitroulopoulou, 2012) and insecticide application (Bukowski and Meyer, 1995; Pentamwa et al., 2011).

Outdoor sources (e.g. industrial emissions, exhaust from vehicles) also contribute to indoor VOCs (Adgate et al., 2004; Talapatra A., 2011). Baek et al. (1997) reported that majority of VOCs measured in indoor environments in two cities of Korea were from outdoor sources. Season and level of urbanization were also shown to have influence on indoor VOC concentration levels (Jia et al., 2008). Similarly, Geiss et al. (2011) showed the effect of geographical and seasonal variations on the indoor air concentrations of VOCs in the statistical analysis of dataset of the indoor pollution of European public buildings and homes.

1.3 Effects of VOCs

VOCs play a vital role in a number of environment and health related issues. These important roles are (ii) halogenated VOCs can deplete O_3 in the stratosphere. (ii) pose potential risks to human health, as some VOCs are toxic. (iii) global-scale increase in VOCs can also induce greenhouse effects and (iv) they can serve as precursors of ground-level photochemical formation of O_3 (Derwent, 1995; Demeestere et al., 2007; Goldstein and Galbally, 2007; Sahu, 2012).

1.3.1 Effects on human health

VOCs may impact human health through: (i) direct effects (ii) indirect impacts via photochemical ozone formation which is also associated with health risks (Choi et al., 2011).

Some VOCs can affect the human senses through their odor and narcotic effect especially at long exposures indoors. VOCs commonly found indoor air like 2-ethyl-1-hexanol are associated with health effects like Sick Building Syndrome (SBS)(Kamijima et al., 2002). This building-related disorder is characterized mainly with subjective symptoms like mild irritation of eyes mucous membranes and the respiratory system, headaches, nausea, drowsiness, fatigue and general malaise (Srivastava et al., 2000).

VOCs belonging to the category of carcinogens are of great concern and are subject to many national and international laws. Some of these VOCs are widely distributed in the ambient atmosphere such as: benzene and 1,3-butadiene (buta- 1,3-diene), as potential leukemia inducing agents, formaldehyde (methanal), as a potential nasal carcinogen, polycyclic aromatic hydrocarbons, as potential lung cancer inducing agents, polychlorinated biphenyl compounds (PCBs) and polychlorinated terphenyl, dioxins and furans (Derwent, 1995).

Another indirect effect of VOCs is through the production of tropospheric ozone. Ozone is known to cause respiratory tract inflammation, reduce respiratory capacity, and increase hospitalization rates related to asthma and other respiratory ailments. There have also been systematic evidences which indicate that short term exposure to ozone is associated with premature mortality following episodes of photochemical smog in the US (Volkamer et al., 2010). Several long term studies showed that the number of attributable deaths due to tropospheric ozone is increased by an estimate of 1–2% on days when the 8-hour mean ozone concentration reaches 100 $\mu g/m^3$ compared to when ozone levels are at a baseline level of 70 $\mu g/m^3$ (the estimated background ozone level). Health effects was observed to become severe and numerous as ozone concentrations increase above the guideline value of 100 $\mu g/m^3$. This effects were reported to occur in places where concentrations are high due to human activities or are elevated during episodes of very hot weather (WHO, 2005).

1.3.2 Stratospheric ozone depletion

Some organic compounds contain chlorine or bromine substituents and have high tropospheric life time. These VOCs are stable enough to survive tropospheric removal processes, and to reach the stratosphere where they undergo the processes of stratospheric photolysis and hydroxyl radical destruction that leads to the release of active ozone-destroying chain carriers. VOCs that contribute to ozone depletion are termed ozone depleting substances (ODS) which includes many chlorinated solvents and refrigerants, and bromine-containing fire retardants and fire extinguishers (Derwent, 1995; Van Langenhove, 2010).

1.3.3 Global warming contribution

Some of the more stable VOCs survive the tropospheric removal process in the atmospheric boundary layer and may be transported into the free troposphere above the boundary layer. Atmospheric boundary layer is the shallow region of the troposphere next to the earth's surface whose depth is typically a few hundred meters in winter to approximately 2 km in mid-summer. Some of these longer-lived VOCs are classed as radiatively active gases and can absorb solar or terrestrial infrared radiation and possess high Global warming Potential (GWP). In this sense, they directly contribute to enhanced greenhouse effect. Many VOCs however are not themselves radiatively active gases, but they have the potential to perturb the global distributions of other radiatively active gases thus acting as secondary greenhouse gases. Organic compounds can behave as secondary greenhouse gases by: (i) reacting with NOx to produce ozone in the troposphere (ii) increasing or decreasing the tropospheric •OH distribution and hence perturbing the distribution of methane. VOCs, thus, can effect an increase of ozone in the free troposphere and this has raised some concern because ozone is an important greenhouse gas (Derwent, 1995).

Ozone can effectively absorb infrared light with a wavelength of around 10 microns and thus efficiently absorbs the infrared rays radiated from the earth. Since these wavelengths do not overlap those for water vapor and carbon dioxide, it makes ozone a powerful greenhouse gas. The extent of global warming property of ozone is shown in Figure 1.2, where global climate forcings of different greenhouse gases are compared. Climate forcing is an index generally used to compare global warming effects of greenhouse gases. It is expressed in Watts per square meter (W/m^2) and is obtained by assessing the extent of reduction of infrared light passing through the tropopause given an increase in concentration of the particular greenhouse gas. From the figure, CO_2 exhibited the largest effect on global warming followed by methane and ozone. Owing to the relative large effect, the Intergovernmental Panel on Climate Change (IPCC) called tropospheric ozone the "third greenhouse gas." (Akimoto et al., 2006)

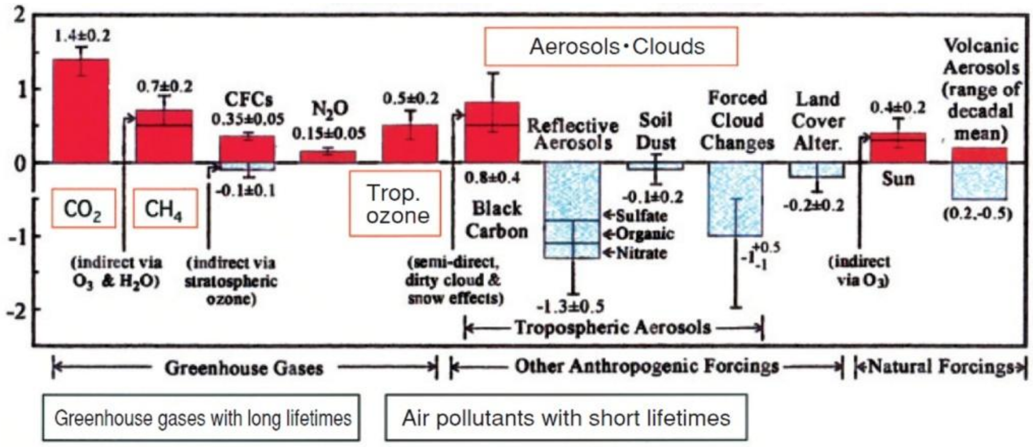

Figure 1.2 Global climate forcings of different greenhouse gases (W/m^2) from 1850 to 2000. Source : Hansen and Sato (2001) as cited by Akimoto et al. (2006)

1.4 Tropospheric ozone formation

As earlier discussed, atmospheric VOCs play an important role in tropospheric chemistry as they lead to the formation of ozone. Tropospheric ozone is formed during the photochemical oxidation of VOCs in the presence of NOx (oxides of nitrogen, NO and NO_2). Formation of ozone via VOC oxidation is linked to the number of transformations of NO to NO_2 by peroxyradicals occurring during the oxidation process (Van Langenhove, 2010; Butler et al., 2011).

1.4.1 Mechanism of formation

The mechanism of tropospheric ozone formation was described by Van Langenhove (2010) and Akimoto et al. (2006) as shown in the figure below.

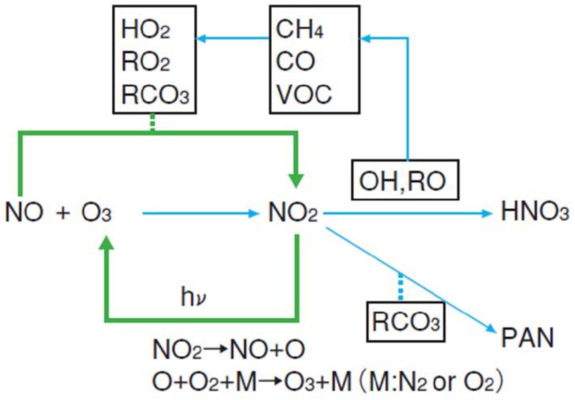

Figure 1.3 Generation and transformation process of ozone and NOx; Note: R = indicates alkyl group, aryl group; PAN = peroxyacetylnitrate

As shown in the figure, when NO_2 is oxidized photo chemically to nitrogen monoxide (NO), oxygen atoms are released which then reacts in a very fast reaction with molecules of oxygen (O_2) thus forming ozone (O_3). The reaction happens only under the influence of ultraviolet light from the sun and thus ozone formation through this reaction only occurs at day time. The net reaction can be stated as:

$$NO_2 + O_2 + h.v \rightarrow NO + O_3 \qquad J \qquad \text{Eqn (1.1)}$$

O_3 can be reduced by NO:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad k \qquad \text{Eqn (1.2)}$$

When steady state is reached, the rate of O_3 production balances the rate of O_3 destruction and thus equilibrium concentration of ozone can be derived:

$$[O_3] = \frac{J[NO_2]}{k[NO]} \qquad \text{Eqn (1.3)}$$

where J and k are rate constants for ozone formation and ozone destruction respectively.

In a clean environment with, only nitrogen oxides and air, equilibrium of generation and decomposition reactions is usually reached when O_3 concentration is around 10 to 20 ppbv. If there are VOCs however, VOC molecules react with O, O_3 and •OH in the photo-oxidation process and would produce oxide radicals (RO) and peroxide radicals (HO_2, RO_2, RCO_3), which in turn are involve in reproducing NO_2 from NO. In this way, VOCs indirectly affect the tropospheric ozone formation.

Since VOCs can undergo a variety of photochemical oxidation process, assessment of impacts of VOCs to ozone formation can be very complicated. Assessing the complex chemistry of atmospheric VOCs in addition to some actual studies indicates that ozone formation is influenced by the VOC/NOx ratio (Finlayson-Pitts and Pitts, 1997; Wu et al., 2009) and with some factors like temperature and humidity (Aneja et al., 2000) and wind speed (Banta et al., 2011).

1.4.2 Estimation of ozone formation

As mentioned, the relationship between O_3, NOx and VOC is rather complex. However knowledge and information regarding the controlling factors in the tropospheric ozone formation are important in understanding regional photochemistry and consequently for applying cost effective control strategies. Photochemical ozone formation depends on the relative abundances of both VOC and NOx. Van Langenhove (2010), for instance, described a specific instance when reducing NO_2 without simultaneous reduction in VOCs can actually lead to increased O_3 levels. In addition, differences in individual VOC reactivity should also be considered because it also affects the O_3 formation. Therefore assessing O_3 formation sensitivity based only on the VOC/NOx ratio may not be sufficient and maybe misleading (Elshorbany et al., 2009).

Most VOC control techniques are traditionally based on reduction of the total mass of organic compounds, without considering the individual reactivity and characteristics of each VOC. However individual VOCs can behave differently in the atmosphere owing to the difference in structure and reactivity, and thus have differing ozone formation potentials. To quantify the relative significance of different VOCs in producing ozone, the concept of reactivity scale was introduced. The incremental reactivity (IR) pertains to the change in ozone formation per unit amount of compound added (Carter, 1994; Russell et al., 1995; Singla et al., 2012).

Some of the reactivity scales currently used to estimate hydrocarbon reactivity towards ozone formation include (i) the maximum incremental reactivity (MIR) scale developed by Carter (Carter, 1994) and (ii) photochemical ozone creation potential, (POCP) developed by Derwent (Derwent et al., 1996).

1.4.2.1 Photochemical ozone creation potential (POCP)

POCP is an incremental reactivity technique developed by using a photochemical trajectory model. Compared to the MIR scale, it examines ozone formation under a more realistic Western European conditions over longer timescales. POCP considers transport effects and spatial variations in NOx emissions by expressing ozone reactivity relative to some reference VOC species. In the technique presented by (Derwent et al., 1996), ethylene was used as reference. A value for photochemical ozone creation potential POCP index for each VOC species, i, can be calculated using the formula:

$$POCP_i = \frac{Mean\ O_{3i} - Mean\ O_{3basecase}}{Mean\ O_{3ethylene} - Mean\ O_{3basecase}} x100 \qquad \text{Eqn (1.4)}$$

where Mean O_3 base case refers to the mean ozone mixing ratio along the 5-day trajectory in the base case, Mean O_{3i} with an additional 2.9% by mass of the *i*th VOC species and Mean O_3ethylene refers to that with the same mass of ethylene. Ethylene was used as a benchmark for the POCP scale because of its well defined degradation pathways, low molecular mass and because it is a relatively important precursor of photochemical ozone with medium reactivity towards hydroxyl. It is also one of the most important ozone forming VOC species in northwest Europe (Xiao and Zhu, 2003; Derwent et al., 2007). An updated listing of POCP values for 178 organic compounds determined for European multi-day conditions was presented by Derwent et al. (2007).

Xiao and Zhu (2003) mentioned that many studies has shown that the POCP is usually a relative value because it is usually derived under a special condition and thus can vary systematically with VOC/NOx ratios, TVOC components, and time scale used. The POCP reactivity then is best suited under the north-western European conditions assumed in its derivation (Elshorbany et al., 2009).

1.4.2.2 Maximum incremental reactivity (MIR)

MIR scale was developed by (Carter, 1994) using a photochemical box model. Incremental ozone reactivity scales were calculated using (i) VOC mixing ratios which were averages of ambient measurements from 39 cities in the USA and (ii) NOx mixing ratios which were adjusted to the level that produced the highest incremental reactivity at the end of 10 hour simulation (Carter, 1994; Hakami et al., 2004; Butler et al., 2011). This is shown in the following equation described by Russell et al. (1995):

$$MIR = \max\left(\frac{\partial[O_3]_p}{\partial E_i}\right) \quad for\ all\ VOCs/NO_x \qquad \text{Eqn (1.5)}$$

Based on the equation, MIR for individual VOCs are defined as the maximum sensitivity of the peak ozone concentration O_3 to a small increase in the initial conditions and emissions of VOC (E_i in equation). The MIRs are found for the input ratio of VOC to NOx that leads to maximum sensitivity to VOCs (Russell et al., 1995). Hakami et al. (2004) suggest that MIR conditions are descriptive of VOC-limited urban air masses, due to its of low VOC-to-NOx ratios and is of practical significance since they represent areas of dense human population.

Another reactivity scale, also developed by Carter (1994) is the maximum ozone incremental reactivity (MOIR), which is estimated by adjusting the NOx to the level that produces maximum ozone concentration for a given VOC mixing ratio. This MOIR conditions on the other hand represents a high VOC/NOx ratio that is typical for aged urban mass (Hakami et al., 2004; Butler et al., 2008).

MIR is widely used in the assessment of ozone formation potential from various VOC compounds (Hung-Lung et al., 2007; Barletta et al., 2008). Its application in the mixed environment was verified by Czader et al. (2008) in their study of VOC reactivity in the Houston-Galveston area in the US. They noted that while there are some places where estimated MIR has lower values than actual reactivity, the comparison of calculated values for the Houston-Galveston conditions with more general MIR scale showed that there was a good agreement for most of the VOC species (Czader et al., 2008).

1.5 Source apportionment and identification

1.5.1 Diagnostic ratios and correlation analysis

Ratios of concentrations of aromatic compounds have been utilized in many studies for the purpose of identification of emission sources or by assessing photochemical age of an air mass (Nelson and Quigley, 1983; Brocco et al., 1997; Khoder, 2007). All these studies used specific ranges of diagnostic ratios that were usually based on past studies. Diagnostic ratios were then use to identify the source of VOCs in ambient air on the basis of the proximity of the samples ratio to the characteristic range of a particular diagnostic ratio.

Benzene-to-toluene concentration ratio (B/T) is a common diagnostic ratio utilized in source identification. Miller et al. (2011) mentioned that reported B/T ratio from recent studies ranges from 0.3 to 0.7 with variations attributed to differences in vehicle type and composition. Gee and Sollars (1998) on the other hand mentioned a range of 0.25 to 0.5 as a common B/T ratio associated with traffic emissions but pointed out that B/T ratio from the samples in Manila and Bangkok were much lower at 0.1 due to high toluene content of the fuel. Recent study in the urban roadside in Hongkong showed that B/T ratio can be as low as 0.1 (Liu et al., 2008a). This shows that B/T ratio can be site specific and depend much on the nature of the source. Source characterization however can still be done as long as the characteristic ratio of the target sources is known.

Aside from B/T, xylene-to-benzene ratio concentration (X/B) (Barletta et al., 2005; Hoque et al., 2008; Buczynska et al., 2009) and xylene-to-ethylbenzene (X/EB) (Nelson and Quigley, 1983; Tiwari et al., 2010) have also been utilized. Use of new diagnostic ratio like VOC/Benzene (VOC/Bz) ratio was also explored by Hoshi et al. (2008) in identifying sources in Tokyo. They found that VOC/Bz ratio can be used in estimating non-registered VOCs such as butane and isopentane and suggested the possibility of estimating emission sources using VOC/Bz ratios from environmental monitoring data.

Correlation analysis is also a useful tool for source identification and can be used to strengthen evaluations offered by diagnostic ratios. A good correlation between atmospheric pollutant concentrations usually indicate common sources and provide additional information of any relationships between pollutants (Morawska et al., 1998; Wang et al., 2002).

Differences between industrial and urban sources were also identified using correlation analysis. For instance Tiwari et al. (2010) noted that good correlations between aromatic species were found in the areas dominated by traffic emissions while industrial areas are characterized by poor correlation. The same observation was also reported by Dollard et al. (2007) who used correlation analysis to identify VOC sources in the United Kingdom. They also found high correlations in areas where traffic was the dominant source and poor correlations were noted in the vicinity of industrial sites. Low correlations associated with multiple emissions were also noted by Chan et al. (2002) and (Barletta et al., 2008).

1.5.2 Receptor Models

As discussed in the last section, diagnostic ratios and correlation are useful tools in identifying emission sources. However, these methods are rather limited since they cannot be used when there are more than two plausible sources (Zalel et al., 2008). However, identification of all possible sources is vital in planning and implementing of effective air emission control strategies and for assessing the impacts on human health (Sanchez et al., 2008). In this case, source receptor models can be utilized in the source apportionment of VOCs in the ambient in cases of multiple sources (Hopke, 1991).

Source receptor models such as Chemical Mass Balance (CMB (Srivastava, 2004; Liu et al., 2008b)), Positive Matrix Factorization (PMF;(Lau et al., 2010; Guo, 2011)), Principal Component Analysis/Absolute Principal Component Scores (PCA/APCS; (Sanchez et al., 2008))have been used in a wide range of studies. However receptor models have more demanding requirements. For example, CMB requires specifications of the complete emission inventory of a region, which may not be always available. The PMF and PCA require sampling of a large number of VOC variables with small uncertainties (Zalel et al., 2008).

1.6 VOCs in the Philippines

The Philippines is one of the most urbanized countries in Southeast Asia, second only to Singapore. It has the sixth highest urbanization rate in the whole Asia. Annual population growth rate in the urban areas is 5.4%, which translates to approximately 2.5 million persons per year. Industrialization has also increased rapidly with a collective annual growth rate of 3.2% for manufacturing, trade, construction, and energy generation between 1988 and 2002. Number of vehicles has also been increasing at an annual rate of about 5 to 6% per year. The rapid industrialization, which occurs mostly in urban areas, has caused increased burden to natural resources, brought detrimental effects to the environment and increased air pollution (ADB, 2006).

1.6.1 Sources of VOCs in the Philippines

There appears very little source on published inventories of VOCs in the Philippines. Two published estimates for VOC emissions in Manila vary a great extent from each other. One estimate for mobile sources for 2005 was reported to be 256 kilo tons per year (ADB, 2006) while another estimate for the year 2002 was even higher at 1,872 kilo tons (Krupnick et al., 2003). The estimated contribution of mobile sources was about 60% which are primarily from gasoline vehicles.

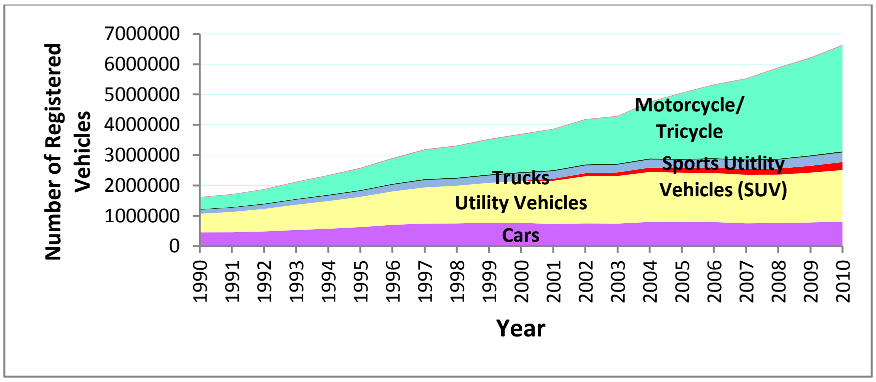

Figure 1.4 Registered motor vehicles in the Philippines, (1990–2010) Data Source: Land Transportation Office 2011(LTO, 2011)

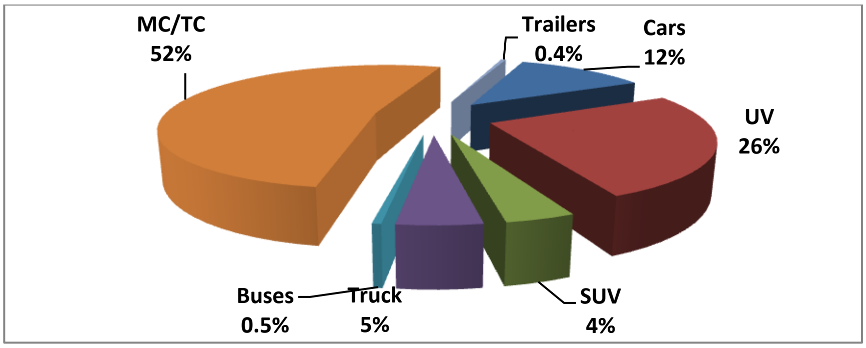

Figure 1.5 % Share of vehicle types in the overall fleet in the Philippines, 2010; MC/TC = motorcycle/tricycle; UV = utility vehicle; SUV= Sports Utility Vehicle % = percent ; Data source: Land Transportation Office 2011 (LTO, 2011)

Diesel vehicles makes up approximately one-third of the total number of vehicles, with another third being gasoline autos, and the rest gasoline utility vehicles and gasoline-oil motorcycles.

1.6.2 Regulations and monitoring

As discussed earlier, VOC has been a major concern in developing countries like the Philippines because of its impact in tropospheric ozone formation along with other effects. The formulation of effective strategies for controlling VOCs requires quantifying the ambient concentrations and the identification of emission sources. However, efforts to improve air quality are currently focused only on criteria pollutants like Total Suspended Particles (TSP) and Particulate Matter (PM). The increasing number of vehicles, the majority of which are gasoline fuelled vehicles, and the limited use of catalytic converters on gasoline vehicles suggest that VOC levels may be high. In addition the high olefin content of petrol (35%) is likely to produce significant exhaust emissions of 1,3-butadiene and even other hazardous pollutants like polycyclic aromatic hydrocarbons (PAHs) (Krupnick et al., 2003; ADB, 2006).

The consensus that PM constitutes the main pollution and health risk problem in Manila leads to downplaying of other pollutants like ozone. The decision to downplay the ozone implies a lesser interest in reducing VOC emissions (from gasoline vehicles primarily), CO emissions (from all mobile sources), and NOx emissions (from both diesel and gasoline vehicles). However, the number of vehicles is increasing at rapid rate specially the gasoline fuelled vehicles which are the main source of VOCs. While ozone has been reported to be generally within the guidelines provided WHO (Krupnick et al., 2003), the levels was based only on one ambient monitoring site in Manila (a private scientific institution), which may not be representative of the whole area. Nevertheless the reported maximum O_3 concentrations also shows that 7 of the 8 maximum readings exceed the national guideline for 1 hour ozone exposure of 140 µg/m3 during an 8 month monitoring from September 2001 to April 2002. A 2004 World Bank report on Philippine air quality noted that ambient concentrations of ozone and nitrogen oxides are on the rise, mostly due to a rapid increase in the number of motor vehicles (WB, 2004).

1.7 VOC analysis

Analysis and quantification of VOCs are important to have a better insight on the occurrence, fate and behavior of VOC in all fields of interest. However, considering the complexity of the environmental air matrix and the usually low concentration of VOCs, from ppbv down to pptv, accurate and precise determination of VOC levels in air require the most efficient and sensitive sampling, pre-concentration and analysis techniques (Demeestere et al., 2007; Ramírez et al., 2010).

Ambient VOCs are commonly monitored by on line, or indirectly after sampling (Palluau et al., 2007; Talapatra A., 2011). There is a broad range of methods for VOC analysis and quantification but basically all the methods vary from each other according to the sampling technique, type of sorbent, method of extraction or preparation and identification technique (Kumar and Víden, 2007).

Selection of the right method or combination of methods may depend on the study design, the compounds of interest, expected concentration range, required sensitivity, accuracy and precision, selectivity, presence of interferences, type of sampling and analytical methods available, power requirements, portability and cost (Demeestere et al., 2007; Ras et al., 2009).

1.7.1 Sampling

The most common techniques used to sample VOCs in air are (a) whole air collection in special containers (b) collection onto solid adsorbents and (c) continuous sampling and on-line analysis (Demeestere et al., 2007; Palluau et al., 2007; Woolfenden, 2010b). Figure 1.6 illustrates some of the techniques for VOC sampling.

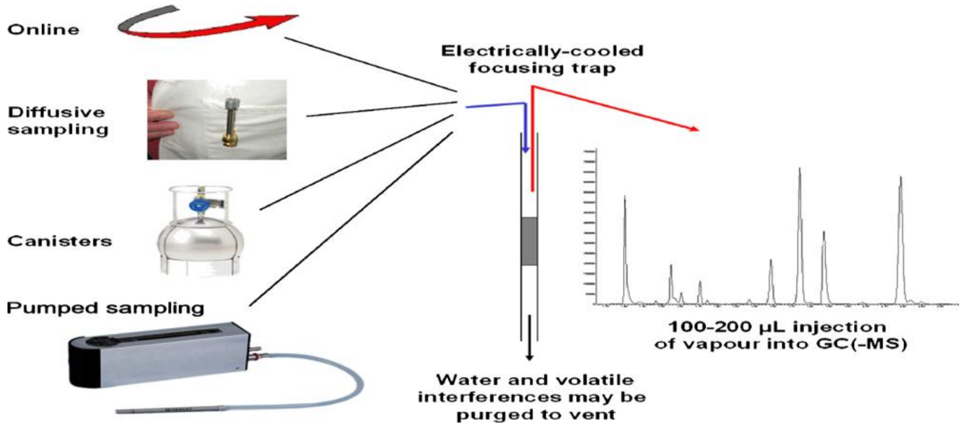

Figure 1.6 Examples of different sampling techniques and schematic overview of the two-stage thermal desorption process for sorbent-based air sampling (Woolfenden, 2010b)

Collecting air samples in a container is the simplest way to collect VOC samples. The samples are usually analyzed later using GC, by direct injection or, more frequently, in combination with a pre-concentration step. Plastics bags (e.g., Tedlar, Teflon or aluminized Tedlar) and metal canisters are the usual containers used. Sample collection in container can also be done with sub atmospheric pressure (passive) or pressurized with a pump (active). The active method allows the sample to be pressurized and the collection of larger sample volumes and not limited by container volume (Ras et al., 2009).

Sorbent adsorption is a technique often used to combine pre-concentration with sampling (active or passive). The VOC portion of the air sample can be selectively collected by trapping it using solid-phase extraction (SPE), through adsorption or reaction of the VOCs with a solid substrate (Harper, 2000; Ras et al., 2009). The use of sorbent tubes is now becoming more popular as they allow a much wider range of compounds to be analyzed. In addition, they also provide greater sample stability as polar compounds are prone to adsorption onto the canister walls (Watson et al., 2011). There are two main sorbent enrichment techniques that are used: active and passive (or diffusive) (Walgraeve et al., 2011).

Continuous sampling and on-line analysis is usually used for kinetic studies, ambient air monitoring and for regulation compliance for monitoring of some compounds like, C_2 to C_{10} hydrocarbon ozone precursors, odorous sulfur compounds and some known potent greenhouse gases like perfluorinated compounds (Watson et al., 2011).

1.7.2 Sample preparation

Different methods for sample preparation has been discussed in detail by Demeestere et al. (2007). They identified some of the different sample preparation (extraction and pre-concentration) techniques which includes cryogenic sample pre-concentration, solvent extraction, immobilized sorbent enrichment combined with thermal desorption (TD), solid phase-micro extraction based techniques (SPME), and membrane extraction.

This study utilized the immobilized sorbent enrichment as pre-concentration coupled with TD. For TD, available sorbents include Tenax TA, chromosorb 106, graphitized carbon and multibed tubes (Harper, 2000). TD is probably the best for low concentration of analytes and it is frequently combined with GC and offers the advantage of lower limit of detections (LODs). This is because (i) the sample can be completely transferred to the chromatographic column if required, and (ii) it avoids the presence of a solvent peaks which can mask analyte peaks (Ras et al., 2009). TD process can also be automated either for online, or for the sequential analysis of canisters/ bags via sorbent traps or the automated desorption of sorbent tubes (Woolfenden, 2010b).

1.7.3 Analysis techniques

The most widely used tool for detecting and quantifying gaseous VOCs is gas chromatography-mass spectrometry, or GC-MS. This technique has been in use for many years and is capable of achieving sensitivities as low as 0.1 pptv. Other detection techniques that can be coupled with gas chromatography include mass spectrometry (MS), flame ionization detection (FID) or electron capture detection (ECD) (Demeestere et al., 2007; Blake et al., 2009).

Another technique usually used for immediate and online measurement of VOCs is Proton Transfer Reaction Mass Spectrometry (PTR-MS). This technique has been used for the detection of a wider spectrum of VOCs in air. In the PTR-MS instrument, ambient air is continuously pumped through a drift tube reactor and the VOCs in the sample are ionized in proton transfer reactions with hydronium ions ($H3O^+$) (Blake et al., 2009; Toscano et al., 2011).

1.7.4 Sorbent enrichment: Active sampling

Active sampling consists of pulling a defined volume of air through a bed of sorbent(s) in a tube where the analytes are retained (Ras et al., 2009; Woolfenden, 2010b). Short term and long term samples can be collected on adsorbents packed in appropriate tube with the use of sampling pump. Sampling pump should be calibrated and should follow well established standards. Active sampling is most commonly used for personal exposure monitoring because all of the equipments required while sampling can be worn by the worker (Kumar and Víden, 2007).

The broad range of number of organic species and variability in concentration of pollutants in ambient air makes analysis difficult. Appropriate choice of sorbent or a good combination of different sorbents may allow the determination of a wide range of target compounds in air samples as well as achieve high breakthrough volumes (Demeestere et al., 2007; Gallego et al., 2010). Some of the main types of sorbents used in air monitoring Types of sorbent materials available commercially are porous organic polymers like Tenax (porous polymer of 2,6-diphenyl-p-phenylene oxide), carbon molecular sieves, graphitized carbon blacks, and activated charcoal. The choice of sorbent(s) mainly considers the volatility of the VOC concerned (Watson et al., 2011). Table 1.1 shows some typical sorbents and their applicable analyte volatility range. Detailed discussion about appropriate sorbent selection and combination is discussed by Woolfenden (2010a).

Table 1.1 Popular sorbents and their respective volatility ranges (Watson et al., 2011)

Sorbent name	Volatility range
Quartz wool/silica beads	C_{30}–C_{40}
Tenax TA	C_7–C_{30}
Carbograph 2TD	C_8–C_{20}
Carbograph 1TD	$C_{5/6}$–C_{14}
Carbograph 5TD	$C_{3/4}$–C_8
Carboxen 1003	C_2–C_5
Carbosieve SIII	C_2–C_5

Physical and chemical characteristics of the VOC studied are not the only considerations when choosing the sorbent, but also on sampling conditions such as the meteorological conditions, time of sampling and sample volume. Combination of several adsorbents may result in better performances. Consequently, if the analysis of the air sample would be done exhaustively, adsorbents that assure a more complete collection with negligible loss of sample would be needed (Gallego et al., 2010). In this regard, recent studies tend to use multiple-bed sorbent cartridges which provide high breakthrough volumes and the quantitative retention and desorption of VOCs over a wide volatility range (Ramírez et al., 2010). Figure illustrates a multi-sorbent sampling tube for VOC sampling.

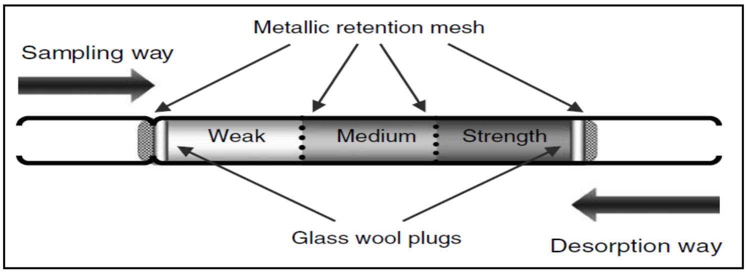

Figure 1.7 Multi-sorbent tube for dynamic sampling of volatile organic compounds(Ras et al., 2009)

Another advantage of using multiple sorbent is its higher breakthrough volume (BTV). The BTV describes the retention capacity of the adsorbent and is defined as the maximum air volume that can be sampled using a trap made with a given quantity of adsorbent, before a compound exits the trap (Do, 2009). Typical volumetric flow rate of air for active sampling ranges from 20–200 ml/min flow rate (optimum is 50 ml/min). Lower limits of flow rate are typically around 10 ml/min (Woolfenden, 2010b). Factors limiting flow rate selection includes (i) analyte diffusion may occur at a rate equivalent to the air flow of approximately 1 ml/min; (ii) analyte diffusion introduces significant errors when using pump flow rates smaller than 10 ml/min; (iii) at high flowrates, there is a significant risk of component exceeding the BTV (Kumar and Víden, 2007). Information of BTV values gives estimate of the maximum sampling volume that ensures a quantitative sampling of a compound using a certain adsorbent at a specific temperature. List of BTVs are usually provided specially for commercial adsorbents (Markes-International, 2006).

Finally, other important factors should be considered when choosing adsorbent. These include: reactivity and artifact formation; water sorption interferences and ozone, storage stability and blank build up. Ozone interferences can result in significant analyte loss especially for reactive, unsaturated compounds. The vulnerability to ozone interference is influenced by the type of adsorbent used for sampling as in the case of Tenax. No significant ozone interferences however has been observed for carbon-based adsorbents (Carbotrap B, Carbotrap C and Carbosieve SIII). Activated carbon is known to be affected by moisture and thus moisture traps should be used when activated carbon is used as sorbent material (Demeestere et al., 2007; Ras et al., 2009).

1.6 Objectives of the Study

Based on the information discussed on the relevant literature, the scope and definition of this study are formulated.

The study aims to provide new information and data on the concentrations of the most concerned VOCs in outdoor and indoor VOCs in an urban and industrial areas in the Philippines by means of (i) sorbent sampling using adsorbent tubes filled with Tenax TA and utilizing the active sampling technique (ii) TD-GC-MS analysis with the IS calibration.

Specifically the study aims to:

i. To assess and make a comparison on the indoor and ambient level of VOCs in the Urban and Industrial environment ;

ii. To evaluate and search for similarities in VOC profiles of the two environments and compare with other studies from the literature;

iii. To utilize diagnostic ratios and statistical approaches in source identification of VOCs and assess the effectiveness and applicability of such tools;

iv. To estimate the ozone formation potential of the measured VOCs in the outdoor sites of industrial and urban areas;

v. To draw meaningful discussion regarding the status and extent of effects of VOCs on air quality in the ambient and indoor environment of urban and industrial areas in the Philippines.

CHAPTER TWO: MATERIALS AND METHODS

2.1 Preparation of sampling materials

2.1.1 Tenax TA sampling tubes (description).

Tenax TA sampling tubes (outer diameter 1/4-inch; length 3.5-inch; 200mg Tenax TA adsorbent ; Markes, Llanstrisant, UK) were used. The adsorbent Tenax TA is a porous polymer resin based on 2,6-diphenylene oxide and is widely used in the determination of VOC's from air and liquids. Tenax is especially applicable in trapping volatile organics from high moisture content samples because it has low affinity with water. Among the other properties provided for Tenax TA include: temperature limit: 350 °C; specific surface area: 35 m^2/g; pore volume: 2.4 cm3/g; average pore size: 200 nm and density 0.25 g/ cm^3. It is usually used in conjunction with the Short Path Thermal Desorption System (SIS, 2011). To ensure adequate seal, the tubes were provided with brass closure caps, with white Teflon ferrules (Alltech SF-400T).

2.1.2 Conditioning of sampling tubes

Thermal conditioning of sampling tubes was done to remove any residual contaminants. The tubes were conditioned by heating in an oven (Carlo Erba Instruments, MFC 500) for 1h at 300°C while helium was allowed to pass through the tubes at flow rate of 22-34 ml/min to ensure no oxygen enter the adsorbent material. Adequate flow rate of helium (around 50 ml/min) was assured by an attached rotameter.

2.1.3 Pump calibration

Active sampling was used for all the samples collected from the urban and industrial sampling sites. For this technique, GILAIR-3 air sampling pump (Gilian R, USA) was utilized. The pump was calibrated 20 times before and after the sampling campaigns to check the consistency of the flow rate. The pump was calibrated to the target volume of 100 ml/min. The air volumetric flow rate was determined using a soap-bubble meter.

2.2 Sampling campaigns

Urban and industrial ambient air samples were collected from different places in the Philippines between August and September 2011. For the urban environment, three representative indoor/outdoor sites were sampled: (i) the indoor environment of a residential house (ii) an outdoor site in a heavy traffic roadside, and (iii) an outdoor site in a park. For industrial environment, three representative indoor/outdoor sites were also sampled: i) the indoor environment of a residential house, (ii) an outdoor site in an industrial zone near a painting plant (Calamba, Laguna), (iii) an outdoor site in an industrial zone and near a printing press (Binan, Laguna). For each site, samples were collected for three days, twice a day at morning (7 am to 10 am) and afternoon (4 pm to 6 pm). Sampling duration was for 30 minutes at pump flow rate of 100 ml/min. Some samples were collected intermittently due to unexpected bad weather and storm.

Table 2.1 summarizes the locations of the sampling sites and the sampling schedule. An overview of the sampling locations is shown in Figure 2.1.

Table 2.1 Sampling sites description and date of sampling for different sampling sites

Sampling Sites		Description of the Sampling Sites	Date	Coordinates
Urban Environment	House Indoor Sample	Two story house about 250 meters away from the roadside in Pasay City Manila	25/8/2011 26/8/2011 3/9/2011	14°32'09.69" N 121°00'09.57" E
	Roadside sample	Busy road MRT train station in EDSA Pasay City Manila	25/8/2011 26/8/2011 (am) 1/9/2011 (pm) 3/9/2011	14°32'15.07" N 121°00'03.07" E
	Park Sample	Rizal park, the largest urban park in Manila about 6 km from roadside sampling site	25/8/2011 26/8/2011 3/9/2011	14°35'03.50" N 120°58'51.91" E
Industrial sites	House Indoor Sample	Two story house located in industrial location 1,	10/9/2011 12/9/2011 13/9/2011	14°11'34.61" N 121°09'23.44" E
	Location 1	Located in in Calamba, Laguna just at the outskirts of an industrial zone (LISP2) and near a painting plant.	9/9/2011 (am) 10/9/2011(pm) 12/9/2011 13/9/2011	14°11'38.89" N 121°09'33.37" E
	Location 2	About 14 kms away from Location 1. Located in Binan Laguna just north of another industrial park in Laguna (LIIP) and near a printing press.	14/9/2011 15/9/2011 16/9/2011	14°17'51.07" N 121°04'45.77" E

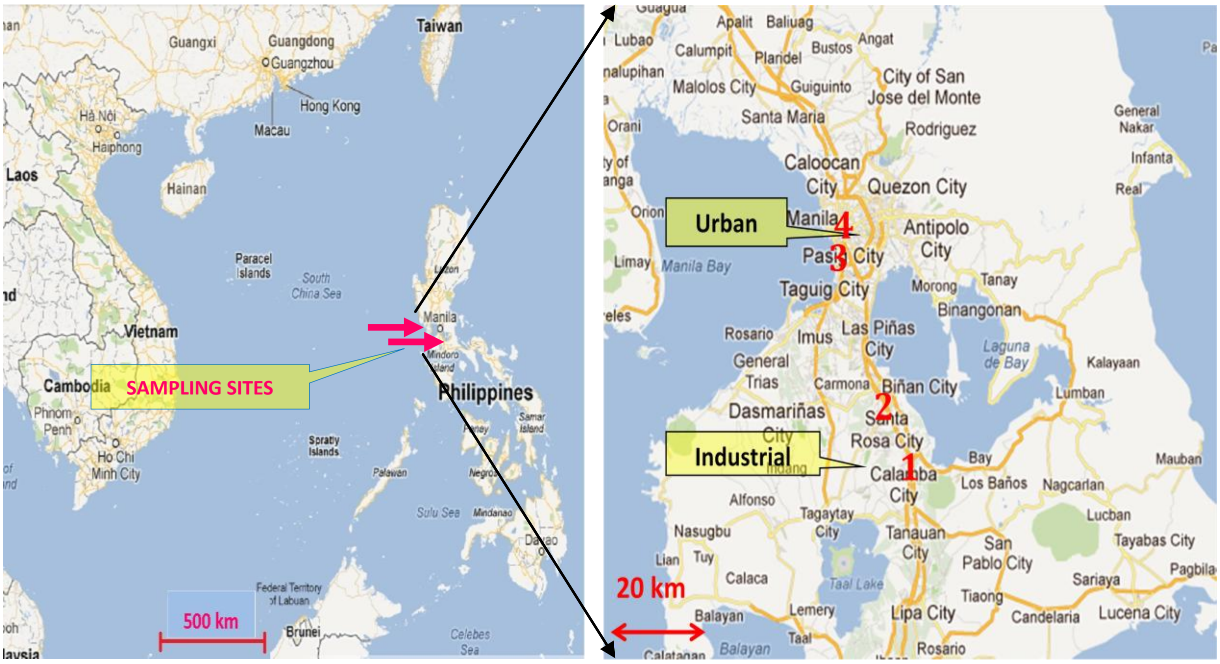

Fig. 2.1. Overview of the urban and industrial sampling locations in the Philippines (1): first industrial sampling site(2): second industrial sampling site (3): urban roadside (4) urban park (Google map 2012)

2.2.1 Urban environment

Manila was chosen as the study area for urban environment. The detailed locations of three sampling sites are shown in Figure 2.2.

Fig.2.2. Location of sites for the urban environment (Manila, Philippines) denoted by (1): Rizal Park, (2): Pasay City Roadside, and (3): Urban House Indoor (Google map 2012).

2.2.1.1 Urban roadside: EDSA MRT in Pasay City Metro Manila

The location serves as intersection point of vehicles coming from four different routes. It is also the intersection of the two train lines in Manila, the Manila Rail Transit (MRT) and Light Rail Transit (LRT). Most of the passing vehicles consist of diesel powered vehicles such as passenger utility jeepneys, buses and trucks and gasoline powered such as cars and motorcycles. West of the site is the Manila bay where sea breeze usually blows from. There are also bus stations in the vicinity. The streets and sidewalks are frequently busy with vendors and pedestrians.

Fig. 2.3. Urban roadside sampling site (EDSA MRT, Pasay City , Metro Manila Philippines)

2.2.1.2 Urban park: Rizal Park

Rizal park, the largest urban park in the country, situated north of Roxas Boulevard, is one of the major tourist attractions of Manila. The east of the park is bounded by Taft Avenue, Padre Burgos Drive and T.M. Kalaw Avenue. To the west is the reclaimed area of the park bounded by the shore of Manila bay. The area is mostly planted with greeneries. The adjacent busy street of

Taft Avenue and Roxas blvd however may contribute in a certain extent to the air quality in the park but the sampling location was chosen in an area far from the busy streets.

Fig. 2.4 Rizal Park , City of Manila Philippines, taken during sampling campaign

2.2.1.3 Urban indoor : house

The house is typical for that of the urban environment in Manila where spaces are limited and the residential areas are congested and crowded. The second floor, where the samples were collected, has natural ventilation. The family of four persons mostly stays in this 20 square meters area which is used as their bedroom and living room. The first floor of the house served as their kitchen.

Fig. 2.5 Indoor sampling, Pasay City Metro Manila Philippines. Left Side : indoor air sampling at the second floor of the house; Right side : outside environment of the sampling point

2.2.2 Industrial environment

Two locations in the province of Laguna, Philippines (about 60 km from Manila) were chosen as sampling sites for industrial environment as seen in Fig 2.6. The sites were chosen to represent the typical industrial zones present in most of sub-urban provinces in the Philippines. Most of the new manufacturing industries are situated in industrial zones in the provinces (non urbanized area) where there are more spaces. This is promoted by the Philippine government to decongest highly urbanized areas and bring more jobs to the provinces.

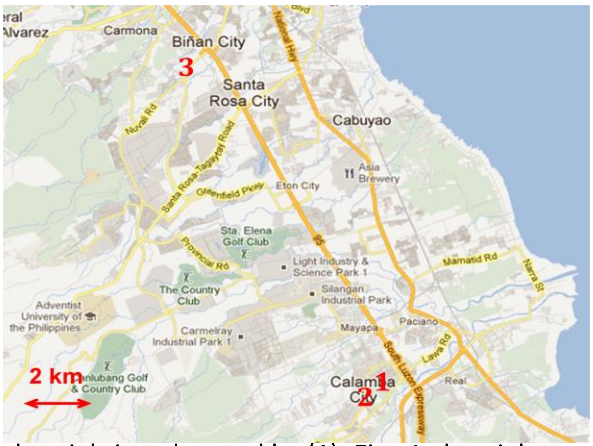

Fig. 2.6. Location of Industrial sites denoted by (1): First Industrial sampling site, (2): Indoor sampling site, and (3) Second industrial sampling (Google map 2012).

2.2.2.1 Industrial Location 1:Calamba Laguna, Philippines

Location 1 is situated in the city of Calamba, Laguna province where several industrial zones are located. The location was chosen because it is on the outskirts of one of the industrial zones and as such is situated near residential and public places like school and city hall. The sampling site is situated about 90 meters away from a factory that manufactures galvanized and painted roofs made from steel sheets. The company uses vast amount of paints and paint thinners and thus have encountered many complaints from the nearby residents. As there are no solid regulations in the Philippines about VOCs or odor emissions, the company operated without any solvent recovery facility in the past but due to frequent number of complaints they have recently installed solvent capturing units designed to capture and adsorbed the released VOCs. The scrubbed air is released via two stacks which are about 8 meters high.

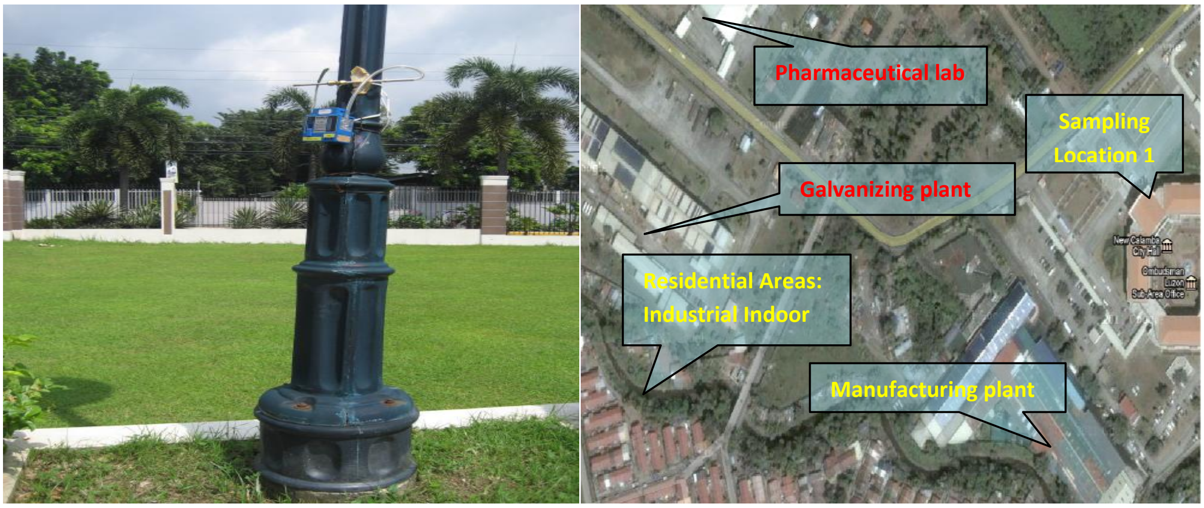

Fig. 2.7 Industrial location 1 (Calamba, Laguna, Philippines). Left :views from the sampling point, Right: aerial view of the vicinity of the sampling site

2.2.2.2 Industrial Location 2: Binan, Laguna, Philippines

Industrial Location 2 is situated in Binan, and just north of one of the industrial zones in Laguna Philippines i.e., Laguna International Industrial Park, (LIIP). This industrial zone is about 117 hectares of land area. Most of the locators are manufacturing facilities for electronics and semiconductor products. Other industries include transport car parts, chemical products, garments rubber and plastics among others. The sampling site is about 90 meters from a printing plant which is behind the front office building. The printing facility is 10-hectare printing complex. It is the largest printing complex in the country which includes printing newspapers and magazines, digital pre-press and printing related enterprise such as ink manufacturing.

Figure 2.8 Industrial location 2 (Binan, Laguna, Philippines). Left: View from the sampling point, Right: Aerial view of the vicinity of the sampling sites

2.2.2.3 Industrial indoor: house (residential)

The indoor sample for the industrial environment was collected from the second floor of a two story house about 350 meters away from the first industrial sampling point. It is within the vicinity of some manufacturing plants, i.e., 260 meters south west of painting and 250 meters away from a pharmaceutical company. The house is around 15 years old and is a typical house structure. The sampling point is a bedroom located in the second floor which is about 10 square meters with natural ventilation. The house is adjacent to other houses as the builders and developers designed it as apartment style. It is located at the edge of the residential complex and near a river and entrance of the subdivision.

Figure 3.9 Indoor sampling (Calamba, Laguna Philippines), Left: View from the sampling point, Right: Aerial view of the vicinity of the sampling site

2.3 Sampling methodology

Active sampling was utilized for this study. The sampling was done using a portable pump sampler.

For outdoor sampling, the tubes were kept at approximately 1.5 meters from the ground to approximate the common breathing level of people. In roadside environment, sampling was carried out at approximately 10 meters away from the traffic lanes to avoid the mixing zone.

For indoor sampling, the sampled tubes were placed at approximately 0.6 meter above the floor and below the ceiling, away from windows, doors, at least 0.5 meter away from bookshelves (Jia et al., 2008).

2.4 Analysis and quantification of Tenax TA sampling tubes

2.4.1 Loading with internal standard

Loading of internal standard was done for quantification purposes and also to account for the detector instabilities. The Tenax TA tubes were loaded with Ethylbenzene-d10 ([2H10]ethylbenzene; 98 % 2H; Sigma-Aldrich, 2010) after the sampling campaign and prior to tube analysis.

Stock solution containing 217.22 ng/µl of ethylbenzene-d10 (EB-d10) was prepared by dissolving 25µl of ethylbenzene -d10 in 100ml methanol. The prepared stock solution was stored in the dark at temperature of -18°C.

2.4.1.1 Preparation of closed two phase system

Preparation of gaseous standards was done by using a closed two-phase system (CTS) as described by Dewulf et al. (1996).

In preparing EB-d10 standard, 20 µL of stock solution was added to 20 mL of deionised water (injected under the water surface) that is previously placed in a 119.8 mL glass bottle. After the addition of the IS, the bottles were immediately sealed by Mininert valve (Alltech, Lokeren, Belgium) to minimize losses. The bottles were then wrapped with aluminum foil to avoid photodecomposition of the IS and incubated in a thermostatic water bath which was maintained at 25.0 ± 0.2 °C for at least 12 hours .

Henry´s constant for ethylbenzene-d10 was experimentally determined by Mturi (2010) using Equilibrium Partitioning in Closed Systems (EPICS) procedure as described by (Gossett, 1987).

Since that the values for mass of EB-d10, volume of the water and gas, and Henry´s law constant at the given temperature (25°C) are known, headspace concentration at equilibrium can be calculated using mass balance in the closed two-phase system (Dewulf *et al.*, 1996).

The closed two-phase mass balance gives :

$$m_{total} = m_{water} + m_{air} = C_{water} * V_{water} + C_{air} * V_{air} \qquad \text{Eqn (2.1)}$$

The Henry´s law constant can be expressed as:

$$H = \frac{C_{air}}{C_{water}} \qquad \text{Eqn (2.2)}$$

Combining the two equations will give:

$$C_{air} = \frac{m_{total} * H}{V_{water} + V_{air} * H} \qquad \text{Eqn (2.3)}$$

Where:
C_{air} is the concentration of EB-d10 at the gaseous space,
C_{water} is the concentration of EB-d10 concentration water phase
V_{air} is the volume of the gaseous phase; V_{water} is the volume of water; H is the Henry's law constant.

Total mass of EB-d10 added to the closed two phase system can be calculated to be

$$m_{total} = V_{stock} * C_{stock} = 20\mu l * (217.22\ ng / \mu l) \quad m_{total} = 4344.35\ ng$$

Henry´s law constant for EB-d10 at 25°C was experimentally determined by Mturi (2010) to be equal to 0.22. Given that V_{water} = 20 mL; V_{air} = 99.8 mL, the concentration of EB-d10 in the headspace can be calculated as 22.78 ng/mL.

2.4.1.2 Loading of Ethyl-benzene d-10

Using a 0.5ml gastight Pressure-Lock VICI precision analytical syringe (Series A, Alltech), 0.5 ml headspace (corresponding to 11.39 ng) of EB-d10 was taken from the closed two phase system and loaded into the sorbent tubes through a customized injection system which was heated at 50 °C. The injection system was flushed with helium at a flow rate of 100 ml/min. The helium flow was held for 3 minutes after injection to ensure that all of the EB-d10 was transferred to the sorbent tubes. After loading, the tubes were tightly sealed with 1/4 inch brass long-term storage end caps, equipped with 1/4 inch one-piece PTFE ferrules.

2.4.2 TD-GC-MS system

Analysis of VOCs adsorbed in the sampling tubes was carried out using TD-GC-MS system(Thermo Desorption- Gas Chromatography- Mass Spectrometry) using the method described by Hayleeyesus (2011) and (Do, 2009).

Masses from *m/z* 29 to 300 were recorded in full scan mode (200 ms per scan) on a Trace DSQ Quadrupole MS (Thermo Finning, Austin, TX, USA), connected to the GC, and operating at an electron impact energy of 70 eV. Chromatograms and mass spectra were processed using XCalibur software (Thermo Finnigan, version 1.4).

Identification of the VOC compounds was carried out on the basis of their fragmentation patterns and by comparison of their mass spectra with the US National Institute of Science and Technology (NIST, Gaithersburg, MD, USA) V2.0 database [NIST/US Environmental Protection

Agency (EPA)/US National Institutes of Health (NIH) Mass Spectral Library], and also through comparison of the retention times with the standards.

2.4.3 Calibration of the TD-GC-MS

Calibration of the TD-GC-MS system was carried out prior to analysis. The 67 target VOC compounds were included in a set of 83 standard compounds used for the calibration. All the standards were purchased from Acros Organics (Geel, Belgium) or at Sigma–Aldrich (Bornem, Belgium) with purity of at least 99.8%. Methanol (LC–MS grade, 99.95%, Biosolve, Valkenswaard, The Netherlands) was used as a solvent for all standard compounds. No further purification of the chemicals was done and thus all the standards were used as provided by the supplier.

Known amount of standards with a known mass of EB-d10 were diluted in methanol to prepare a stock solution. The standards were divided into 4 groups to avoid co-elution of compounds with almost similar retention times. A volume of 1 µL of the stock solution was then loaded into each Tenax TA sampling tubes corresponding to specific loaded mass of the standards (ranges from 31.3 ng to 81.2 ng).

The sample response factor (SRF), defined in chromatography as the signal output per unit concentration or mass of a substance entering the detector, is calculated as:

$$SRF_i = \frac{A_i}{m_i} \qquad \text{Eqn (2.4)}$$

where, *Ai* is the peak area and m_i is the mass (ng) of substance i on the sorbent tube. Since the sensitivity of TD-GC-MS system has been to have low stability, introducing an internal standard with which a relative response of the sample can be compared has been shown to improve the precision of external calibration (Demeestere et al., 2008). RSRF (relative sample response factor) is defined as the ratio of sample response factor of the analyte (SRF_a) and that of internal standard. In this study, ethylbenzene-d10 was used as the internal standard for the final quantification.

$$RSRF = \frac{SRF_a}{SRF_{st}} = \frac{\left(A_a / m_a \right)}{\left(A_{st} / m_{st} \right)} \qquad \text{Eqn (2.5)}$$

Relative sample response factor of the standard compounds in relation to EB-d10 is shown in Table 3.2. Take note that these are obtained using a liquid phase mixture of standards. However, as shown by Demeestere et al. (2008), relative sample response factors determined by the analysis of sorbent tubes loaded with both the analytes and internal standard in liquid phase ($RSRF_{L,L}$) are shown to be a reliable alternative for quantification of airborne VOCs sampled on sorbent tubes first loaded with gaseous internal standard. i.e., $RSRF_{L,L} \approx RSRF_{G,G}$.

2.4.4 Quantification

From equation 3.5, it can be seen that if relative sample response factor of an analyte to a known internal standard is known, then the mass of the analyte can be determined. Rearranging equation 2.5 gives:

$$m_a = \frac{A_a * m_{st}}{RSRF_i * A_{st}} \qquad \text{Eqn (2.6)}$$

The mass of target compound (m_a) can thus be calculated since all the other variables are known i.e., the mass of internal standard injected in the sample (11.39 ng as calculated in section 2.1.4), the peak area of the analyte and the IS, and the $RSRF_{L,L}$ from the calibration of TD-GC-MS.

The concentration of the air drawn into the sampling tubes (C_a) can be calculated as:

$$C_a = \frac{m_a}{Q*t} = \frac{m_a}{V} \qquad \text{Eqn (2.7)}$$

The concentration of the analyte C_a is determined by dividing the calculated mass of the analyte (m_a) in the sampling tube by the volume of the air (V) which is the product of the volumetric flow rate of the air sampler and the sampling time.

Limits of detection (LOD) and limits of quantification (LOQ) were defined on the basis of the signal to noise ratio (S/N) of the peak of a component in the SIM (Selective ion monitoring) chromatogram. Whenever a component was quantified in the blanks, i.e. S/N bigger than 10, a blank correction was performed by subtracting the quantified amount of the analyte in the blanks from the mass quantified in the sampling tubes.

2.5 Statistical Analysis

SPSS Statistical software package (IBM Corporation 2011) was used to determine the statistical significant difference among the concentration levels and fir the correlation analysis among the VOC concentration. Given the number of samples, Shapiro-Wilk test was used to test for normality of distribution of samples. When normality of samples could be assumed, independent sample t-test was used, otherwise non-parametric Mann-Whitney U test was utilized.

CHAPTER THREE: RESULTS AND DISCUSSION

Measurement of volatile organic compounds (VOCs) was carried out in industrial and urban areas in the Philippines. Air samples were collected in August and September 2011 and were analyzed using TD-GC-MS (see Chapter 3). From the 67 target VOCs, 37 were identified from the samples collected in the different areas.

Results of the VOC identification and quantification analysis are presented in this chapter. First, concentration profiles of the different VOCs present in the different sampling sites were brought forward. Second, discussion of the typical VOCs detected was presented. Third, total volatile organic compounds (TVOCs) and benzene, toluene, ethylbenzene, and xylene (BTEX) levels were also discussed. Fourth, indoor to outdoor concentration (I/O) ratio for the TVOCs and for the four most prominent groups of VOCs (alkanes, aromatic compounds, oxygenated compounds and terpenes) was also determined and evaluated. Next, source identification with the use of diagnostic ratios and correlation analysis was also done. Finally, ozone formation potential (OFP) of the VOCs in the outdoor environment were estimated using the latest maximum incremental reactivity scale (MIR_{2010}) (Carter, 2010) to assess the extent of potential health hazards of VOCs.

3.1 Results of VOC concentration analysis

The summary of the measured VOC concentrations are shown in tables 3.1 and 3.2. Actual concentration values can be found in Appendix B to D. Undetected target VOCs were not included in the tables. These include furan, carbondisulfide, dimethylsulfide, dichloromethane, 1,1,2 trichlorotrifluoroethane, isobutyraldehyde, chloroform, tetrahydrofuran, 1,2-dichloroethane, 3-methylbutyraldehyde, 1,2-dichloropropane, hexamethyldisiloxane, n-propylacetate, trimethoxymethylsilane, 3-methyl-1-butanol, dimethyldisulfide, 1,1,2-trichloroethane, 1-pentanol, 1,1,1,2-tetrachloroethane, chlorobenzene, 1-bromo-4-fluorobenzene, 5-methyl-3-heptanone, 2-octanone, 1,3-dichlorobenzene, 1-octanol, 5-nonanone, linalool, methylbenzoate, 1,2,4-trichlorobenzene, 1,3,5-triisopropylbenzene.

A summary of percent contribution of the different VOC groups ((cyclo-)alkanes, aromatic hydrocarbons, halogenated compounds, oxygen containing hydrocarbons and terpenes) to TVOC is shown in Table 3.1. It can be noted from the table that among the VOCs identified, the aromatics has the highest percent contribution in all the sampling sites. (Cyclo-)alkanes accounted for the next most abundant group in all sites except for the samples collected in one industrial area where a relatively higher level of alcohols was observed. Oxygenates (e.g., ketones, aldehydes and other oxygenated compounds) were also detected. Halogenated compounds were also found in all sampling sites due mainly to the presence of carbon tetrachloride (CCl_4) but other halogenated compounds were also detected in high frequency specifically from the industrial areas.

Table 3.1 Mean concentration of Detected VOCs (µg/m^3) and percent contribution of VOC group to the TVOC in the sampling area, (%= percent contribution, AVE = mean concentration in µg/m^3)

Component Name	Urban park		Urban roadside		Urban indoor (house) All*		Urban indoor (house) 4 samples		Industrial Indoor (house)		Industrial loc 1 Ambient		Industrial loc 2 Ambient	
	%	AVE	%	AVE	%	AVE	%	AVE	%	AVE	%	AVE	%	AVE
(Cyclo-)alkanes	20	5.7	21	26.9	71	282.6	37	27.6	9	9.8	6	14.5	27	22.2
Aromatic compounds	43	12.5	66	85.1	20	79.9	42	31.5	59	65.1	58	143.9	57	46.4
Aldehydes	18	5.2	7	8.5	2	6.6	6	4.8	2	2.6	1	2.9	3	2.8
Alcohols	6	1.8	0	0.0	0	0.8	2	1.2	13	14.3	21	53.1	3	2.1
Ketones	11	3.3	6	7.2	6	24.0	7	5.1	4	4.8	7	16.3	7	6.0
Other oxygenated compounds	0	0.1	0	0.0	0	0.0	0	0.0	9	10.1	7	16.71	1	0.6
Halogenated compounds	1	0.4	0	0.1	0	0.2	0	0.1	1	0.6	0	0.21	1	1.2
Terpene	1	0.2	1	0.8	1	2.8	6	4.2	3	2.9	0	0.05	0	0.30
TVOC		**29**		**129**		**397***		**74.6**		**110**		**248**		**82**

*includes the two urban indoor samples with very high TVOC concentration

3.2 Characteristic VOCs in the sampling environments

The discussion for characteristic VOCs in the sampling sites are presented in the following manner: (i) the ambient VOC for the urban environment (roadside and park), (ii) the ambient VOC for the industrial environment (the two industrial sampling sites) and (iii) the indoor VOCs for the urban and industrial sites.

Typical VOCs detected in each sampling environment are discussed in this section. A summary of the relative abundance of each VOC groups in the sampling sites and the frequency of detection of each VOC to give an idea of their prevalence in the sampling sites, were first presented in section 3.2.1. Detailed discussions regarding the detected VOCs in the urban ambient, industrial ambient and indoor samples (both urban and industrial) were presented in sections 3.2.2 to 3.2.4.

3.2.1 Frequency of detection

Table 3.2 summarizes the mean concentration and frequency of detection of the VOCs measured for all sampling sites. Overall detection frequencies were also shown to illustrate the spatial distribution and occurrence of the VOCs.

Table 3.2 Mean concentration of detected VOCs (µg/m^3) and Detection Frequencies in the six sampling sites (DF= Detection Frequencies in %, AVE = mean concentration in µg/m^3)

Component Name	**Overall DF (%)**	**Urban Park**		**Urban roadside**		**Urban Indoor All***		**Urban Indoor 4 samples**		**Industrial Indoor**		**Industrial Loc 1 Ambient**		**Industrial Loc 2 Ambient**	
		DF	**AVE**	**DF**	**AVE**	**DF**	**AVE**	**DF**	**AVE**	**DF**	**AVE**	**DF**	**AVE**	**DF**	**AVE**
(Cyclo-)alkanes															
n-Hexane	76	17	0.1	100	2.7	33	0.2	25	0.0	100	4.0	100	3.8	100	3.6
n-Heptane	100	100	0.4	100	3.2	100	2.6	100	0.9	100	0.6	100	1.6	100	0.8
n-Octane	100	100	0.3	100	1.8	100	7.6	100	0.9	100	0.5	100	1.2	100	0.6
n-Nonane	100	100	0.9	100	3.0	100	49.7	100	4.2	100	0.7	100	1.2	100	1.6
n-Decane	100	100	1.3	100	3.2	100	98.4	100	7.7	100	0.6	100	1.3	100	3.1
n-Undecane	100	100	1.2	100	4.6	100	74.4	100	7.8	100	0.8	100	1.4	100	5.8
n-Dodecane	97	100	1.3	100	5.1	100	49.6	100	6.0	83	0.1	100	1.0	100	4.9
2-Methylpentane	71	0	0.0	100	2.3	17	0.0	25	0.0	100	1.6	83	1.9	100	1.3
Methylcyclopentane	65	17	0.0	100	0.8	0	0.0	0	0.0	100	0.5	67	0.7	83	0.4
Cyclohexane	88	83	0.1	100	0.2	50	0.1	25	0.0	100	0.5	100	0.4	100	0.3
Aromatic compounds															
Benzene	100	100	0.9	100	7.0	100	1.2	100	1.3	100	2.2	100	2.8	100	1.4

Component Name	Overall DF (%)	Urban Park		Urban roadside		Urban Indoor				Industrial Indoor		Industrial Loc 1 Ambient		Industrial Loc 2 Ambient	
						All*		4 samples							
		DF	AVE	DF	AVE	DF	AVE	DF	AVE	DF	AVE	DF	AVE	DF	AVE
Toluene	100	100	3.2	100	20.5	100	10.4	100	9.5	100	9.3	100	12.6	100	5.7
Ethylbenzene	100	100	0.6	100	5.5	100	4.1	100	2.1	100	5.0	100	26.8	100	8.2
m,p-Xylene	100	100	1.9	100	16.1	100	13.2	100	5.5	100	17.3	100	61.0	100	8.9
o-Xylene	100	100	1.0	100	8.3	100	8.3	100	3.0	100	8.8	100	27.7	100	3.9
Styrene	100	100	0.3	100	2.0	100	0.4	100	0.5	100	0.6	100	0.5	100	0.3
Propylbenzene	100	100	0.3	100	2.9	100	5.2	100	0.9	100	1.6	100	0.8	100	2.1
1,2,4 Trimethylbenzene	100	100	2.0	100	17.7	100	30.6	100	5.4	100	16.3	100	9.8	100	12.7
Benzonitrile	100	100	0.8	100	2.4	100	2.1	100	1.1	100	2.0	100	1.1	100	1.7
Phenol	100	100	1.6	100	2.6	100	4.4	100	2.4	100	1.9	100	0.9	100	1.4
Aldehydes															
n-Butyraldehyde	82	83	0.3	67	0.3	100	0.4	100	0.2	100	0.3	83	0.7	67	0.1
Hexanal	68	67	0.3	67	0.0	83	0.5	75	0.3	67	0.0	50	0.1	83	0.1
Heptanal	18	67	0.5	0	0.0	50	1.2	25	0.0	17	0.0	0	0.0	0	0.0
Benzaldehyde	100	100	4.2	100	8.2	100	4.6	100	4.3	100	2.2	100	2.2	100	2.5
Alcohols															
1-Butanol	18	0	0.0	0	0.0	0	0.0	0	0.0	33	8.0	67	52.8	0	0.0
2-Ethyl-1-hexanol	94	100	1.8	67	0.0	67	0.8	100	1.2	100	6.3	100	0.3	100	2.1
Ketones															
2-Butanone	100	100	0.6	100	0.7	100	0.9	100	0.9	100	2.8	100	12.1	100	2.6
2-Hexanone	71	67	0.0	100	0.1	83	0.1	100	0.1	50	0.0	50	0.0	67	0.0
2-Heptanone	97	83	0.1	100	0.4	100	3.2	100	0.6	100	0.0	100	0.1	100	0.1
Acetophenone	100	100	2.5	100	6.0	100	19.8	100	3.5	100	2.0	100	4.0	100	3.3
Other oxygenated compounds															
Ethylacetate	35	0	0.0	0	0.0	0	0.0	0	0.0	50	10.0	83	16.7	67	0.6
2-Methyl-furan	32	17	0.1	50	0.0	33	0.0	50	0.0	83	0.2	0	0.0	0	0.0
Halogenated compounds															
Carbon tetrachloride	100	100	0.2	100	0.1	100	0.2	100	0.1	100	0.2	100	0.2	100	0.2
Trichloroethylene	15	17	0.0	0	0.0	17	0.0	0	0.0	50	0.4	17	0.0	0	0.0
Tetrachloroethylene	24	17	0.2	0	0.0	0	0.0	0	0.0	17	0.0	0	0.0	100	1.0
Terpene															
α-Pinene	100	100	0.0	100	0.0	67	0.1	100	0.1	100	0.1	100	0.0	100	0.0
Limonene	100	100	0.2	100	0.8	83	2.8	100	4.1	100	2.8	100	0.0	100	0.3

*includes the two urban indoor samples with very high TVOC concentration

From the 37 VOCs detected, 29 were identified in all sampling locations (including indoors) with an average detection frequency of 71 to 100 percent. The other eight VOCs have detection frequencies of around 18 to 65 percent and are found localized in some sites indicating that these are associated with specific local sources (Jia et al., 2008). It must be taken note that the mean concentration values of the replicate measurements for each location were approximated by taking a value of zero for the samples where the signal to noise ratio are less than 10 (S/N<10). This means that samples which were detected but did not reach the limit of quantification (LOQ), were also assigned a value of zero. Discussion of the possible local sources of some VOCs is presented in the next sections.

3.2.2 Ambient VOCs in urban environment

Tables 3.1 and Table 3.2 give an overview of the most common VOC present in the urban environment of Manila (detailed values of concentration can be found in appendix B). The large difference of TVOC concentration in the two urban sampling sites (urban park and roadside) shows the dependence of concentration on the local source. For the urban park, the highest contributor to the TVOCs is benzaldehyde which contributes to about 15% of the total VOCs present at a mean concentration of 4.2 µg/m^3. While most VOCs present in the park can be inferred to come mostly from vehicular emissions in the urban area, the difference in the relative contribution of the specific VOC to the TVOCs profile between the two urban sampling sites shows that other mechanism aside from simple diffusion and dilution were occurring.

The mean TVOC concentration of the roadside sampling site is the second highest among all the sites sampled (mean concentration: 129 µg/m^3). For this sampling site, toluene is the highest contributor (16%). The relative high contribution of toluene in the roadside environment in Manila was also reported by Balanay and Lungu (2009) in their study of the occupational effect of vehicular emissions in 2005 and by Gee and Sollars (1998) in the measurement done in Manila in 1995 as part of a study conducted to determine VOC levels in some major cities in Asia and Latin America. The difference between the VOC profile of the park (where benzaldehyde was dominant) and the roadside VOC profile (where toluene was dominant), can be possibly attributed to the formation of benzaldehyde in the air through photochemical oxidation of toluene and other aromatic hydrocarbons (Han et al., 2003; Sun et al., 2009; HSDB, 2011). Highly reactive VOCs from vehicular emissions, must have reacted while it dispersed and diffused to lower concentration areas. This may explain why benzaldehyde in the park is higher in terms of percent contribution in the TVOC compared to the roadside.

Another compound that shows high concentration in both the park and roadside sampling sites is 1,2,4-trimethylbenzene. This compound is produced during petroleum refining as a major component of the C9 aromatic hydrocarbon fraction and is primarily used as gasoline additive along with other industrial applications such as solvent in coatings, cleaners, pesticides, printing and inks (Harley et al., 1992; U.S.EPA, 1994). Other compounds present like benzonitrile, acetophenone, styrene and phenol could be attributed to automobile exhausts (Seizinge.De and Dimitria.B, 1972; Jüttner, 1994; Schuetzle et al., 1994). Phenol and others carbonyls were possibly produced through the atmospheric reaction of hydroxyl (•OH) radicals with benzene (Berndt and Boge, 2006).

The aromatic compounds and the rest of the VOCs that have high detection frequencies in the two urban areas are also commonly identified with the automobile exhaust except for carbon tetrachloride (CCl_4) and 2-ethyl-1-hexanol. Therefore, further discussions of those two VOCs were given.

CCl_4 was a widely used industrial compound and was utilized as a solvent for asphalt, benzyl resin, bitumens, cleaning agent for machinery and electrical equipment, and other chlorination processes until most of the uses are discontinued due to toxicity problems and its high ozone depletion potential (Allen et al., 2009; HSDB, 2011). It is already banned in developed countries since 1995 but is still allowed for use in the Philippines until end of 2010 following the mandates of the Montreal Protocol. However CCl_4, is also known for its high persistence in the environment, with an approximate atmospheric half life of 366 years based on OH reactivity (Atkinson, 1976) as cited in (HSDB, 2011). Thus, although there are no known significant natural sources of CCl_4, it is expected to be detected in the ambient air of an area in a rather homogeneous concentration, assuming there are no immediate sources of emissions. In the sampling campaign conducted, the levels of CCl_4 tend to be homogeneous (concentrations were not statistically different) in the urban areas with the mean concentration of 0.17 and 0.14 µg/m^3 for the urban park and the roadside respectively. The relative stability of CCl_4 concentration was also reported by Class and Ballschmiter (1986) in their study of chlorinated hydrocarbons in air over the Atlantic ocean. The same observation was also noted by Montecastro (2008) who found no spatial nor temporal variability for CCl_4 in the VOC monitoring in six sites in Seattle, Washington.

The compound 2-ethyl-1-hexanol was also observed to occur in the ambient urban environment, specifically the urban park, but was barely detected in all the roadside samples. This VOC is however mostly associated with indoor environment (Sakai et al., 2006) and outdoor ambient data are quite few. It was detected and quantified however in the VOC sampling campaign done in Vietnam but it was not detected in sampling done in Ethiopia (Do et al., 2011). Sartin et al. (2001) also reported 2-ethyl-1-hexanol as among the biogenic VOCs detected in the ambient coastal air in Ireland. It was also identified as one of the biogenic VOCs emitted by some plants (Batten et al., 1995) which can possibly explain its presence in the park and some sites where greeneries are present. Although this compound is not normally found in automobile exhaust or regular vehicular fuel, it may soon become ubiquitous in the outdoor air because of its presence in the biodiesel vapor, which is being promoted by a lot of countries including the Philippines (Peng et al., 2006; Garcia et al., 2010).

3.2.3 Ambient VOCs in industrial environment

Industrial sources also contribute to ambient VOCs and several papers have been published regarding VOC emissions from these stationary sources (see section 1.2). These studies show that industries can be major contributors of VOCs and can affect the exposure of people especially when the residential areas are adjacent with these industrial sites.

Tables 3.1 and 3.2 give mean concentration values of typical VOCs found in the sampling campaign from two industrial sites in the Philippines (detailed values of concentration can be found in appendix C). The two locations are both in the outskirts of two main industrial parks in Laguna, Philippines. Sampling site for industrial location 1 (Calamba , Laguna) which is situated near a roof galvanizing and painting facility among other industries, showed the highest TVOCs among the sites sampled with mean TVOC of 248 µg/m^3. The high concentration is mostly contributed by aromatic hydrocarbons and alcohols that must have come from the intensive solvent used in the painting activities. In particular, 1-butanol is found only in this area which suggests a localized stationary source of emissions. (m+p)-Xylene was the main contributor to the TVOC (61%), suggesting the high usage of this VOC in the painting activity. On the other hand, sampling site in industrial location 2, which is situated near a newspaper and magazine printing complex, showed a relatively lower average TVOCs with an average of 82 µg/m^3. However, samples from industrial location 2 showed the presence of tetrachloroethylene in all samples suggesting the usage of this compound from the printing facility or possibly from nearby industries in the industrial park. It should be noted that the International Agency for Research on Cancer (IARC) has classified tetrachloroethene as a Group 2A carcinogen, which means that it is probably carcinogenic to humans (IARC, 2012). In addition, 1,2,4-trimethylbenzene showed the highest concentration in the second industrial site followed by xylenes. While 1,2,4-trimethylbenzene can be emitted from vehicle exhausts, the smaller concentration of toluene compared to 1,2,4- trimethylbenzene in the second industrial sampling site, suggests that it is also used as material in the industrial printing press from the use of inks and solvents or from other industries located in the area (U.S.EPA, 1994). This is also supported by one study done to determine the occupational exposure of employees in a printing press in Hongkong where the presence of 1,2,4-trimethylbenzene was identified in the working environment(Leung et al., 2005). Another compound, ethylacetate, was detected only in all industrial sampling sites and never in the urban area. This compound is mostly used as industrial solvent and its presence in the industrial environment indicates its usage in the surrounding industries(NPI, n.d). CCl_4 is also found in the all samples in the industrial environment. As discussed earlier, it is a ubiquitous compound which is expected to be found in the ambient air. The level of CCl_4 is almost homogenous in the two industrial areas at the mean concentration of 0.2 μg/m^3 for both the sampling sites, although they are about 14 kms apart. This homogeneity of concentration was also observed from among the sampling sites in the urban area as discussed earlier. However, when all sample concentrations data of CCl_4 from the urban area were pooled and compared with the pooled concentration data of CCl_4 from the industrial area (including the indoors), it can be observed that the industrial environment has statistically significant higher level of CCl_4 ($p<0.01$). This gives an indication on the influence of industrial activities in the increased level of CCl_4 and possibly other stable volatile organic compounds used in manufacturing activities, in areas near industrial complexes. Although this compound is officially phased-out in the country since end of 2010, its high persistence in the environment specially surrounding the industrial areas in the country still put residents living near industrial sites at higher risk of exposure to this toxic chemical. This observed spatial dependence of CCl_4 can be further explored to possibly correlate the levels of CCl_4 with presence or contribution of industrial activities to ambient VOC levels.

Table 3.3 Comparison of mean concentration of CCl_4 (μg/m^3) in all Sampling Locations

	Sampling location					
	Urban park	**Urban roadside**	**Urban Indoor**	**Industrial indoor**	**Industrial Loc 1**	**Industrial Loc 2**
Ave CCl_4 conc (μg/m^3)	0.17	0.14	0.14	0.23	0.21	0.21

3.2.4 Indoor VOCs (urban and industrial environments)

While indoor VOCs have been widely studied in developed countries, indoor VOCs are just recently gaining interest in the developing nations (Tang et al., 2005). This research work reports probably for the first time indoor concentration levels of multi-class VOCs in urban and industrial air environments in the Philippines.

Tables 3.1 and 3.2 show the detected VOCs and the mean concentrations for the two indoor sampling sites. The two sampling sites show a mean concentration of 248 and 110 μg/m^3 for the industrial area indoor and urban indoor samples, respectively. It should be noted however that the TVOC for the urban indoor sample is based only from four samples because two samples were excluded in estimating the mean concentration. This was done because the two samples were found to have mean concentration of 1042 µg/m^3, which is about 14 times higher than the mean concentration of the other samples. The very high concentration of the two samples was inferred to be associated with the use of insecticides in the house before the sampling day. Although the two samples were excluded, further discussion on the effects of insecticide use will be discussed at the last part of this section. Implications of the possible influence of insecticide use in the indoor VOC profile will also be mentioned in the discussion of I/O ratio and also in the correlation analysis in the succeeding section.

Like the outdoor ambient samples, the predominance of aromatic compounds in the total VOCs were observed for the two indoor samples. Table 3.1 shows that aromatic compounds contributed to about 42 and 59 % of the TVOCs for the urban indoor and industrial area indoor samples respectively.

Some VOCs were mostly found in higher concentration in the two indoor environments compared in the ambient samples, like alpha-pinene and limonene. Limonene is used as a flavor and fragrance additive in food, household cleaning and polishing products, while alpha pinene, a naturally occurring terpene, can be associated with wood-based products, aerosol paint, cleaning and sanitation products, paints and varnish removers (Kotzias D, 2005). This high concentration of terpenes in indoor environment was attributed to the increased use of terpenoid solvents and scents during the recent years (Weschler, 2009). Chlorinated compounds like trichloroethylene and tetrachloroethylene were also detected in the indoor samples most notably in the indoor sample from industrial area. In the industrial indoor sampling site, presence of 2-methyl-furan was also noted and can be associated with the presence of smoker in this indoor sampling location (Xie et al., 2003; Van Berkel et al., 2008).

The presence of 2-ethyl-1-hexanol is also apparent in both indoor sampling sites with mean concentration of 1.2 and 6.3 µg/m^3 for the urban area indoor and industrial area indoor samples respectively. This compound is of concern in Europe and Japan as it is considered to be a major causative factor of Sick Building Syndrome (Norbäck et al., 2000; Kamijima et al., 2002). It is mostly considered to be emitted from building materials made from PVC and that the main mechanism of emission is through the alkali hydrolysis of di-2-ethylhexylphtalate (DEPH), a plasticizer which is major component of PVC along with the residual emission from industrial-quality DEPH (Sakai et al., 2006; Chino et al., 2009).

Indoor use of insecticides

One important source of indoor VOCs is the use of insecticide spray which is a common practice in many households in the Philippines. The tropical climate of the country is conducive for proliferation of insects which leads to a high amount of insecticide usage in homes (Pentamwa et al., 2011). During the rainy season for instance, dengue fever epidemic, which is caused by mosquitoes, is common in the Philippines and as such, most households use insecticide sprays and burn mosquito coils indoors to ward off mosquitoes. Figure 5.1 shows the chromatogram for the two samples from urban house indoor.

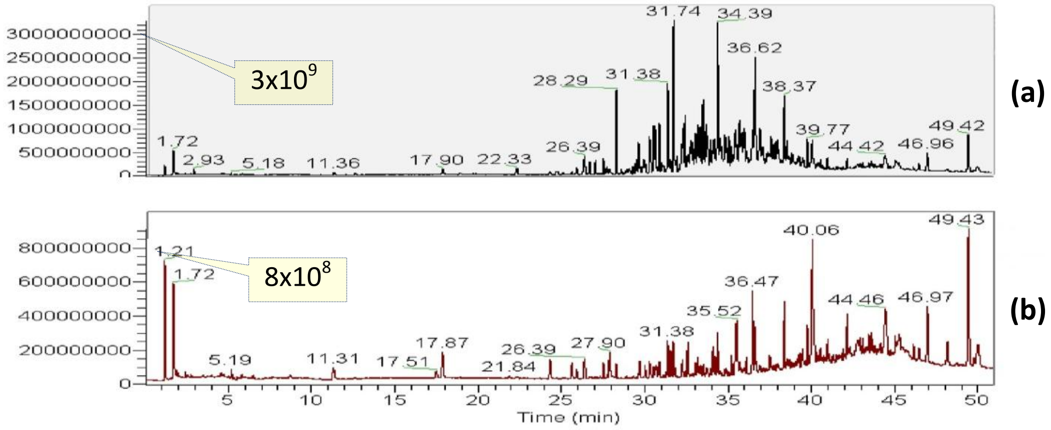

Figure 3.1 Comparison of chromatograms of two indoor samples from urban area showing the difference in scales of peaks. (a) sample chromatogram of excluded sample due to high concentration (after insecticide application) (b) chromatogram of a normal sample from urban indoor

The large difference between the peak scales of the two samples was noticeable. The high peaks on the first sample (Fig 5.1- a) was attributed to insecticide use due to onset of rains that encouraged breeding of mosquitoes during the sampling campaign. This was evident in the trace smell of insecticide noticed during the third sampling day. Examination of the VOC profile of the excluded samples showed that the high TVOC level for the last two samples (average concentration 1042 µg/m^3) was mainly due to increase of alkane concentration. There was also an observed increased of concentration of 1,2,4-trimethylbenzene, acetophenone, 2-heptanone and phenol for the two samples compared to the other ones. On another note, it was also observed that the elevated concentrations of these VOCs precluded the detection of lower concentration VOCs that were normally observed in the other indoor samples like 2-ethyl-1-hexanol, α-pinene and limonene. This maybe because the high signal of the elevated compounds may have rendered the relatively lower signal from the low concentration VOCs to be detected as noise. The high concentrations of alkanes and 1,2,4-trimethylbenzene indicates their use as the carrier solvent for the insecticide spray while ketones like acetophenone and phenol may have been part of the insecticide formulation due to their insect repellant properties (Erbilgin et al., 2008).

Indeed the insecticide application is one of the important sources of indoor air pollution and indoor VOCs (U.S.EPA, 1995) as shown by the very high concentration of the last two urban indoor samples (see Table 3.1 and Appendix C). In a simulation study done by Bukowski and Meyer (1995), it was reported that indoor VOC level can reach up to 328,000 and 20,500 µg/m^3 (depending on the type of spray), following insecticide application. Residents are thus placed into high health risk with the use of these insecticide sprays or mosquito coils due to high concentration of irritant and possibly toxic VOCs. For instance, one study suggests that exposure to mosquito coil smoke can post significant acute and chronic health risks comparable to environmental tobacco smoke. It was reported that emission of toxic VOCs from burning one mosquito coil is equivalent to emissions from 51 cigarettes (Liu et al., 2003).

(a) (b)

Figure 3.2 Some of the typical sources of VOCs in tropical countries. (a) : burning mosquito coil; (b) : spraying of insecticides . (Photo from Tenenbaum (2003) and http://accidentinsurancethailand.com/)

3.3 TVOCs and BTEX

In this section, the TVOCs (based on the 67 target compounds) and BTEX of the different sampling sites are discussed. Comparisons of TVOC levels and profiles among the sampling sites and with other studies are presented.

3.3.1 TVOC level

Figure 3.3 shows the box plot of the TVOCs concentration of the samples collected from the six sampling sites.

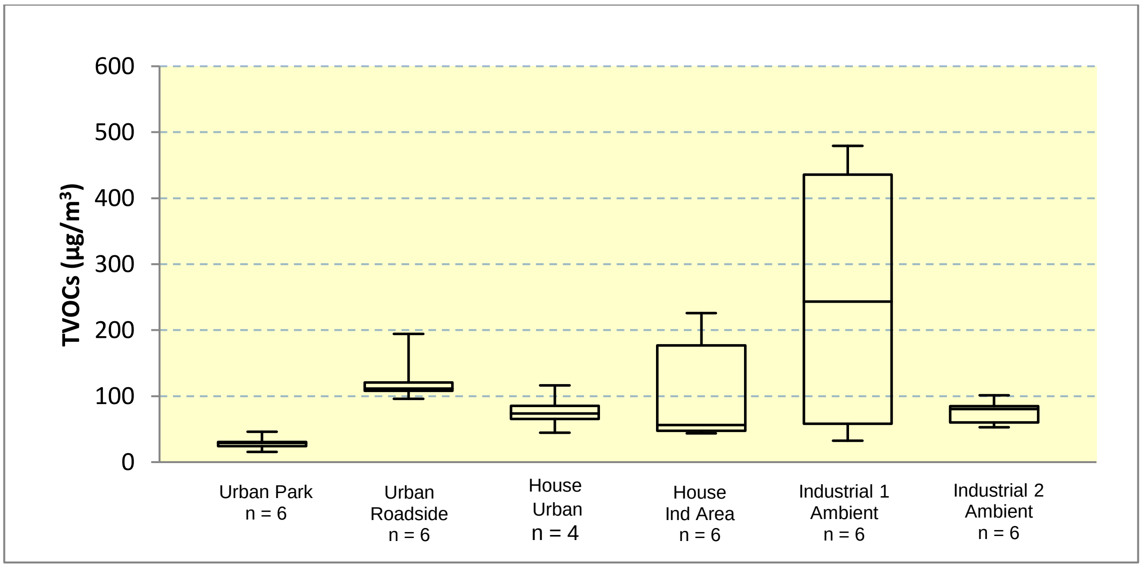

Figure 3.3 Box plot of TVOCs (µg/m^3) measured in the six sampling sites(middle line: median, box: 25% -75%; whisker: non-outlier range)

As mentioned earlier, industrial location 1 recorded the highest TVOC concentration at an average of 249 µg/m^3. However the values of VOC concentration in this industrial area is also highly dispersed which may indicate an intermittent and periodic emission from the nearby sources. The second sampling site for industrial area which is also in the outskirts of one of the main industrial parks in the country and near a printing facility, showed a lower average TVOC at around 82 µg/m^3. This may be due in part to efficient scrubbing mechanisms of nearby industry (the printing facility) compared to the first industrial sampling site where emission cleaning system may not be enough to handle the amount of emissions from the painting facility.

The high variation observed in the TVOCs concentration within and between the industrial sampling sites shows the significance of different factors in the industrial environment. For instance, the difference between the levels of VOCs and the type of VOCs identified between the two industrial sites demonstrates the effect of the type of industrial sources of VOCs. The extent of fugitive emissions which is mainly dependent on the efficiency of the scrubbing system of an industrial source and how enclosed the industrial emission source is may also explain the difference in the levels of TVOCs between the two industrial areas (Van Deun et al., 2007). Intermittent and periodic emissions which are related to manufacturing activities may also be a factor in the observed variability of concentrations. Furthermore, the meteorological factors such as wind strength and the direction should also be considered. In the first industrial location for example, the wind speed and direction may have affected the concentration of TVOCs since it was observed that the direction and speed of wind was constantly changing during the sampling. The observation regarding the high variability of the concentration of VOCs in the industrial area was also mentioned in studies done on the ambient VOCs in industrial areas in Thailand and France (Pimpisut et al., 2003; Xiang et al., 2012). Despite the high variation, industries can indeed be a significant source of VOC in ambient environment. For instance, in a study conducted in roadside microenvironments in Hongkong, the maximum concentration was found to be highest in the industrial district. This was attributed to the additional sources of VOC from the industries present (Chan et al., 2002).

3.3.2 BTEX level

Among the aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylene (BTEX) are cited to be the most abundant among the aromatic hydrocarbons and are of great concern because of their role in tropospheric chemisty and the risks they posed to human health (Brocco et al., 1997; Buczynska et al., 2009; Franco et al., 2012; Singla et al., 2012).

Table 3.4 shows some reported mean BTEX concentration for industrial and roadside ambient air samples from different countries, most of which are from Asia. Industrial area near the painting plant in Calamba, Laguna showed a relatively high level of BTEX compared to other industrial locations from the studies listed. The high concentration is mainly due to elevated level of ethylbenzene and xylenes. The BTEX level of the second industrial location on the other hand is comparable to the BTEX levels reported in the industrial areas located in Guangdong China, Rayong, Thailand, Ulsan South Korea and Yokohama Japan. It must be taken note however that analytical and sampling methodologies used in these studies vary from one study to another.

Table 3.4 Mean BTEX concentration (µg/m^3) for sampling sites areas (B: Benzene, T:Toulene, EB; Ethylbenzene, (m+p)-X: (m+p)-Xylene, o-X: o-Xylene)

REFERENCES	Site Description	Site/ Location	Average Concentration (µg/m^3)					Total BTEX	RATIO	
			B	T	EB	(m+p) X	o-X		B/T	(m+p)X/ EB
This Study (2012)	Industrial Area (near painting plant)	Calamba , Laguna, Philippines	2.8	12.6	26.8	61.0	27.7	**130.9**	0.23[d]	2.51[d]
This Study (2012)	Industrial Area (near printing press)	Binan, Laguna, Philippines	1.4	5.7	8.2	8.9	3.9	**28.2**	0.27[d]	1.30[d]
Xiang et al. (2012)	Industrial	Dunkerque, France	0.40	1.22	0.37	0.86	0.30	**3.15**	0.33	2.32
Tiwari et al. (2010)[b,c]	Industrial (near Petrochemical plant)	Yokohama , Japan	2.6	9.3	4.9	3.7	1.6	**22.0**	0.28	0.76
Roukos et al.(2009)	Industrial	Dunkerque, France	1.55	2.10	0.56	0.82	0.32	**5.35**	0.74	1.46
Liu et al. (2008a)[c]	Industrial (near Petrochemical plant - rush hour)	Kaohsiung, Taiwan	27.0	453.7	88.0	33.7	38.0	**640.4**	0.06	0.38
Chan et al. (2006)	Industrial	Guangdong, China	2.8	13.5	2.0	4.9	1.2	**24.4**	0.21	2.45
Chan et al. (2006)[a]	Industrial suburban	Guangdong, China	1.3	7.3	0.8	1.7	0.5	**11.6**	0.18	2.13
Pimpisut et al. (2003)	Industrial	Rayong, Thailand	6.4	20	0.9	4.3	-	**31.6**	0.32	4.78
Hawas et al. (2002)[c]	Industrial	Brisbane, Australia	10.5	39.9	5.9	21.2	8.3	**85.8**	0.26	3.59
Na et al., (2001)[a]	Industrial	Ulsan, South Korea	6.7	14.7	3.9	16.5	4.8	**46.6**	0.46	4.23
Kalabokas et al.,(2001)[b,c]	Industrial near refinery	Athens, Greece	1.9	4.7	1.0	2.3	2.0	**11.9**	0.40	2.30
This Study (2012)	Urban Roadside	Manila , Philippines	7.0	20.5	5.5	16.1	8.3	**57.5**	0.34[d]	2.94[d]
Do et al. (2011)	Urban Roadside	Gent, Belgium	2.0	10.7	1.0	3.0		**16.7**	0.19	3.00
Do et al. (2011)	Urban Roadside	Ababa, Ethiopia	18.3	40.7	7.6	28.5		**95.1**	0.45	3.75
Do et al. (2011)	Urban Roadside	Hanoi, Vietnam	32.2	119.3	19.5	63.2		**234.2**	0.27	3.24
Liu et al. (2008a)[c]	Urban (near traffic rush hour)	Kaohsiung, Taiwan	53.5	599.0	136.0	81.0	78.6	**948.1**	0.09	0.60
Wang and Zhao (2008)	Urban Roadside	Nanjing, China	15.8	38.2	7.0	9.3	7.1	**77.4**	0.41	1.33
Ho et al. (2002)	Urban Roadside	HKPU, Hongkong	4.85	28.81	3.11	3.98	2.85	**43.6**	0.17	1.28
Chan et al. (2002)	Urban (commercial near traffic)	Mongkok, Hongkong	28.9	70.0	2.1	10.6	2.2	**113.8**	0.41	5.05
Wang et al. (2002)	Urban (near traffic)	Guangzhou, China	51.5	77.3	17.8	82.2		**228.8**	0.67	4.62
Wang et al. (2002)	Urban (I near traffic)	Macao, China	34.9	85.9	24.1	95.6		**240.5**	0.41	3.97
Wang et al. (2002)	Urban (near traffic)	Nanhai, China	20	39.1	3.0	14.2		**76.3**	0.51	4.73

a= sampling point taken away from known direct source but within the vicinity of industrial and traffic sources. ;b =average of several industrial sites c = converted to µg/m^3 from ppbv; µg/m^3 = (12.187 *MW/(273.15 + T (ºC)) x ppbv, (assuming 25 ºC and 1 atm) where MW :molecular weight of compound; d = average of individual sample ratios

There is a high variability in terms of BTEX levels among different industrial locations as seen in table 3.4. Generally, except for the sample collected from Calamba, Philippines and that from Kaohsiung, Taiwan (Liu et al., 2008a), BTEX levels tends to be lower in the industrial area compared to the urban roadside BTEX level.

Urban BTEX values of the roadside from the street of Pasay City, Manila were lower compared to samples taken from urban roadside samples of other countries like Vietnam, Ethiopia, China and Taiwan but it is still higher compared to BTEX levels from developed countries like Belgium and Hongkong (see Table 3.4).

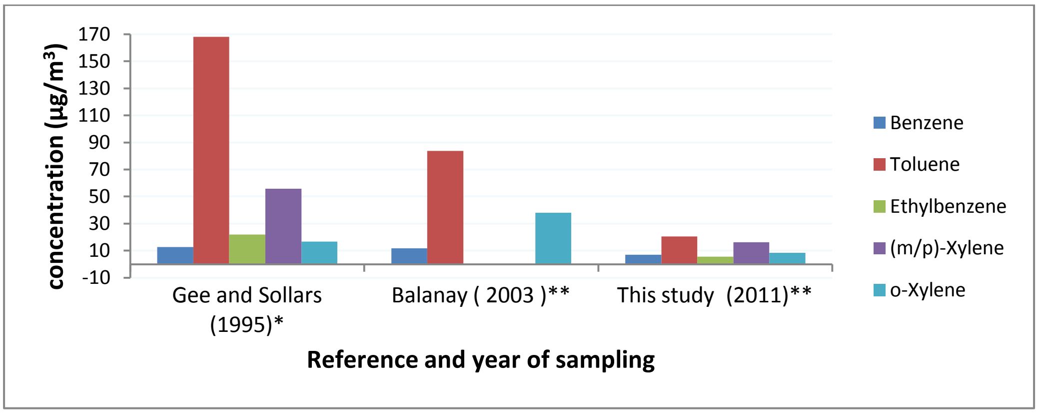

Figure 3.4 Trend of BTEX concentration in Manila (*samples from roadside and locations remote from traffic; ** all samples taken from roadside)

Figure 3.4 shows the trend on BTEX levels in Manila using the data from Gee and Sollars (1998), Balanay and Lungu (2009) and this study. Based on the figure, a general improvement of BTEX levels can be noted in the roadside environments of Manila. The perceived improvement can be much higher considering that the data from Gee and Sollars (1998) were averaged not just from roadside data but from sampling points far from the traffic sites. Roadside data however can be approximated on the maximum data from the study where maximum values of 47.5, 807.0, 80.3, 170.3, 41.9 µg/m^3 for benzene, toluene, ethylbenzene, (m,p)-xylene and o-xylene respectively were reported. Comparing these values to the roadside levels of BTEX in the current study, and considering that samples in this study were collected during the rush hours and thus possibly represent the higher levels of the present BTEX concentration range, a vast improvement in terms of BTEX levels can be observed. This is despite the fact that the vehicle fleet is increasing in the country at the rate of about 6 percent and 5 percent per year for the diesel fuelled and gasoline fuelled vehicles respectively (ADB, 2006). The general improvements may be the results of a law passed in 1999 (Philippine Clean Air Act of 1999) in response to the very poor quality of air in Manila during the 1990s. However, this apparent trend should also be interpreted with caution as the concentration in the sampling site may have been affected by meteorological factors like the presence of the sea breeze from the nearby Manila bay (see Figure 2.2 for the map of sampling location) which can have a diluting effect (Zhao et al., 2004). Thus analysis of ambient samples from other various roadside and urban places in Manila should be done if this observation is to be validated.

The benzene concentration in the roadside (7.0 µg/m^3) is higher than that observed from the two industrial sampling sites (2.8 and 1.4 µg/m^3 for Industrial Location 1 and 2 respectively). The mean benzene concentrations for the two indoor samples were 1.2 and 2.2 µg/m^3 for the urban indoor and industrial area indoor samples. All the sampling sites in the urban and industrial areas (except for the park : mean concentration of 0.8 µg/m^3) , still exceeds the benzene levels of 1.7 µg/m^3 associated with an excess lifetime risk of 1/100,000 of the population (WHO, 2000).

3.3.2 TVOC profile

Figure 3.5 shows the relative contribution (%) of each group of pollutants to the TVOCs (μg/m^3) during each sampling campaign. It can be seen from the figure that aromatics account for the highest percentages of contribution for all the six sampling sites. Alkanes, on the other hand, are the second largest contributors except for the first industrial location where alcohols and oxygenated compounds showed substantial contribution to TVOCs.

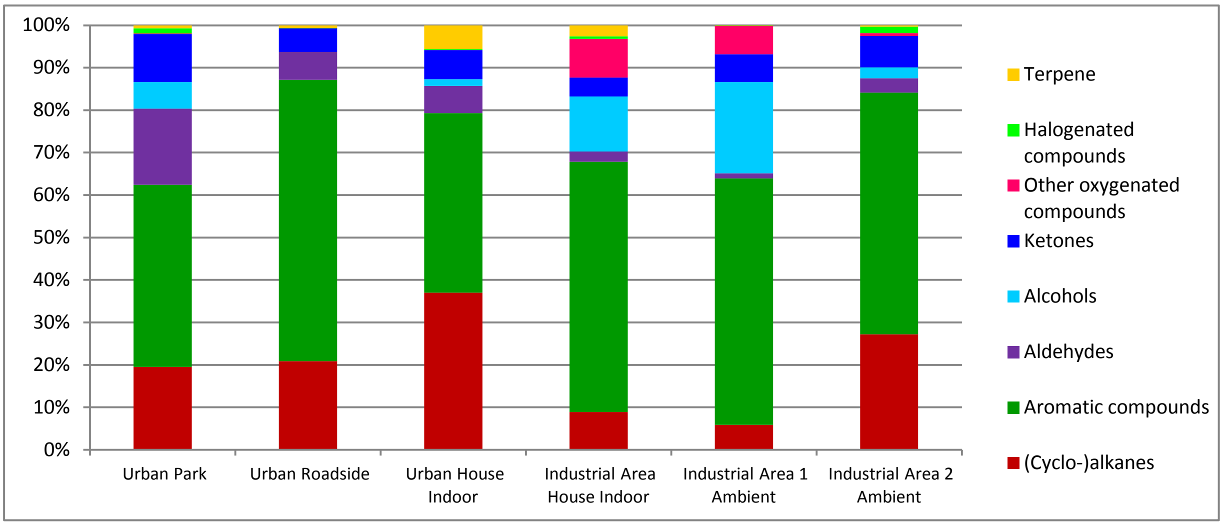

Figure 3.5 Stacked column of percent contribution of each group to the TVOCs in the six sampling locations

It is worth noting that the two indoor sampling sites were situated within the vicinity of the two ambient sampling locations. Urban house indoor was located about 250 meters from the urban roadside traffic while the indoor sample from industrial area was located some 260 meters away from the first industrial sampling site. Given this, the extent of influence of outdoor source on the indoor profile can thus be examined. As can be shown in Fig 3.5, outdoor sources may have major influence on the indoor air basing on the similarity of the profiles of VOCs of the two indoor environments to the nearby outdoor ambient air VOC profile. The apparent deviation however can be attributed to the presence of additional indoor sources of VOC like terpenes and 2-ethyl-1-hexanol. In addition, the relatively higher contribution of alkanes in urban indoor environment may have been due to residual petroleum based solvent from insecticide used. Although the two samples with high concentration of VOCs were excluded, it can be inferred that the particular household where the sampling was conducted may have used insecticide intermittently and residual VOCs may have persisted indoors long after the application.

Variations of TVOC profile depending on the sources are reported in some studies for both industrial or traffic related sources of emissions. For instance, aromatic compounds were observed to be the most abundant group in the TVOC in the two industrial sites in the Philippines measured in this study and in the samples obtained from industrial sites involving steel manufacturing, shoemaking and cement production in Guangdong China (Chan et al., 2006) and in the industrial site near the petrochemical complex in Kaohsiung, Taiwan (Liu et al., 2008a). However there are also some studies that show other VOC groups can dominate the

TVOC concentration. In the industrial ambient air sample near petrochemical industry in Yokohama, Japan, the dominant VOCs were the alipathics (Tiwari et al., 2010). In another industrial sampling in Brisbane alkanes contributed the highest to TVOCs compared to the aromatics (i.e., 45% compared to 12% contribution, respectively) (Hawas et al., 2002). On the other hand, ambient air sample from an industrial complex dominated by petroleum refinery in Ulsan, South Korea showed that oxygenated hydrocarbons contributed the most to TVOCs (Na et al., 2001) while another refinery in Taiwan reported alkanes as the dominant VOCs (Chen et al., 2006).

In the case of traffic related emissions, aromatics are usually reported to be the significant contributor to TVOCs. However, there is also a variation in exhaust emission as a result of the differences in fuel and vehicle fleet types from region to region(Verma and des Tombe, 2002). Gee and Sollars (1998) in their study on VOC levels in Asian and Latin American countries showed that aromatic levels in fuels used in Asian countries are higher than those used in Latin American cities which they correlated with the higher BTEX levels in ambient air in Asian cities. The difference in profiles of vehicle exhausts depending on the fuel type, on the other hand, was reported by Schuetzle et al. (1994); Caplain et al. (2006). In a study to determine VOC profiles and levels in Shing Mun Tunnel in Hong Kong, Ho et al. (2009) found out that alkanes were the highest contributor to TVOC followed by alkenes.

3.3.3 Indoor-to-outdoor concentration ratio (I/O)

Indoor to outdoor (I/O) ratios for the urban and industrial sites are presented in Table 3.5. The mean ratio for each site was calculated by getting the ratio of the mean concentration of each compound group from the indoor to that of the mean concentration from the outdoor. For statistical analysis of the difference between indoor and outdoor, non-parametric Mann Whitney-U test was used from the pooled data from each site. For the urban house indoor, VOC level was compared with the level at roadside sampling site which is around 250 m away from the house sampling site and at the urban park , which is about 6 km away. For the industrial area, house indoor VOC level was compared with the level at the nearby industrial sampling site 1 (Calamba, Laguna) which is about 260 m away from the house and with the second industrial sampling site (Binan, Laguna) which is about 14 km away.

Table 3.5 : Mean concentration of TVOC groups and I/O ratios of the six sampling sites in the Philippines (H : house indoor, P: Park, I1 : Industrial Location 1, Industrial Location 2)

	Urban Area			Industrial area			I/O Ratio			
Compound\Group	H	P	R	H	I1	I2	Urban Area		Industrial Area	
							H/P	H/R	H/I1	H/I2
(Cyclo-)alkanes	27.6	5.7	26.9	9.8	14.5	22.2	4.8*	1.0	0.7	0.4*
Aromatic compounds	31.5	12.5	85.1	65.1	143.9	46.4	2.5*	0.4*	0.5	1.4
Oxygenated compounds	11.1	10.4	15.6	32.0	89.1	11.5	1.1	0.7	0.4	2.8
Terpenes	4.21	0.20	0.80	2.89	0.05	0.30	21.0*	5.3*	61.3*	9.5*
TVOCs	**74.6**	**29.2**	**128.5**	**110.4**	**247.8**	**81.5**	2.6*	0.6*	0.4	1.4

*: indicates significant difference at level of 0.05

It can be seen from table 3.5 that for both indoor samples, the I/O ratio for TVOCs and most of the groups except terpenes, are less than or equal to 1 when the indoor sample is compared to the site with a known immediate source of emission like the traffic site and the painting facility (i.e., H/R and H/I1). When compared to an outdoor sample with no known or little sources of emission, the I/O ratio of TVOC and most of the compound groups is greater than 1 for both the urban and industrial sampling areas. The less than 1 I/O ratio implied a stronger outdoor source of VOCs compared to indoor sources. On the other hand, comparison with background ambient sampling site like the park shows that there were also indoor sources that contributed to the levels of VOCs in the indoor environment. Referring back to table, we can see that the I/O ratio for the terpene group are both high for both the urban and industrial areas since there are low levels detected in outdoor air compared to levels of terpenes indoor. As discussed in section 3.2.3, high level of terpenes can be attributed to the use of household cleaning , sanitation and polishing products, perfumes etc (Kotzias D, 2005; Weschler, 2009). Indoor level of (cyclo)-alkanes and aromatics in the urban house is also statistically higher than the concentration in the park. It was discussed earlier that residual VOCs from pesticide usage must have made the urban indoor concentration of alkanes relatively higher. The noticeable absence of significant difference of the house indoor concentration with that of the outdoor concentration in the industrial area despite the difference in the concentration level is probably due to the high variation in both the indoor and outdoor concentration data in the first industrial sampling location. The variation shows the extent of influence of the outdoor emission to the indoor levels as indoor air was obviously affected by outdoor intermittent emission possibly from the nearby painting facility. The infiltration of pollutants and apparent fluctuation in the indoor VOC levels may also be a function of the high exchange rates of air since the house was properly ventilated by windows. This natural ventilation is typical for houses in the Philippines due to its tropical condition and windows are almost always open. The significant effect of the outdoor air pollution to the indoor air was also described by Sarigiannis et al. (2011) and Srivastava et al. (2000) who reported that the extent of effect can be influenced by prevailing wind direction, ventilation type and the kind of indoor activity. Geographical and seasonal effects was evaluated in the statistical analysis of indoor air of eleven European cities (Airmex) and it was mentioned that indoor levels of VOC with known indoor sources, like terpenes, tends to be lower in the summer possibly due to higher ventilation rate and reaction with ozone that penetrated from outdoor air . However they also reported that the intrusion of outdoor air due to increased ventilation rates in summer contributed to the indoor levels of aromatic compounds (Geiss et al., 2011). Related observations or the seasonal extent of effect of outdoor air to indoor air was also described by Pekey and Arslanbaş (2008) and Schlink et al. (2004).

The broad range of factors affecting the indoor air thus makes generalization of I/O ratio difficult. In this study the indoor to outdoor ratio was seen to vary depending on the location where the house indoor level was compared. As Do et al. (2011) pointed out, I/O ratios of VOCs may not be as uniform as it has been frequently proposed in the earlier literature and suggested that sampling region, specific indoor and outdoor location and type of pollutants should be considered in indoor and outdoor VOC comparisons. In addition, based on the observation in this study and the literature sources mentioned above, the interaction and combination of the following factors may affect major influence over I/O ratio. These include (i) the strength and presence of known sources of VOC in the outdoor air (ii) the proximity of the known outdoor source (iii) the strength and presence of indoor sources (iii) ventilation provision and type of ventilation (iv) wind /disturbance. Consideration of the presence or absence or combination of these factors may be useful in estimating the possible I/O VOC relationship. For instance, a high I/O ratio can be expected when there is no immediate outdoor source, ventilation is low and presence of indoor VOC sources is noted. Less than 1 I/O ratio on the other hand can be expected if the outdoor sampling point has an immediate VOC source like traffic fleet or industrial emission, indoor sources are of far distance from outdoor source and there is no wind blowing from the outdoor source and no strong indoor sources. High ventilation i.e. prolonged opened windows, (such as in the case in the Philippines and other tropical countries and summertime in temperate regions) and lack of indoor VOC sources on the other hand will tend to equilibrate the indoor and outdoor VOC levels rendering the ratio to be near unity and the correlation of VOC species between indoor and outdoor to be high. The relationship of this factors and its effect on the I/O ratio can thus be further studied.

3. 4 Source Identification

For effective emission controls and health risks assessment, identification of all possible sources of VOCs is important (Sanchez et al., 2008). Use of diagnostic ratios and correlation coefficient to identify VOC source as well as comparison of spatial variability is discussed in this section. Difference between the urban and industrial area in relation to the difference in diagnostic ratios and correlation coefficients will also be evaluated.

3.4.1 Diagnostic ratios

As discussed in section 1.4, a number of literature utilized diagnostic ratios of certain VOCs like BTEX to identify VOC source (Brocco et al., 1997; Barletta et al., 2008; Buczynska et al., 2009) as well to make estimation on the age of the air mass (Nelson and Quigley, 1983; Khoder, 2007).

Table 3.6 shows the mean characteristic ratio of samples taken from each sampling site for the three sampling days. Effect of temporal variations on the ratios is not considered.

Table 3.6: Mean ratios of the indicator compounds in the six sampling points

Sampling location	Mean ratio*	
	B/T	$X_{(m+p)}$/EB
Urban park	0.29	2.93
Urban roadside	0.34	2.94
Urban indoor	0.13	2.76
Industrial indoor	0.28	3.16
Industrial location 1	0.23	2.51
Industrial location 2	0.27	1.30

* mean of individual ratio for each sample

3.4.1.1 Benzene-to- toluene (B/T)

As discussed in Chapter 1, specific range of the benzene to toluene ratio (B/T) has been used as an indicator of traffic emissions in past studies. Miller et al. (2011) mentioned a range of 0.33 to 0.67 as the typical range of B/T ratio as an indicator of traffic dominated source of emission while Buczynska et al. (2009) reported a lower range of 0.22 to 0.26 for areas with intensive street traffic. Barletta et al. (2008) on the other hand proposed a specific B/T ratio of < 0.20 as an indicator of air samples strongly affected by industrial emissions.

The B/T ratio for the ambient urban sample of park (0.29) and roadside (0.34) are within the proposed range that characterized the influence of vehicular emission. However the B/T ratio for the urban house indoor (0.13) is well below this range and indicates significant source of VOCs from indoor. As discussed earlier, it was inferred that the insecticide usage may have left residual VOCs thus influencing the indoor VOC profile. This was verified by examining the B/T ratio of the two excluded samples which were associated with insecticide spraying. The B/T ratios for these two samples were found to be 0.10 which is close to the four other samples confirming the influence of insecticide as the major indoor source. This observation also indicates that residual VOCs from insecticide application can persist long after the application.

The B/T ratios in the industrial environment, (0.23 and 0.27 for Industrial location 1 and industrial location 2 respectively), are slightly above the B/T cutoff of <0.2 ,proposed by Barletta et al. (2008) to be the characteristic ratio of ambient air highly influenced by industrial emissions. For industrial location 1, although the emission from inside painting plant has a very low B/T ratio of 0.05, the higher ambient B/T of 0.23 is an indication of influence of multiple sources. This may be because industrial emissions are not limited to industrial VOC solvent usage in the manufacturing process but also emissions from stationary diesel fired power plants for industries with intensive electricity and heating requirements. For instance a galvanizing plant is present near sampling location 1 and the combustion process for other industrial activities may have influence the ambient air in terms of B/T ratio. In addition benzene may be emitted in some manufacturing process within industrial area.

Several studies for industrial and urban roadside environment from different countries in Table 3.4 showed that B/T ratio can range from 0.09 to 0.67 and 0.06 to 0.74 for urban roadside and industrial environment. Again this shows the difficulty of generalizing B/T ratio in characterizing effect of traffic or industrial emission influence in terms of a specific range of values since the ratio is dependent on wide range of factors like the fuel and vehicle type and industries present and thus a particular area, depending on the sources, will have its own characteristic B/T. Source identification can be facilitated if the characteristic ratio of the source is known.

Comparison of ratio however can also be useful in characterizing the age of an air mass or distance from a known source of emission on the basis of difference of the degradation rate with •OH radical. Since toluene degrades five times faster than benzene(Atkinson, 1989), B/T ratio of an aged air mass tend to increase compared to the ratio of a source and thus can be a gauge of the extent of degradation and the nearness of pollution source (Korte and Klein, 1982;

Gelencsér et al., 1997; Miller et al., 2011). B/T ratio may also be used as a tracer to predict long-range transport (Srivastava, 2005).

3.4.1.2 (m+p)-Xylene-to- ethylbenzene ((m+p)-X/EB)

It was proposed that the ratio of (m+p)-xylene and ethylbenzene can also be used in assessing the photochemical age of an air mass from anthropogenic emission sources based on the observation that (i) these VOCS also occur in significant concentrations and constant relative proportion in the major anthropogenic sources of emissions and (ii) there is also difference of the degradation rate with •OH radical. It was further reported that it tends to be constant in a particular location and ranges from 3.3 to 4.7 in various cities of developed countries and value less than 2 indicates an aged air mass from a distant emission source. The lower value is expected for an aged air mass since the degradation rate constant for ethyl-benzene is lower than that for xylenes (Nelson and Quigley, 1983; Atkinson, 1986).

Referring to Table 3.6 we can see that the mean ratio of (m+p)-X/EB for the ambient urban sampling sites are very similar (2.93 and 2.94 for the park and roadside respectively) while the ratios from the industrial ambient locations were dispersed and at notably lower values (2.51 and 1.30 for industrial location 1 and 2 respectively). The relatively low (m+p)-X/EB ratio in the ambient industrial area samples compared to the urban environment may indicate that the sources of VOCs in the industrial area have different characteristic composition than vehicle exhaust and thus like the B/T ratio, generalization using a specific range is difficult. The lower range of (m+p)-X/EB observed in the industrial ambient is comparable to the other published (m+p)-X/EB ratios on industrial ambient air from various countries. For instance, Tiwari et al. (2010) observed that (m+p)-X/EB ratio was steady at all three industrial locations measured in industrial location in Japan with a range of 1.24–1.44.

The higher (m+p)-X/EB in the industrial indoor sample compared to the nearby ambient sample in the first industrial area may indicate other indoor sources of xylenes. On the other hand the lower (m+p)-X/EB in the urban indoor compared to the urban ambient, may be indicative of relatively aged air.

3.4.2 Correlation analysis

Correlation analysis of different VOCs was also found to be useful in identification of prevailing emission sources (Brocco et al., 1997; Wang et al., 2002). Pearson’s correlation of the concentrations of seven aromatic compounds for the six sampling sites was then utilized to evaluate and assess the source of VOCs. The results of the correlation analysis (2 tailed) are summarized in table 3.7.

Table 3.7 Summary of Pearson Correlation Coefficient (r) at the different sampling sites (B: Benzene, T:Toulene, EB; Ethylbenzene, X: (m+p+o)-Xylene, S: Styrene, PB : Propylbenzene, TMB: 1,2,4-Trimethylbenzene)

Aromatic Compounds	B	T	E	X	S	PB	TMB
Urban Park							
Benzene	1.00						
Toluene	0.79	1.00					
Ethylbenzene	0.74	0.96**	1.00				
Xylenes	0.83*	0.93**	0.98**	1.00			
Styrene	0.95**	0.86*	0.86*	0.92**	1.00		
Propylbenzene	0.83*	0.78	0.83*	0.91*	0.85*	1.00	
1,2,4-TMB	0.80	0.75	0.78	0.86*	0.79	0.99**	1.00
Urban Roadside							
Benzene	1.00						
Toluene	0.99**	1.00					
Ethylbenzene	0.90*	0.88*	1.00				
Xylene	0.91*	0.91*	0.97**	1.00			
Styrene	0.43	0.44	0.71	0.74	1.00		
Propylbenzene	0.99**	0.99**	0.93**	0.96**	0.53	1.00	
1,2,4-TMB	0.95**	0.97**	0.91*	0.97**	0.59	0.98**	1.00
Urban Indoor							
Benzene	1						
Toluene	0.93	1					
Ethylbenzene	0.94	1.00**	1				
Xylene	0.97*	1.00**	0.99**	1			
Styrene	1.00**	0.93	0.93	0.96*	1		
Propylbenzene	0.97*	0.99**	0.99*	1.00**	0.97*	1	
1,2,4-TMB	0.97*	0.97*	0.95	0.98*	0.98*	0.99*	1
Industrial area Indoor							
Benzene	1.00						
Toluene	-0.61	1.00					
Ethylbenzene	0.86*	-0.38	1.00				
Xylene	0.85*	-0.38	1.00**	1.00			
Styrene	0.13	-0.33	0.32	-0.34	1.00		
Propylbenzene	0.80	-0.40	0.99**	0.99**	-0.35	1.00	
1,2,4-TMB	0.79	-0.4	0.98**	0.99**	-0.36	1.00**	1.00
Industrial Location 1							
Benzene	1						
Toluene	0.78	1					
Ethylbenzene	0.71	0.84*	1				
Xylene	0.66	0.77	0.99**	1			
Styrene	0.80	0.36	0.30	0.31	1		
Propylbenzene	0.49	0.33	0.72	0.81	0.49	1	
1,2,4-TMB	0.61	0.59	0.92**	0.96**	0.38	0.93**	1
Industrial Location 2							
Benzene	1.00						
Toluene	0.86*	1.00					
Ethylbenzene	0.35	0.34	1.00				
Xylene	0.40	0.37	1.00**	1.00			
Styrene	0.15	-0.08	-0.52	-0.51	1.00		
Propylbenzene	-0.62	-0.33	-0.43	-0.45	-0.06	1.00	
1,2,4-TMB	-0.64	-0.34	-0.45	-0.48	-0.21	1.00**	1.00

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

From the table we can see that, generally, very good correlation exists for aromatic species in the urban area. Except for styrene which curiously, has poor correlation with other species in the roadside, all species in the urban environment (i.e. park, roadside and indoor) have good correlation among each other which indicates that their primary source of origin is similar. This corroborates the initial observations using diagnostic ratios that traffic is the main source of

VOC exposure in the three urban environments monitored. (Hoque et al., 2008; Tiwari et al., 2010). The poor correlation of styrene in the roadside might probably indicate another source of styrene in the particular sampling site.

While there was a good correlation among the species in the urban areas, industrial areas were characterized with very poor correlation which indicates multiple origins of VOC emissions. Comparing the correlation of species in the indoor environment with the nearby ambient sampling location in industrial area 1 (Calamba, Laguna), it can be seen that there are also differences in terms of correlation of some species. For instance toluene is slightly correlated with some of the aromatic species in the ambient sampling point but it is totally not correlated with any aromatic species in the indoor environment. This suggests that indoor is affected by more sources like the indoor emission, tobacco smoking, emission from a nearby galvanizing plant and pharmaceutical company. Very poor correlation was also observed for Industrial area 2 (Binan, Laguna), where almost all species are not correlated except for some good correlation observed between ethylbenzene and xylene , benzene and toluene, and propylbenzene and 1,2,4-trimethylbenzene. This is also reveals the variety of sources that affects the ambient air in the second industrial location.

Remarkably, there were also some species that exhibits good correlation for both the industrial and urban areas. Referring again to table 3.7, xylene and ethylbenzene showed a very strong and significant correlation ($p<0.01$) in all sites for both the urban and industrial areas. This corroborates the observed consistency of (m+p)-X/EB diagnostic ratios discussed earlier. Combining the analysis from the diagnostic ratios, this implied that the main source for the urban ambient areas is the traffic fleet with characteristic ratio of 2.94 which is possibly a function of the predominant vehicle fuel mixture in Manila. The lower (m+p)-X/EB ratio in the urban indoor house then can be inferred to be sign of photochemical aging of the diffused air mass from the traffic source or from the insecticide spray with characteristic (m+p)-X/EB ratio of 3.55. From the discussion of diagnostic ratios however, it was mentioned that the major source for the urban indoor VOCs was probably the residuals of insecticide spray. For the industrial environment, the observed average (m+p)-X/EB ratio of 2.5 is in agreement with the (m+p)-X/EB ratio of the air inside the painting facility (data not included in the table) which implies that the lower ratio in the industrial environment cannot be taken as a sign of photochemical aging but rather a unique ratio of TVOCs in that particular industrial area. This may also be the case for the second industrial location which has a low value of (m+p)-X/EB (1.3) compared to the typical ratio from traffic fleet. The consistent good correlation of (m+p)-X/EB ratio for both urban and industrial areas was also reported (Tiwari et al., 2010). In addition to xylene and ethylbenzene correlation, it is interesting to note that xylene/propylbenzene and xylene/1-2-4 trimethyl benzene show significantly strong relationship for both industrial and urban areas except for industrial location 2 which indicates multiple sources for these VOCs. Propylbenzene for example is used for textile dyeing and printing (HSDB, 2011) and thus the printing press and some textile industries located in the nearby industrial park in industrial location 2 may have contributed to its presence in the ambient air. Nevertheless, the consistent strong correlation of this species can also be considered in analysis of diagnostic ratios for ambient air.

The observation in this study regarding good species correlation in the traffic dominated urban region and poor correlation in the industrial environment is also reported in other studies done by Dollard et al. (2007) , (2010) and Chan et al. (2002), all of whom inferred that additional or multiple sources of individual VOCs are utilized in various manufacturing activities.

This study shows that source identification using specific diagnostic ratios like the usually used B/T ratio may be a bit difficult because of the observed site-specific BTEX patterns which imply different unique sources in different sites. Combining the data with correlation analysis however helps in interpretation and assessment of possible nature of the source. Nevertheless, diagnostic ratios and correlation analysis are only useful as long as no more than two plausible sources of specific VOCs are considered (Zalel et al., 2008) since precise source identification may be precluded by multiple sources as seen by poor correlation in the industrial environment. Other source apportionment techniques like Chemical Mass Balance(CMB), Positive Matrix Factorization (PMF) and variants of Principle Component Analysis (PCA) can be considered since methods commonly used for allocation of VOCs in cases of multiple sources (Hopke, 1991) as cited by (Zalel et al., 2008).

3.5 Ozone formation potential

As mentioned in chapter 1, ozone, is an important air pollutant, which plays an important role in tropospheric chemistry. It is produced in the troposphere from the reactions between ozone precursors, nitrogen oxides (NOx), and nonmethane volatile organic compounds (NMVOCs) in the presence of sunlight (Aneja et al., 2000). It is thus imperative to measure and monitor the levels of ozone as it is an important health risk. However, in many developing countries, ozone monitoring may not be always available and thus assessment of ozone concentration using appropriate estimation models may prove to be beneficial.

As discussed in chapter 1, Maximum Incremental Reactivity (MIR) is a widely used method for estimating tropospheric ozone formation as function of different VOCs in the ambient air (Hung-Lung et al., 2007). MIR values of different VOCs are based on their specific reactivity and thus more reactive species have higher MIR Values. Ozone formation potential (OFP) gives an approximation of the contribution of each VOC to O_3 formation and is calculated from the summation of the product of specific VOC concentration and its corresponding MIR (Carter, 1994).

Table 3.8 shows the ozone formation potential for each VOC species calculated from the latest maximum incremental reactivity data (MIR_{2010}). (Carter, 2010)

Table 3.8 Estimated OFP of the six sampling sites [a: MIR 2010 maximum incremental reactivity (g O^3/g VOC) (Carter 2010); [b] Ozone formation potential ($\mu g/m^3$)= VOC concentration * MIR]

	Average Concentration (ug/m^3)					**Ozone Formation Potential (MIR 2010)[b]**			
Compound Name	Urban Park	Urban Road side	Industrial Loc 1	Industrial Loc 2	**MIR (2010)[a]**	Urban Park	Urban Road side	Industrial Loc 1	Industrial Loc 2
(Cyclo-)alkanes									
n-Hexane	0.1	2.7	3.8	3.6	1.24	0.08	3.36	4.71	4.43
n-Heptaan	0.4	3.2	1.6	0.8	1.07	0.43	3.38	1.76	0.80
n-Octane	0.3	1.8	1.2	0.6	0.90	0.30	1.58	1.05	0.51
n-Nonane	0.9	3.0	1.2	1.6	0.78	0.68	2.35	0.97	1.22
n-Decane	1.3	3.2	1.3	3.1	0.68	0.89	2.16	0.90	2.12
n-Undecane	1.2	4.6	1.4	5.8	0.61	0.76	2.82	0.86	3.54
Dodecane	1.3	5.1	1.0	4.9	0.55	0.73	2.79	0.56	2.69
2-methylpentane	0.0	2.3	1.9	1.3	1.50	0.00	3.45	2.79	1.97
Methylcyclopentane	0.0	0.8	0.7	0.4	2.19	0.00	1.76	1.43	0.78
Cyclohexane	0.1	0.2	0.4	0.3	1.25	0.18	0.30	0.55	0.32
Aromatic hydrocarbons									
Benzene	0.9	7.0	2.8	1.4	0.72	0.61	5.05	2.04	1.03
Toluene	3.2	20.5	12.6	5.7	4.00	12.69	82.01	50.41	22.82
Ethylbenzene	0.6	5.5	26.8	8.2	3.04	1.92	16.65	81.49	25.02
m+p Xylene	1.9	16.1	61.0	8.9	7.80	14.60	125.75	475.76	69.71
o-Xylene	1.0	8.3	27.7	3.9	7.64	7.48	63.72	211.33	29.52
Styrene	0.3	2.0	0.5	0.3	1.73	0.47	3.47	0.82	0.52
Propylbenzene	0.3	2.9	0.8	2.1	2.03	0.59	5.92	1.66	4.28
1,2,4 Trimethylbenzene	2.0	17.7	9.8	12.7	8.87	17.67	157.43	86.50	112.48
Benzonitrile	0.8	2.4	1.1	1.7					
Phenol	1.6	2.6	0.9	1.4	2.76	4.43	7.27	2.43	3.87
Aldehydes									
n-Butyraldehyde	0.3	0.3	0.7	0.1	5.97	1.72	1.57	3.98	0.65
Hexanal	0.3	0.0	0.1	0.1	4.35	1.12	0.00	0.24	0.59
Heptanal	0.5	0.0	0.0	0.0	3.69	1.70	0.00	0.00	0.00
Benzaldehyde	4.2	8.2	2.2	2.5	-0.67	-2.83	-5.49	-1.49	-1.69
Alcohols									
1-Butanol	0.0	0.0	52.8	0.0		0.00	0.00	0.00	0.00
2-Ethyl-1-Hexanol	1.8	0.0	0.3	2.1	2.00	3.68	0.00	0.60	4.17
Ketones									
2-Butanone	0.6	0.7	12.1	2.6	1.48	0.92	1.06	17.96	3.80
2-Hexanone	0.0	0.1	0.0	0.0	3.14	0.08	0.28	0.01	0.04
2-Heptanone	0.1	0.4	0.1	0.1	2.36	0.27	0.93	0.26	0.25
Acetophenone	2.5	6.0	4.0	3.3		0.00	0.00	0.00	0.00
Other oxygenated compounds									
Ethylacetate	0.0	0.0	16.7	0.6	0.63	0.00	0.00	10.53	0.37
2-Methyl-Furan	0.1	0.0	0.0	0.0	8.30	0.46	0.10	0.00	0.00
Halogenated compounds									
Carbon tetrachloride	0.2	0.1	0.2	0.2	0.00	0.00	0.00	0.00	0.00
Trichloroethylene	0.0	0.0	0.0	0.0	0.64	0.00	0.00	0.00	0.00
Tetrachloroethylene	0.2	0.0	0.0	1.0	0.03	0.01	0.00	0.00	0.03
Terpene									
α-Pinene	0.0	0.0	0.0	0.0	4.51	0.00	0.06	0.11	0.13
Limonene ((R)-(+)-Limonene)	0.2	0.8	0.0	0.3	4.55	0.91	3.57	0.11	1.25
TOTAL						**73**	**493**	**960**	**297**

Highest OFP was calculated in industrial location 1 in Calamba, Laguna followed by urban roadside in Pasay City, Manila. While OFP is a function of both MIR and VOC concentration, it can be seen that the trend follows closely with that of the VOC concentration primarily because all locations has high percentage of aromatics which contributes the most to total OFP as can be in Figure 3.6.

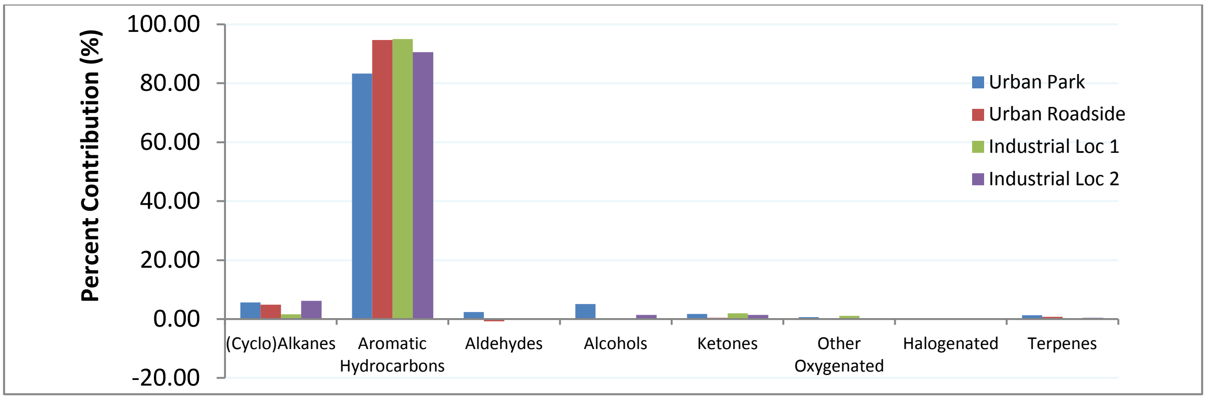

Figure 3.6 Percent contribution of different VOC groups to ozone formation in the four ambient sampling sites in the Philippines.

The relatively high contribution of aromatic compounds to the total OFP was also noted by Do et al. (2011) in the study done in Belgium, Ethiophia and Vietnam and by Hung-Lung et al. (2007) in a study done in Taiwan.

Calculated OFP values for the six sampling sites are shown in Figure 3.7. It can be seen that all sampling sites, with the exception of the park area exceeds the 8 hour threshold value of 100 µg/m^3 set by World Health Organization (WHO, 2005). Furthermore according to WHO, concentration equivalent to and above 240 µg/m^3 already has significant health effects and substantial proportion of vulnerable populations are also affected. The high level at industrial sites as well as in the roadside environment poses great risks for people in these areas.

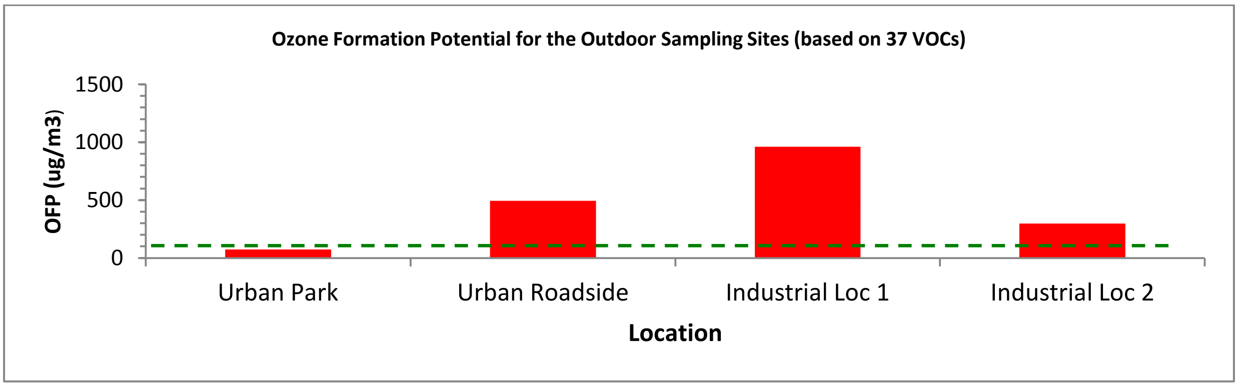

Figure 3.7: Comparison of ozone formation potential of the four ambient sampling site; Green dashed line denotes WHO recommended level for ambient ozone <100 µg/m^3

The relative contribution of six aromatic compounds to the total OFP for each site is shown in Figure 3.8. It can be noticed that 1,2,4-trimethylbenzene is a significant contributor to the total OFP for the urban park, roadside and industrial location 2, owing to its high maximum incremental reactivity. On the other hand xylene contributes the most to the total OFP in industrial location 1 due to its very high concentration in that specific area.

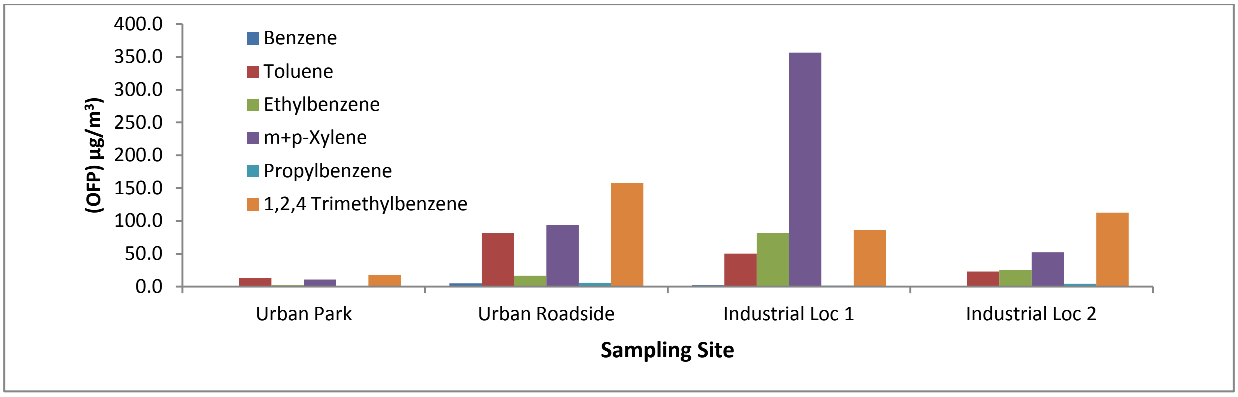

Figure 3.8 Relative contribution of the 6 aromatic compounds on of ozone formation potential of the four ambient sampling site

Ozone formation potential values of the ambient air in samples from the Philippines are also compared to other OFPs from different cities around the world. It can be seen that the calculated OFP for the sampling sites in the Philippines are comparable to other cities. The roadside data from the Philippines is higher than the estimated level in Beijing China and Jimma, Ethiopia but lower than the calculated OFP from Hanoi and Addis Ababa, Ethiopia. The figure also demonstrates that industrial emissions can also be a significant source of tropospheric ozone which may adversely affect the health of residents within the vicinity of industrial areas.

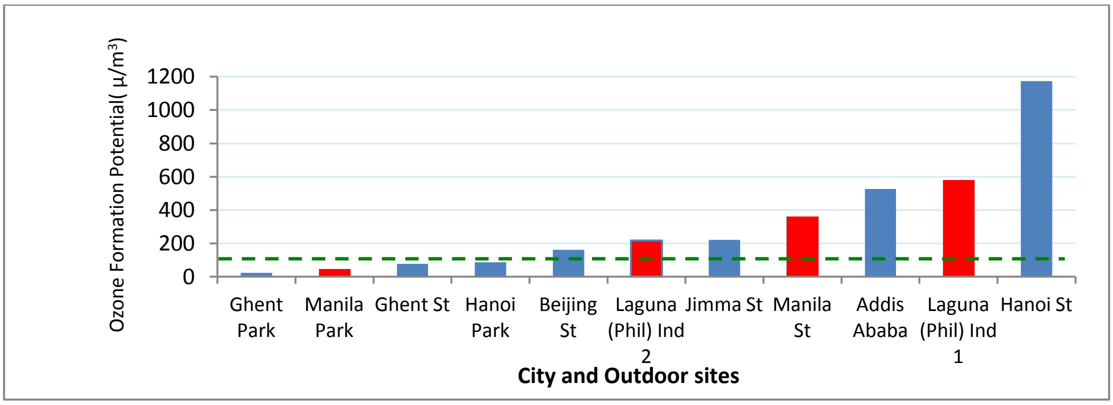

Figure 3.9 Comparison of OFP of the sampling sites in the Philippines with other cities (based on six aromatic VOCs) ; Green dashed line denotes WHO recommended level for ambient ozone <100 µg/m^3

In addition to VOCs other factors like meteorological parameters that influence local ozone concentration can also be considered in risk assessments in a particular area. Hung-Lung et al. (2007) for example, discussed the lowering effect of humidity and enhancement of ozone formation with increased wind speed and temperature. Nevertheless, OFP potential calculated is a good estimate of the total ozone risks and the information can be useful in local zoning and planning and pollution reduction strategies.

GENERAL CONCLUSIONS

Atmospheric concentration levels of 37 VOCs (i.e. alkanes, aromatic hydrocarbons, halogenated compounds, oxygen containing hydrocarbons and terpenes) were measured at indoor and outdoor sites in urban and industrial areas in the Philippines. Active sampling was done by means of sorbent tubes filled with Tenax TA. The analysis was carried out by TD-GC-MS using internal standard calibration. In spite of the limited data set, the following conclusions can be drawn from the work.

This study provides new information regarding the VOC concentration levels in urban and industrial areas in the Philippines. Aromatic hydrocarbon was observed to be the most abundant group in all sampling sites ranging from 43 to 67% of the TVOC. However, evaluation of the detected VOCs shows that presence of VOCs varied from one site to another depending on the main source. Most VOCs detected in the outdoor urban sampling sites were characteristics of VOCs from vehicle emissions. On the other hand, some VOCs like ethyl acetate, 1-butanol and tetrachloroethylene were found mostly in the industrial areas suggesting local sources and usage in the manufacturing activities. Terpenes (i.e.limonene and α-pinene) and 2-ethyl-1-hexanol were found to be highest in the indoor environments which were linked to common indoor sources. Insecticide spraying, a common practice in tropical countries, was also seen as a significant source of indoor VOCs. CCl_4 was detected in all sites for both the urban and industrial areas but it was found to be significantly higher in industrial area ($p<0.01$). The spatial stability of CCl_4 concentration was also noted and it was suggested that it can be used as an indicator of the extent of effect of industrial emission sources.

The level of TVOCs (based on 67 target compounds), was found to be highest in one of the industrial areas (248 $\mu g/m^3$) which shows that emissions from industries can be a significant source of VOCs. This should be noted since most of the manufacturing activities are found highly concentrated in industrial zones which may be located near residential areas. The second highest concentration TVOCs among the sites was measured at a roadside site in the urban area of Manila, with a mean level of 129 $\mu g/m^3$. The highest BTEX concentration was found in the first industrial sampling site and at the roadside environment. Benzene levels are below the EU regulation limit of 5.0 $\mu g/m^3$ (EU, 2009) for all sampling sites except for the urban roadside level which has a mean benzene concentration of 7.0 $\mu g/m^3$. However, it must be noted that according to World Health Organization, there are no established safe levels for benzene exposure below which no adverse effects can be observed. With a continuously increasing vehicle fleet in the country, the level of this compound and other possible toxic VOCs like 1,3-butadiene are recommended to be monitored.

There is an apparent improvement in terms of BTEX levels in Manila when the result of the study was compared to two other previous measurements done in 1995 and 2005. However, while it appears that there is a significant reduction of VOCs in the roadside data, more sampling campaigns should be done to validate this observation. Regular monitoring of VOCs in sites with significantly high emission should also be considered by the country.

Indoor-outdoor concentration ratio for TVOCs and for some compound groups are not consistently higher than 1.0 as reported in most studies. As discussed, a number of possible factors like enhanced ventilation, the location of the outdoor ambient air site, presence of significant indoor sources can influence the I/O ratio.

Diagnostic ratios were utilized to identify the sources of emissions. The urban ambient samples were found to have B/T ratio in the range that was reported to be linked to traffic related emissions. Samples from industrial area however (BT ratio 0.23 to 0.28), did not conform to the <0.20 B/T ratio that was proposed in some literature to be indicative of industrial sources of emission. The urban ambient (m+p)-X/EB ratio was found relatively constant with mean values 2.93 and 2.94 for park and roadside ambient samples respectively indicating a common source. Diagnostic ratios were also utilized for the two indoor environments and it was inferred that indoor sources may be the major influence for the indoor air VOCs.

This study shows that diagnostic ratios can be used in evaluating source of VOC emissions. However source identification using specific values of diagnostic ratios from the literature may prove to be difficult because of the observed site-specific BTEX patterns which imply different unique sources in different sites. Presence of multiple and nearby point sources also makes identification via diagnostic ratios problematic. When using diagnostic ratios, caution is needed to ensure that they are not being biased by nearby point source emissions. Evaluation of sample sources using the diagnostic ratios together with correlation analysis helps in drawing better conclusions regarding the nature of the source.

Correlation analysis of aromatic compounds shows that the urban ambient VOCs were highly correlated. This is indicative of a common source which is most probably the traffic emissions. On the other hand, industrial areas are characterized by very poor correlation which implies multiple and varied sources of emissions possibly because of the wide range of industries present in the sampling locations.

Highest OFP was calculated at Industrial location 1 (960 $\mu g/m^3$) followed by the level measured at the roadside (493 $\mu g/m^3$). Industrial location 2 also showed significant level of OFP at 297 $\mu g/m^3$. This study shows that industrial activities can be a significant source of photochemical ground level ozone. It is thus imperative that, like traffic emission, careful attention and consideration should also be given to industrial emission sources.

To the best of our knowledge, no specific regulations are provided in the Philippines for ambient levels of emissions of VOCs. However based on this study, traffic and industries emit significant amount of VOCs that could cause immense health risks to population residing near the emission sources. It is thus recommended that VOCs be included in the list of criteria pollutants that are monitored and regulated. This study may provide helpful information in assessing current environmental policies for air quality and can serve as reference when conceptualizing development programs, planning and implementing regulations and pollution reduction strategies.

RECOMMENDATIONS FOR FURTHER RESEARCH

Given the reported spatial and temporal variability of VOC concentrations, sampling and monitoring in more locations and over a longer period of time can be considered to further substantiate the initial findings of this work and to have appropriate data set for human health risks assessment on the exposure to some toxic VOCs. Effect of meteorological factors and seasonal variation (rainy and summer seasons) should also be done as these could provide useful and practical information in VOC assessment in the Philippines.

Further study on diagnostic ratios and correlation analysis in source identification of VOCs can be done. In addition use of diagnostic ratios which relates source characteristic ratio, photochemical aging in combination with meteorological factors like wind direction and speed can be explored in assessing the extent of spatial influence of known sources of emission (like traffic and industrial sources). This could be a good tool for predicting and estimating the impact of emissions in developing countries where monitoring stations are hardly available.

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APPENDICES

APPENDIX A

The 67 standard VOCs used for calibration of the TD-GC-MS are shown together with their characterizing ions, the loaded mass, the retention time and RSRF-ethylbenzene-d10 (dimensionless)

Compounds	Ion (SIM)	mass (ng)	RT (min)	RSRF Ethylbenzene-d10
(Cyclo)Alkanes				
n-hexane	41, 71, 86	32.95	5.88	0.13
n-heptane	70, 71, 100	34.20	12.64	0.34
n-octane	71, 85, 114	35.15	22.33	0.31
n-nonane	57, 85, 128	35.90	28.28	0.37
n-decane	75, 85, 142	36.50	31.71	0.11
n-dodecane	57, 85, 170	37.65	36.61	0.45
n-undecane	57, 85, 156	37.00	34.36	0.39
2-methylpentane		32.65	4.74	0.27
methylcyclopentane	55, 70	37.45	7.23	0.06
cyclohexane	84, 15	38.95	9.32	0.16
Aromatic hydrocarbons				
benzene	52,63,77,78	43.70	8.73	0.77
toluene	65, 91, 92	43.30	17.89	1.17
ethylbenzene	91, 106	43.35	25.91	1.01
p-xylene	91, 105, 106	43.30	26.44	1.17
m-xylene	91, 105, 106	43.40	26.39	1.21
o-xylene	91, 105, 106	43.90	27.52	1.21
styrene	51, 78, 104	45.45	27.32	1.03
n-propylbenzene	91, 92, 120	43.10	30.02	1.25
1,2,4-trimethylbenzene	105, 120	44.00	31.37	1.29
1-bromo-4-fluorobenzene	75, 95, 174, 176	79.65	28.59	0.85
Phenol	65, 66, 94	53.50	30.68	0.51
Oxygenated compounds				
Aldehydes				
hexanal	44, 56, 72, 82	40.75	20.26	0.22
heptanal	44, 70, 96	41.00	27.48	0.20
benzaldehyde	77, 105, 106	52.50	29.70	0.76
n-Butyraldehyde (butanal)	41, 44, 45, 72	40.85	4.90	0.17
Isobutyraldehyde	41, 43, 72	39.50	4.01	0.26
3-methylbutyraldehyde	41, 42, 43, 58, 71, 86	39.80	7.75	0.20
Alcohols				
1-butanol	28,31,33,56	40.50	8.90	0.13
1-pentanol	29, 31, 55, 75, 70	40.55	20.65	0.12
2-ethyl-1-hexanol	31, 56, 70, 83, 112	41.65	32.23	0.38
1-Octanol	68, 69, 70, 83, 84, 112	41.35	33.31	0.34
3-methyl-1-butanol	29, 31, 42, 70	40.00	15.00	0.18
Ketone				
2-butanone	72, 11	40.30	5.04	0.29
2-hexanone	43, 71, 85, 100	40.60	19.35	0.32
2-heptanone	43, 71, 85, 100	41.00	26.99	0.24
2-octanone	58, 113, 128	40.95	30.88	0.24
5-nonanone	85, 100, 142	41.00	33.31	0.32
5-Methyl-3-heptanone	85, 100, 142	41.15	29.30	0.86
acetophenone	77, 105, 120	51.50	33.05	0.79
Esters				
ethyl acetate	61, 70, 88	45.10	5.96	0.11
n-propylacetate	61, 73	44.00	12.74	0.13
methylbenzoate	77, 105, 136	54.00	33.93	1.02
Other oxygenated compounds				
Furan	39, 68, 69	46.80	3.04	0.27
2-methylfuran	53, 81, 82	45.50	5.71	0.45
tetrahydrofuran	41, 71, 72	44.45	6.69	0.28
Halogenated compounds				
Chloroform	47, 83, 85	74.60	6.11	0.38
carbon tetrachloride	117,119,121	79.70	9.11	0.22

Compounds	Ion (SIM)	mass (ng)	RT (min)	RSRF Ethylbenzene-d10
dichloromethane	49, 84, 86	66.25	3.52	0.21
chlorobenzene	77, 112, 114	55.38	24.77	0.67
1,3-Dichlorobenzene		64.40	31.64	1.01
1,2,4-trichlorobenzene	145, 180, 182, 184	72.70	10.91	0.93
1,3,5-Triisopropylbenzene		42.70	38.82	1.41
1,1,2-trichlorethane	61, 97, 99, 132	71.75	3.70	0.32
1,2-dichloroethane	62, 64, 98, 100	62.65	7.32	0.16
1,2 Dichloorpropaan	62, 64, 98, 100	57.80	36.25	0.20
1,1,2-trichlorotrifluoroethane	101, 103, 151, 153	78.50	17.06	0.06
1,1,1,2 Tetrachloorethaan	101,103,151,153	79.90	24.80	0.55
trichloroethylene	95, 97, 130, 132	73.00	11.66	0.64
tetrachloroethylene	95,97,130,132	81.15	22.37	0.55
chlorobenzene	131, 164, 166, 168	55.38	24.77	0.67
1,2,4-trichlorobenzene	77, 112, 114	72.70	10.91	0.93
Sulfur Containing Compounds				
Dimethyldisulfide	45, 79, 94	53.13	15.20	0.00
Carbondisulfide	44, 76	63.00	3.79	0.31
Nirogen Containing Compound				
Benzonitrile	76, 103, 104	50.50	30.32	0.98
Silicon Containing Compound				
Trimethoxymethylsilane	91, 105, 121	48.00	13.97	0.20
Hexamethyldisiloxane	73, 147, 148, 149	38.20	11.63	1.32
Terpene				
α-pinene	92, 93, 121, 136	42.90	29.66	0.77
limonene	68, 93, 107, 121, 136	43.50	34.11	0.33
Linalool	71, 93, 121, 136	43.50	34.11	0.33
Internal standard				
tolueen-d8 (Tol-d8)	98, 100	47.00	17.53	1.13
ethylbenzene-d10 (Eb-d10)	98, 116			1.00

APPENDIX B - Ambient VOC concentration in the urban environment

Appendix B-1: VOC concentrations (µg/m^3) measured at Urban park- (Manila Philippines , 2011)
(D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location		**Urban Park**					
Sampling Date		**8/25/2011**	**8/25/2011**	**8/26/2011**	**8/26/2011**	**9/3/2011**	**9/3/2011**
Sampling Time		**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature		28.6	29.4	29.3	28.4	30.4	30.8
Ave Relative Humidity %		81.3	80.1	80.8	78.8	79.6	74.8
(Cyclo-)alkanes							
n-Hexane		ND	ND	ND	ND	ND	0.4
n-Heptane		0.9	0.4	0.4	0.3	0.1	0.3
n-Octane		0.6	0.4	0.3	0.3	0.1	0.3
n-Nonane		1.7	0.8	0.8	0.8	0.4	0.7
n-Decane		2.9	1.7	0.7	1.0	0.1	1.4
n-Undecane		2.1	2.2	0.8	0.7	0.2	1.5
Dodecane		2.5	2.5	0.7	0.9	D	1.4
2-Methylpentane		ND	ND	ND	ND	ND	ND
Methylcyclopentane		ND	ND	ND	ND	D	ND
Cyclohexane		0.2	0.1	0.0	ND	0.0	0.6
	Total	**10.7**	**8.0**	**3.7**	**4.2**	**1.0**	**6.6**
Aromatic compounds							
Benzene		1.6	1.0	0.7	0.5	0.5	0.8
Toluene		5.7	3.3	2.9	3.1	2.5	1.5
Ethylbenzene		1.1	0.6	0.7	0.6	0.5	0.3
m+p-Xylene		3.4	1.9	2.1	1.6	1.1	1.1
o-Xylene		1.7	0.9	1.1	0.9	0.6	0.6
Styrene		0.8	0.2	0.2	0.2	0.0	0.2
Propylbenzene		0.5	0.4	0.3	0.2	0.1	0.2
1,2,4 Trimethylbenzene		3.0	2.6	2.3	1.5	0.9	1.6
Benzonitrile		0.8	0.9	0.9	0.7	1.0	0.7
Phenol		1.5	1.6	2.0	1.9	0.6	2.0
	Total	**20.1**	**13.4**	**13.3**	**11.2**	**8.0**	**9.1**
Aldehydes							
n-Butyraldehyde		1.1	ND	D	D	D	0.6
Hexaldehyde		1.0	D	0.1	ND	ND	0.5
Heptaldehyde		1.3	0.1	ND	0.28	ND	1.1
Benzaldehyde		5.8	4.2	4.9	3.3	1.6	5.4
	Total	**9.2**	**4.3**	**5.0**	**3.6**	**1.6**	**7.6**
Alcohols							
1-butanol		ND	ND	ND	ND	ND	ND
2-ethyl-1-hexanol		1.0	1.7	2.9	1.2	3.3	0.9
	Total	**1.0**	**1.7**	**2.9**	**1.2**	**3.3**	**0.9**
Ketones							
2-butanone		1.4	0.4	0.6	0.2	0.2	0.9
2-Hexanone		ND	0.0	0.0	0.1	ND	D
2-heptanone		D	D	0.2	D	ND	0.5
Acetophenone		3.2	2.8	2.6	2.1	1.2	3.1
	Total	**4.6**	**3.2**	**3.5**	**2.4**	**1.4**	**4.6**
Other oxygenated compounds							
Ethylacetate		ND	ND	ND	ND	ND	ND
2-Methyl-Furan		ND	ND	0.3	ND	ND	ND
	Total	**0.00**	**0.00**	**0.3**	**0.00**	**0.00**	**0.00**
Halogenated compounds							
CCl_4		0.2	0.2	0.1	0.2	0.1	0.2
Trichlororethylene		ND	ND	D	ND	ND	ND
Tetrachlororethylene		ND	ND	1.1	ND	ND	ND
	Total	**0.2**	**0.2**	**1.3**	**0.2**	**0.1**	**0.2**
Terpene							
α-pinene		D	D	D	D	D	D
Limonene		0.4	D	0.3	0.2	0.1	0.3
	Total	**0.4**	**0.0**	**0.3**	**0.2**	**0.1**	**0.3**
TVOCs		**46**	**31**	**30**	**23**	**16**	**29**

Appendix B-2 VOC concentration (µg/m^3) measured at roadside (Pasay City- Manila Philippines , 2011)(D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location	**Urban Roadside**					
Sampling Date	**8/25/2011**	**8/25/2011**	**8/26/2011**	**9/1/2011**	**9/3/2011**	**9/3/2011**
Sampling Time	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature	30.1	30.5	31.05	26.6	31.85	29.7
Ave Relative Humidity %	70.1	71.6	73.6	85.6	60	74
(Cyclo-)alkanes						
n-Hexane	1.9	1.7	2.0	6.5	1.9	2.3
n-Heptane	2.5	2.5	2.8	5.9	2.5	2.8
n-Octane	1.6	1.6	1.4	3.3	1.3	1.4
n-Nonane	2.7	2.9	3.2	4.8	2.5	2.0
n-Decane	3.1	4.1	2.7	4.1	2.4	2.8
n-Undecane	4.2	4.3	4.2	6.6	3.8	4.7
Dodecane	4.6	4.7	4.6	7.2	4.0	5.3
2-Methylpentane	1.4	1.2	1.9	5.7	1.5	2.1
Methylcyclopentane	0.3	0.4	D	2.8	0.4	0.8
Cyclohexane	D	0.2	0.4	0.6	D	0.3
Total	**22.2**	**23.4**	**23.1**	**47.7**	**20.3**	**24.4**
Aromatic compounds						
Benzene	5.7	5.5	6.3	13.5	5.3	5.8
Toluene	16.3	17.2	16.9	38.6	15.6	18.5
Ethylbenzene	5.4	5.6	5.4	8.0	4.3	4.2
m+p-Xylene	14.5	17.1	15.3	24.4	12.7	12.8
o-Xylene	8.2	9.4	6.1	12.8	7.1	6.4
Styrene	2.5	2.8	1.3	2.7	1.6	1.1
Propylbenzene	2.4	2.8	2.6	5.0	2.3	2.5
1,2,4 Trimethylbenzene	15.9	18.0	15.4	26.0	14.6	16.5
Benzonitrile	2.8	2.7	2.3	2.8	1.5	2.1
Phenol	2.8	3.9	2.0	2.4	2.3	2.4
Total	**76.5**	**85.0**	**73.6**	**136.0**	**67.3**	**72.2**
Aldehydes						
n-Butyraldehyde	0.3	ND	0.4	0.5	ND	0.4
Hexaldehyde	D	ND	D	D	D	ND
Heptaldehyde	ND	ND	ND	ND	ND	ND
Benzaldehyde	8.7	8.2	8.2	10.2	5.9	7.9
Total	**9.0**	**8.2**	**8.6**	**10.7**	**5.9**	**8.3**
Alcohols						
1-butanol	ND	ND	ND	ND	ND	ND
2-ethyl-1-hexanol	D	D	ND	D	D	ND
Total	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Ketones						
2-butanone	0.7	0.6	0.9	1.1	0.5	0.6
2-Hexanone	0.1	0.1	0.1	0.2	0.1	0.1
2-heptanone	0.6	D	0.4	1.0	0.3	D
Acetophenone	6.3	6.9	5.7	6.0	4.7	6.1
Total	**7.7**	**7.5**	**7.1**	**8.3**	**5.5**	**6.8**
Other oxygenated compounds						
Ethylacetate	ND	ND	ND	ND	ND	ND
2-Methyl-Furan	D	ND	D	0.07	ND	ND
Total	**0.0**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**
Halogenated compounds						
CCl4	0.1	0.1	0.1	0.2	0.1	0.2
Trichlororethylene	ND	ND	ND	ND	ND	ND
Tetrachlororethylene	ND	ND	ND	ND	ND	ND
Total	**0.1**	**0.1**	**0.1**	**0.2**	**0.1**	**0.2**
Terpene						
α-pinene	D	D	D	0.1	D	D
Limonene	0.9	0.9	0.6	1.1	0.3	0.7
Total	**0.9**	**0.9**	**0.6**	**1.2**	**0.3**	**0.7**
TVOCs	**116**	**125**	**113**	**204**	**100**	**113**

APPENDIX C Ambient VOC concentration in the industrial environment

Appendix C-1 : VOC concentration (μg/m^3) measured at industrial location 1 -(Calamba, Laguna Philippines , 2011) (D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location	**Industrial location 1 (Calamba, Laguna)**					
Sampling Date	**9/9/2011**	**9/10/2011**	**9/12/2011**	**9/12/2011**	**9/13/2011**	**9/13/2011**
Sampling Time	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature	33.2	29	32.3	33.6	28.4	27.8
Ave Relative Humidity %	64.5	82.1	61.2	60.5	79.3	84.8
(Cyclo-)alkanes						
n-Hexane	1.5	0.2	4.5	3.3	5.4	7.9
n-Heptane	1.8	0.9	1.7	0.9	2.0	2.7
n-Octane	1.4	0.5	0.9	0.6	1.8	1.9
n-Nonane	1.5	1.0	1.5	1.4	1.0	1.1
n-Decane	1.6	0.7	0.8	3.4	0.5	0.9
n-Undecane	2.2	0.7	0.9	3.9	0.4	0.3
Dodecane	2.3	0.7	0.6	2.2	0.3	D
2-Methylpentane	0.4	ND	2.9	1.0	2.8	4.0
Methylcyclopentane	ND	ND	0.9	0.1	1.1	1.8
Cyclohexane	0.3	0.1	0.3	0.5	0.6	0.8
Total	**13.0**	**4.7**	**14.9**	**17.3**	**15.9**	**21.5**
Aromatic compounds						
Benzene	3.1	1.4	3.4	1.6	3.2	4.3
Toluene	12.1	7.8	10.6	7.1	19.9	18.1
Ethylbenzene	47.8	1.4	2.2	7.2	46.2	56.0
m+p-Xylene	120.7	4.3	6.0	18.7	101.8	114.4
o-Xylene	57.6	2.2	3.0	8.5	44.6	50.1
Styrene	0.6	0.1	0.9	0.2	0.4	0.6
Propylbenzene	1.4	0.5	0.7	0.6	0.8	0.9
1,2,4 Trimethylbenzene	18.7	3.8	4.6	5.5	11.5	14.4
Benzonitrile	1.8	0.8	1.1	0.5	1.0	1.4
Phenol	2.2	0.8	1.0	0.8	0.3	0.3
Total	**266.05**	**23.23**	**33.44**	**50.67**	**229.71**	**260.51**
Aldehydes						
n-Butyraldehyde	1.1	ND	0.3	0.3	0.9	1.3
Hexaldehyde	ND	ND	0.2	0.0	0.1	ND
Heptaldehyde	ND	ND	ND	ND	ND	ND
Benzaldehyde	4.1	1.3	3.2	1.3	1.6	1.8
Total	**5.2**	**1.3**	**3.7**	**1.6**	**2.6**	**3.2**
Alcohols						
1-butanol	94.3	ND	ND	8.4	96.5	117.9
2-ethyl-1-hexanol	D	0.8	0.8	0.2	D	D
Total	**94.3**	**0.8**	**0.8**	**8.6**	**96.5**	**117.9**
Ketones						
2-butanone	11.1	0.4	2.1	2.1	27.5	29.6
2-Hexanone	D	ND	0.0	0.0	ND	ND
2-heptanone	0.2	0.0	0.1	D	0.1	0.1
Acetophenone	8.9	1.8	2.6	3.1	2.4	5.2
Total	**20.2**	**2.2**	**4.9**	**5.2**	**30.0**	**35.0**
Other oxygenated compounds						
Ethylacetate	38.8	ND	0.5	3.9	23.1	33.9
2-Methyl-Furan	ND	ND	ND	ND	ND	ND
Total	**38.8**	**0.0**	**0.5**	**3.9**	**23.1**	**33.9**
Halogenated compounds						
CCl4	0.2	0.2	0.2	0.2	0.2	0.2
Trichlororethylene	ND	ND	ND	D	ND	ND
Tetrachlororethylene	ND	ND	ND	ND	ND	ND
Total	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**	**0.2**
Terpene						
α-pinene	D	0.1	D	0.1	D	0.0
Limonene	D	0.1	D	D	D	D
Total	**0.0**	**0.2**	**0.0**	**0.1**	**0.0**	**0.0**
TVOCs	**438**	**33**	**59**	**88**	**398**	**472**

Appendix C-2: VOC concentration (μg/m^3) measured at industrial location (Binan, Laguna Philippines , 2011) (D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location	**Industrial location 2 -(Binan ,Laguna)**					
Sampling Date	**9/14/2011**	**9/14/2011**	**9/15/2011**	**9/15/2011**	**9/16/2011**	**9/16/2011**
Sampling Time	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature	31.4	31.1	29.8	31.4	31.2	32.7
Ave Relative Humidity %	63.8	62.1	76.6	71.9	70.4	63.8
(Cyclo-)alkanes						
n-Hexane	3.9	4.0	2.0	4.5	3.7	3.2
n-Heptane	0.5	0.9	0.7	1.0	0.8	0.5
n-Octane	0.4	0.5	0.4	0.7	0.9	0.5
n-Nonane	0.9	1.1	1.1	1.5	2.5	2.3
n-Decane	1.6	2.1	3.2	2.8	4.6	4.5
n-Undecane	2.3	3.0	3.3	16.6	3.7	6.0
Dodecane	0.7	1.0	2.0	16.5	1.9	7.3
2-Methylpentane	1.1	1.5	1.2	1.9	1.3	0.8
Methylcyclopentane	0.3	0.5	ND	0.7	0.4	0.3
Cyclohexane	0.4	0.2	0.1	0.2	0.4	0.3
Total	**12.3**	**14.6**	**14.0**	**46.5**	**20.1**	**25.6**
Aromatic compounds						
Benzene	1.2	1.6	1.8	1.6	1.4	1.0
Toluene	4.0	6.0	10.0	6.0	4.3	3.9
Ethylbenzene	3.6	3.2	14.5	5.8	19.1	3.3
m+p-Xylene	5.3	5.4	13.5	7.6	16.9	4.9
o-Xylene	2.3	2.7	5.5	3.5	6.5	2.7
Styrene	0.3	0.7	0.2	0.2	0.2	0.2
Propylbenzene	1.1	1.9	1.3	1.0	0.8	6.6
1,2,4 Trimethylbenzene	9.8	12.3	9.7	7.7	7.6	29.0
Benzonitrile	1.9	2.4	1.3	1.6	1.0	2.0
Phenol	1.6	0.7	1.1	2.0	2.4	0.6
Total	**31.2**	**36.8**	**59.0**	**37.0**	**60.1**	**54.2**
Aldehydes						
n-Butyraldehyde	0.2	ND	D	ND	0.4	D
Hexaldehyde	D	ND	0.0	0.2	0.6	D
Heptaldehyde	ND	ND	ND	ND	ND	ND
Benzaldehyde	3.0	2.7	1.6	2.3	3.6	1.9
Total	**3.3**	**2.7**	**1.6**	**2.6**	**4.5**	**1.9**
Alcohols						
1-butanol	ND	ND	ND	ND	ND	ND
2-ethyl-1-hexanol	4.5	D	2.7	0.6	3.8	0.9
Total	**4.5**	**0.00**	**2.7**	**0.6**	**3.8**	**0.9**
Ketones						
2-butanone	0.8	0.6	0.6	0.9	10.6	1.9
2-Hexanone	0.0	D	ND	0.01	0.05	ND
2-heptanone	0.1	0.1	0.1	0.1	0.2	0.1
Acetophenone	3.3	2.1	3.1	3.5	6.9	1.1
Total	**4.2**	**2.8**	**3.8**	**4.5**	**17.8**	**3.1**
Other oxygenated compounds						
Ethylacetate	1.5	1.0	ND	0.7	ND	0.2
2-Methyl-Furan	ND	ND	ND	ND	ND	ND
Total	**1.5**	**1.0**	**0.0**	**0.7**	**0.0**	**0.2**
Halogenated compounds						
CCl4	0.21	0.22	0.23	0.18	0.20	0.20
Trichlororethylene	ND	ND	ND	ND	ND	ND
Tetrachlororethylene	1.48	1.83	0.22	1.10	0.19	0.96
Total	**1.7**	**2.1**	**0.4**	**1.3**	**0.4**	**1.2**
Terpene						
α-pinene	0.1	0.1	D	D	D	0.0
Limonene	1.1	0.2	0.2	D	0.2	D
Total	**1.1**	**0.3**	**0.2**	**0.00**	**0.2**	**0.0**
TVOCs	**60**	**60**	**82**	**93**	**107**	**87**

Appendix D Indoor VOC concentration - Urban and industrial Environment

Appendix D-1 Indoor VOC concentration (µg/m3) measured at urban area- (Pasay City Manila Philippines , 2011) (D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location	**Indoor sample (Urban area) -Pasay City ,Manila**					
Sampling Date	**8/25/2011**	**8/25/2011**	**8/26/2011**	**8/26/2011**	**9/3/2011***	**9/3/2011***
Sampling Time	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature	30.1	30.2	28.2	31.4	31.1	30.3
Ave Relative Humidity %	77.8	79.9	78.9	75.6	74.3	77.3
(Cyclo-)alkanes						
n-Hexane	ND	0.1	ND	ND	ND	0.8
n-Heptane	0.6	1.9	0.6	0.4	5.2	7.1
n-Octane	0.8	1.6	0.8	0.5	18.3	23.8
n-Nonane	3.7	6.6	4.0	2.5	124.4	157.0
n-Decane	7.2	10.8	8.3	4.7	229.0	330.7
n-Undecane	7.1	10.1	9.2	4.8	169.5	245.6
Dodecane	6.1	6.6	7.6	3.6	105.8	167.9
2-Methylpentane	ND	0.2	ND	ND	ND	ND
Methylcyclopentane	ND	ND	ND	ND	ND	ND
Cyclohexane	ND	0.0	ND	ND	D	0.6
Total	**25.4**	**37.9**	**30.5**	**16.4**	**652.1**	**933.4**
Aromatic compounds						
Benzene	1.0	2.3	1.2	0.6	1.2	1.2
Toluene	9.9	15.7	6.9	5.3	11.6	12.9
Ethylbenzene	2.0	3.9	1.3	1.1	7.1	9.1
m+p-Xylene	5.3	9.6	4.0	2.9	24.9	32.8
o-Xylene	3.0	5.3	2.3	1.5	15.5	22.4
Styrene	0.4	0.9	0.5	0.2	0.2	0.3
Propylbenzene	0.9	1.5	0.7	0.5	9.0	18.5
1,2,4 Trimethylbenzene	5.3	8.1	5.1	3.2	63.3	98.8
Benzonitrile	1.0	1.5	1.1	0.7	3.0	5.1
Phenol	2.5	3.2	2.4	1.5	5.8	10.7
Total	**31.2**	**51.9**	**25.5**	**17.5**	**141.5**	**211.8**
Aldehydes						
n-Butyraldehyde	D	0.6	D	0.3	0.5	0.8
Hexaldehyde	ND	1.0	0.2	0.1	0.7	0.9
Heptaldehyde	ND	D	ND	ND	2.6	4.5
Benzaldehyde	3.4	6.9	4.4	2.5	3.7	6.8
Total	**3.4**	**8.4**	**4.6**	**2.9**	**7.5**	**12.9**
Alcohols						
1-butanol	ND	ND	ND	ND	ND	ND
2-ethyl-1-hexanol	D	D	3.2	1.4	ND	ND
Total	**0.0**	**0.0**	**3.2**	**1.4**	**0.0**	**0.0**
Ketones						
2-butanone	1.0	1.2	0.9	0.4	0.9	1.2
2-Hexanone	0.1	0.3	0.1	0.1	0.1	ND
2-heptanone	0.5	0.9	0.5	0.3	6.8	9.9
Acetophenone	3.2	4.9	3.6	2.3	35.6	69.1
Total	**4.8**	**7.4**	**5.1**	**3.1**	**43.5**	**80.2**
Other oxygenated compounds						
Ethylacetate	ND	ND	ND	ND	ND	ND
2-Methyl-Furan	ND	D	0.06	ND	ND	ND
Total	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**	**0.0**
Halogenated compounds						
CCl4	0.1	0.1	0.2	0.1	0.2	0.2
Trichlororethylene	ND	ND	ND	ND	ND	0.1
Tetrachlororethylene	ND	ND	ND	ND	ND	ND
Total	**0.1**	**0.1**	**0.2**	**0.1**	**0.2**	**0.2**
Terpene						
α-pinene	0.1	0.1	0.1	D	ND	ND
Limonene	5.6	4.5	4.2	2.3	D	ND
Total	**5.7**	**4.6**	**4.3**	**2.3**	**0.0**	**0.0**
TVOCs	**71**	**110**	**74**	**44**	**845**	**1239**

**Samples were excluded in the determination of average urban indoor air concentration due to very high concentration*

Appendix D-2 Indoor VOC concentration (µg/m^3) measured at industrial location 1 (Calamba, Laguna Philippines , 2011) (D= Detected, ND = Not Detected, TVOCs = Total Volatile Organic Compounds)

Sampling Location	**Indoor sample(Industrial area) -Calamba Laguna**					
Sampling Date	**9/10/2011**	**9/10/2011**	**9/12/2011**	**9/12/2011**	**9/13/2011**	**9/13/2011**
Sampling Time	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**
Ave Temperature	33.2	29	32.3	33.6	28.4	27.8
Ave Relative Humidity %	64.5	82.1	61.2	60.5	79.3	84.8
(Cyclo-)alkanes						
n-Hexane	5.1	4.7	5.4	2.6	2.2	4.2
n-Heptane	1.3	0.9	0.4	0.5	0.5	0.3
n-Octane	0.9	0.8	0.3	0.3	0.3	0.3
n-Nonane	0.7	0.6	0.7	0.9	0.7	0.7
n-Decane	0.2	0.1	1.2	0.9	0.4	0.5
n-Undecane	0.2	0.3	1.6	1.2	0.6	0.7
Dodecane	ND	D	0.2	0.2	D	D
2-Methylpentane	2.1	2.0	1.9	0.8	1.2	1.9
Methylcyclopentane	0.8	0.5	0.7	D	0.1	0.6
Cyclohexane	0.5	0.6	1.0	0.4	0.2	0.4
Total	**11.6**	**10.5**	**13.4**	**7.8**	**6.1**	**9.7**
Aromatic compounds						
Benzene	3.2	2.5	2.1	1.5	2.3	1.6
Toluene	7.8	6.6	8.2	17.4	7.3	8.4
Ethylbenzene	13.4	11.3	1.1	1.5	1.7	0.9
m+p-Xylene	47.7	40.6	3.3	4.8	4.8	2.8
o-Xylene	24.5	21.1	1.7	2.2	2.2	1.4
Styrene	0.5	0.5	0.6	0.5	0.8	0.5
Propylbenzene	4.1	4.3	0.4	0.4	0.4	0.3
1,2,4 Trimethylbenzene	42.3	46.3	2.4	2.9	2.2	1.8
Benzonitrile	3.0	2.9	1.5	1.2	1.8	1.6
Phenol	0.8	0.8	2.8	1.8	2.9	2.4
Total	**147.3**	**137.0**	**24.0**	**34.2**	**26.4**	**21.7**
Aldehydes						
n-Butyraldehyde	0.5	0.5	D	0.3	0.3	0.3
Hexaldehyde	0.0	ND	0.1	ND	0.1	0.0
Heptaldehyde	ND	ND	ND	ND	0.3	ND
Benzaldehyde	2.5	3.0	2.0	1.2	2.6	2.2
Total	**3.1**	**3.4**	**2.1**	**1.5**	**3.3**	**2.5**
Alcohols						
1-butanol	26.2	22.0	ND	ND	ND	ND
2-ethyl-1-hexanol	2.3	2.8	5.3	8.7	10.9	7.8
Total	**28.6**	**24.8**	**5.3**	**8.7**	**10.9**	**7.8**
Ketones						
2-butanone	6.0	4.7	2.2	0.7	2.1	1.2
2-Hexanone	ND	ND	0.0	0.0	ND	0.0
2-heptanone	D	D	D	0.1	0.2	D
Acetophenone	3.2	2.9	1.7	1.3	1.4	1.3
Total	**9.2**	**7.6**	**3.9**	**2.2**	**3.7**	**2.5**
Other oxygenated compounds						
Ethylacetate	26.8	32.2	ND	ND	ND	0.9
2-Methyl-Furan	ND	D	0.2	0.1	0.5	0.2
Total	**26.8**	**32.2**	**0.2**	**0.1**	**0.5**	**1.1**
Halogenated compounds						
CCl4	0.2	0.2	0.2	0.2	0.2	0.2
Trichlororethylene	ND	0.3	ND	1.9	ND	0.1
Tetrachlororethylene	ND	ND	ND	ND	ND	0.1
Total	**0.2**	**0.5**	**0.2**	**2.1**	**0.2**	**0.4**
Terpene						
α-pinene	D	D	0.1	0.1	0.2	0.1
Limonene	0.1	0.5	1.7	1.9	8.0	4.6
Total	**0.1**	**0.5**	**1.8**	**2.0**	**8.2**	**4.7**
TVOCs	**227**	**217**	**51**	**59**	**59**	**50**