Modeling of Ground-level Ozone Formation in Urban Air-sheds of Sri Lanka

Doctor of Philosophy Thesis

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Modeling of Ground-level Ozone Formation in Urban Air-sheds of Sri Lanka

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by

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DECLARATION

The work submitted in this dissertation is the result of my own investigation, except where otherwise stated.

It has not already been accepted for any degree, and is also not being concurrently submitted for any other degree.

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We endorse the declaration by the candidate.

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ABSTRACT

Physical phenomenon of the relation among ground-level ozone (O_3), oxides of nitrogen (NO_X) and volatile organic compounds (VOC) is governed by complex nonlinear photochemistry. To predict and control O_3 concentration, it is vital to know, how O_3 concentration changes in response to prescribed changes in source emissions of NO_X and VOCs. In this research, a theoretical model was developed and validated for ground-level O_3 formation in urban air-sheds of Sri Lanka. Hourly averaged weekly results of ambient pollutant concentration data of eleven cities in the base years 2013, 2014 and 2015 in Sri Lanka was assessed and an urban air shed model was developed. The model was calibrated using influential parameters measured. Then Colombo as the most complicated urban air-shed in Sri Lanka was analyzed in detail. Model was validated using measured 24-hour air quality monitoring data from the mobile air quality monitoring stations at major traffic locations in Colombo in the year 2018 and 2019. Operational schedules of emission sources including train scheduled data, working hours of the thermal power plants, and vehicle counts were conducted at identified critical locations in Colombo to investigate the responsible sources. Gases from the exhaust line of different types of vehicles was collected and analyzed using Gas Chromatography Mass Spectroscopy (GCMS).

Results confirm that there exist two regimes of NO_X-VOC-O_3 sensitivity as NO_x-sensitive regime and VOC-sensitive regime. The urban air-shed model is capable of estimating the ground-level steady state ozone concentration (O_{3ss}) and contributions from each regime. The univariate linear regression model using predicted and observed O_3 values confirmed that O_{3ss} concentration was significantly correlated with the predicted O_3 concentration. Analysis of urban air shed in Colombo also confirms the predicted and observed O_{3ss} concentration were significantly correlated. This research provides a detailed understanding of photochemical degradation on formation of ground-level O_3 in urban air-sheds of Sri Lanka and provides critical information for the scientific community and decision-makers to formulate air pollution mitigation policies.

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LIST OF ABBREVIATIONS

AEA	Atomic Energy Authority
AirMAC	Air Resource Management Centre
ATS	American Thoracic Society
CAI-Asia	Clean Air Initiatives in Asia
CB4	Carbon Bond Mechanism 4
CB5	Carbon Bond Mechanism 5
CEA	Central Environmental Authority
CEB	Ceylon Electricity Board
CFC-11 (CCl_3F)	Chlorofluorocarbons
CFC-12 (CCl_2F_2)	Chlorofluorocarbons
CNG	Compact Natural Gas
CH_3CN	Methyl Cyanide
CH_4	Methane
CMC	Colombo Municipal Council
CO	Carbon monoxide
CO_2	Carbon dioxide
°C	Celsius
COPD	Chronic obstructive pulmonary disease
DMT	Department of Motor Traffic
FID	Flame Ionization Detection
FIDs	Flame Ionization Detectors
FSRU	Floating Storage Regasification Unit
FT	Free troposphere
GC	Gas Chromatograph

GCMS	Gas Chromatograph/Mass Spectrometer
GHG's	Greenhouse Gases
GOSL	Government of Sri Lanka
GWP	Global warming potential
HCHO	Formaldehyde
HCN	Hydrogen Cyanide
HEI	Health Effects Institute
HO_2	Hydro-peroxy radicals
IAP	Indoor air pollution
IARC	International Agency for Research on Cancer
IPCC	Intergovernmental Panel on Climate Change
IT	Interim targets
ITI	Industrial Technology Institute
JICA	Japan International Cooperation Agency
LRT	Light Rail Transport
LNG	Liquid Natural Gas
LPG	Liquid Petroleum Gas
MCM	Master Chemical Mechanism
MIM	Mainz Isoprene Mechanism
MW	Mega Watt
$\mu g/m^3$	Micro gram for cubic meter
μm	Micro meter
mm	Mile meter
MOF	Ministry of Finance
MTBE	Methyl Tertiary Butyl Ether

N_2	Nitrogen
N_2O	Nitrous oxide
N_2O_5	Dinitrogen pentoxide
NBRO	National Building Research Organization
NEA	National Environmental Act
NH_3	Ammonia
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_3	Nitrate radical
NOU	National Ozone Unit
NO_X	Oxides of nitrogen
O(1D)	Excited oxygen atom
O(3P)	Ground state oxygen atom
O_2	Oxygen
O_3	Ozone
OH	Hydroxyl radical
OVMs	Organic Vapour Monitors
OVOCs	Oxygenated Volatile Organic Compounds
PBL	Planetary Boundary Layer
PCBs	Polychlorinated biphenyls
PID	Photo Ionization Detection
PIDs	Photo-Ionization Detectors
PM	Particulate matter
PM_{10}	Particulate matter less than 10 microns (µm) in diameter
$PM_{2.5}$	Particulate matter less than 2.5 microns (µm) in diameter

POCP	Photochemical Ozone Creation Potentials
POPs	Persistent Organic Pollutants
PPCP	Photochemical PAN Creation Potentials
ppm	Parts per million
pptv	Parts-per-trillions by volume
PTR-MS	Proton-transfer-reaction mass spectrometry
R	Alkyl radical
RACM	Regional Atmospheric Chemistry Mechanism
RO	Alkoxy radical
RO_2	Peroxy radicals
RPM	Respirable Particulate Matter
RTS	Rapid Transit System
SAPRC	Statewide Air Pollution Research Centre
SEI	Stockholm Environment Institute
SLAQI	Sri Lanka Air Quality Index
SLVET	Sri Lanka vehicle emission testing program
SMEs	Small and Medium Enterprises
SO_2	Sulfur dioxide
SOA	Secondary organic aerosols
SPM	Suspended Particulate Matter
SVOCs	Semi Volatile Organic Compounds
TSP	Total Suspended Particulates
UK	United Kingdom
UNEP	United Nations Environment Programme
USA	United States America

USEPA	United States Environmental Protection Agency
UV	Ultra-Violet
VOC	Volatile Organic Compound
VOCs	Volatile Organic Compounds
VOHAPs	Volatile Organic Hazardous Air Pollutants
vol/vol	Volume to volume
VVOCs	Very Volatile Organic Compounds
WHO	World Health Organization
WRMPPP	Western Region Mega Polis Plan

CHAPTER 1

INTRODUCTION

Work flow chart of the Thesis outline is presented in Figure 1.

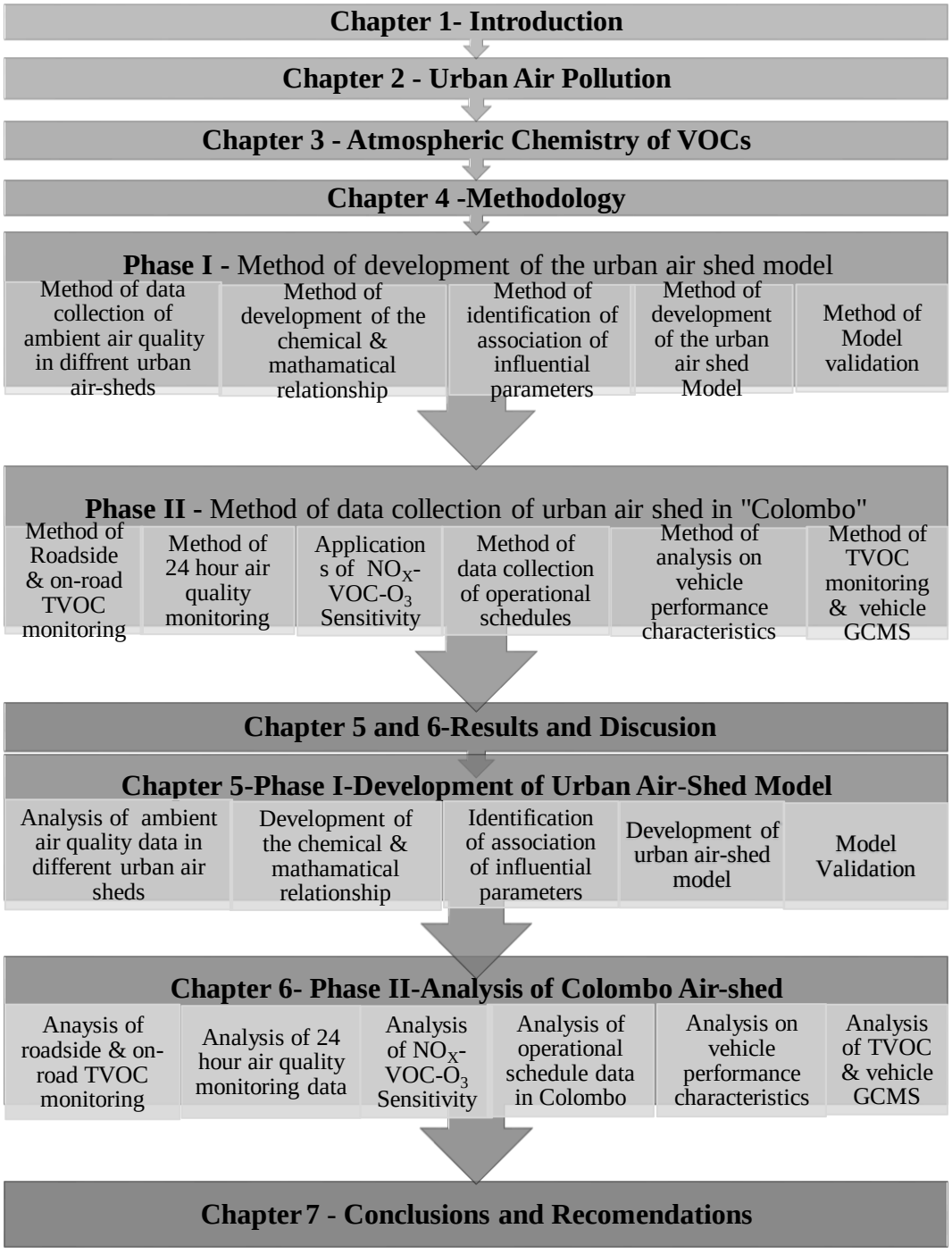


Figure 1: Work flow chart of the Thesis outline

1.1 BACKGROUND

Global estimates suggest that nearly 800,000 deaths are because of contributions from urban air pollution worldwide each year [1, 2 and 3]. This burden is not evenly distributed because of the high percentage of deaths are in the developing countries of Asia [1, 2]. Evidently, health and environmental effects of exposure to polluted air have become an important area identified in Sri Lanka at present years [4].

Outdoor air pollution arises from a spectrum of sources in urban environments [5] where the population density is high as compared to semi-urban or rural environments [6]. Rapid urbanization and industrialization of Sri Lanka has increased urban transportation, establishment of various factories, power plants and many other sources of outdoor air pollutants as main contributory factors for excessively high air pollution. Greater dependence on fossil fuels as the main source of energy supply in aforesaid sectors has resulted in increased atmospheric pollution. Sri Lanka at present meets approximately 50% of its total energy needs from fossil fuels, namely petroleum products and coal [7]. The incresing use of fossil fuels for energy applications has resulted in both environmental and energy-related challenges. A major contributor to urban air pollution is vehicular emission and it contributes to 60% of the ambient air pollution in Colombo [4].

United States Environmental Protection Agency (USEPA) has identified six major air pollutants that are hazardous to the environment and public health. They are namely particulate matter (PM), nitrogen dioxide (NO_2), Ozone (O_3), sulfur dioxide (SO_2), lead (Pb), and carbon monoxide (CO) [8]. Of the collection of air pollutants in the urban air, PM and SO_2 are the most widespread and cause acute health risks in Colombo [4]. In recent years air pollution due to invisible pollutants such as volatile organic

compounds (VOCs) have encountered great attention. Experience to date suggested that VOCs that are released into the urban air can lead to serious problems such as respiratory diseases, lung cancer, and even heart diseases [9]. People living in urban areas are experiencing the worst. VOCs on the Earth's atmosphere are emitted from a wide variety of biogenic and anthropogenic sources. The main concerns on indoor VOCs are due to adverse health impact while outdoor VOCs is due to the ability to create photochemical smog under certain conditions.

In the presence of sunlight, oxides of nitrogen (NO_X) and VOCs react in the atmosphere to produce a mass amount of tropospheric O_3 that is responsible for photochemical air pollution [10, 11]. The number of studies investigating VOCs degradation on tropospheric O_3 formation remains comparatively limited due to the complexity of the atmospheric chemical degradation and composition. Standards on VOCs emissions are yet to be implemented in air pollution regulations in Sri Lanka. There is a lack of data and understanding of the behavior and reactions of VOCs though it is a major concern affecting both health and the environment. The severity of the problem has compelled the national level and the political hierarchy to give special attention to control tropospheric O_3 pollution countrywide. An appropriate urban air quality modeling is an important area identified and heavily used internationally to predict and control tropospheric O_3 pollution beyond the above-mentioned control strategies, although local attention in this context is lacking.

1.2 PROBLEM STATMENT

Urban air quality modeling is a complex phenomenon to implement which needs multifactor inputs for wide range of relationships of the governing parameters. Despite the significant contribution from urbanization to air pollution from NO_X, VOCs, only limited number of studies aimed specifically at the investigation of simulating "urban air-sheds". Since the behaviour of the atmosphere is complex, and cannot be readily studied in the laboratory environment, an appropriate numerical modeling of NO_X, VOC and O_3 pollutants supported by data collected from onsite measurements could be applied. This phenomenon could be quantified, if certain measurable species can be introduced for $NO_X - VOC - O_3$ sensitivity.

There are many thousands of VOCs emitted in to the atmosphere. Each of these VOCs has its own decomposition mechanism that determines the effects of the VOC on O_3 production. The existing models are serving as a connection between the available laboratory studies and the chemical models. Therefore none of the models have identified all VOC reactions and many of the reactions which have identified also have not been studied experimentally to provide the rate constants in the governing relationships.

Development of interventions for the control of O_3 has become a challenging task for the policy makers and regulatory agencies in Sri Lanka. This is mainly due to the lack of clear understanding on physical phenomenon among O_3, NO_X and VOC interactions. There is no comprehensive air quality modeling tools with sufficient accuracy to generate information to support further research and decision making in air quality management.

1.3 AIM AND OBJECTIVES

Aim:

Aim of this study is to simulate an 'urban air-shed' to describe the photochemical degradation that would assist in implementing air pollution mitigation interventions in urban environments of Sri Lanka.

Objectives:

The objectives are to;

1. Identify key parameters and governing mechanisms influencing photochemical degradation.
2. Establish a mathematical model that describes the formation of ground-level ozone through photochemical reactions in urban air sheds.
3. Produce critical information through the mathematical model for the formulation of a comprehensive air quality model in different urban air-sheds in Sri Lanka.

1.4 METHODOLOGY:

The methodology of the research consists of two phases as explained in detail in Chapter 4: Phase I of the methodology described the method of development of the urban air shed model. Phase II of the methodology described the method of data collection and detail analysis of the urban air-shed in Colombo. In the phase I, the weekly ambient air quality data in 2013, 2014 and 2015 were collected from the mobile air quality monitoring station for selected cities covering different provinces in Sri Lanka. Selected locations are Jaffna, Anuradhapura, Colombo, Ratnapura, Kurunegala, Gampaha, Matara, Badulla, Kandy, Nuwaraelliya and Pollonnaruwa. Based on the trend patterns for the $NO, NO_2, NMHC, CH_4$ and O_3 air pollutants with subsequent metrological parameters, different regimes were identified for $NO_X - VOC - O_3$ sensitivity. The chemical and mathematical relation-ships were developed for the identified regimes. Furthermore relation-ship of air pollutants and influential parameters were studied using MATLAB version 2015 and SPSS version 16 softwear. Based on the chemical and mathematical relation-ships, the theoretical urban air shed model was developed and the developed model was validated using weekly ambient air quality data from the selected locations.

In Phase II, urban air shed in "Colombo" was studied in detail. The developed model was applied for the urban air shed in "Colombo". Variety of emission sources have been explored prior to the field measurements to identify critical locations in Colombo and based on the findings identified locations are Dehiwala, Kollupitiya, Fort, Maradana, Borella, Narahenpita, Grandpass and Nugegoda. Data collection of the urban air-shed in Colombo was conducted as follows. Field measurements of predominantly transport induced hourly VOC concentrations using MiniRAE Lite TVOC monitor were conducted

at selected locations as a pilot measurements in year 2014. 24-Hour ambient automated air quality monitoring was conducted at selected locations as detail measurements in year 2017, 2018 and 2019. Measured air pollutants were namely $PM_{2.5}$, PM_{10}, NMHC, CH_4, NO_2, NO, CO, SO_2 and O_3 with subsequent meteorological parameters of air solar radiation, relative humidity, temperature, wind speed, and wind directions with their distribution patterns (wind-rows).

Operational schedules of emission sources including train scheduled data, working hours of the thermal power plants at Kelanithissa and vehicle counts were conducted at identified critical locations in Colombo. Further vehicle counts were conducted simultaneously with air quality monitoring, considering the different type of vehicles and as a total in each location in Colombo for two week-days and one weekend-day. Furthermore additional information was calculated considering the fuel economy with passenger kilometers, based on the active vehicle fleet data collected at this research. Representative random sample (434,497 vehicles) of vehicle exhaust hydrocarbon data from Department of Motor Traffic in 2013 in Sri Lanka were analyzed using SPSS version 16 software. Real time TVOC measurements for 10 minutes (reporting every minuted data) in fourteen sites were carried out using Photo Ionization Detectors (PID), EW technologies, USA. Furthermore air from the exhaust line of randomly selected 50 different types of vehicles was collected using Teflon air bags and analyzed using GCMS.

1.5 RESULTS AND DISCUSSION

Chapter 5 and 6 schedules the results and discussion as in two phases with various graphical relationships of air pollutants and visualization tools. Chapter 5-Phase I, schedules the "development of urban air-shed model" and Chapter 6- Phase II, schedules the analysis of the urban air-shed in Colombo.

As in Chapter 5, ambient real-time air quality data and meteorological parameters of different cities in Sri Lanka signify that two concepts exist for NO_X–VOC– O_3 sensitivity. In certain environments, the course of O_3 formation is controlled entirely by NO_X and is mainly independent of VOC. This condition is considered as NO_X- sensitive regime. NO_X-sensitive regime has comparatively low NO_X and high VOC concentrations and O_3concentration rises with rising NO_X. Nevertheless, O_3 concentration changes slightly in response to rising VOC. Accordingly, in Colombo, Kurunegala, Jaffna, Matara, Badulla, Polonnaruwa, and Gampaha show the NO_X-sensitive regime. On the other hand, in certain other environments, the course of O_3 formation rises with rising VOC. Further, the course of O_3 formation rises or occasionally even reduces with rising NO_X. This condition is considered as VOC-sensitive regime. In Ratnapura, Anuradhapura, Kandy and Nuwara Eliya show the VOC- sensitive regime. The chemical pathways were derived and calculated for NO_X − VOC − O_3 sensitivity mathematically for two regimes. From the developed steady-state ozone concentration (O_{3ss}), both regimes could be calculated. Relationships of meteorological parameters of air temperature, solar radiation, and wind speed with NO_X − VOC − O_3 sensitivity was identified. Furthermore, the air shed model was validated with the measured O_3 concentration.

In Chapter 6, schedules the analysis of the urban air-shed in Colombo. Roadside weekly average TVOC hourly median concentrations in ppb were 226.5, 205.6, 194.5, 190.0, 99.0, 91.5, and 72.5, at the locations; Grandpass, Fort, Maradana, Borella, Dehiwala, Narahenpita, and Kollupitiya respectively. The corresponding on-road TVOC concentrations in ppb were 536.0, 321.5, 216.0, 195.0, 189.0, and 183.0 between Narahenpita to Grandpass, Maradana to Borella, Borella to Narahenpita, Fort to Maradana, Kollupitiya to Fort, and Dehiwala to Kollupitiya, respectively. TVOC levels were high on-road (273.4ppb) than beside the road (132.8ppb). Air pollution data analysis in the city of Colombo shows that the emissions from power stations in Kelanithissa could be affecting the high $PM_{2.5}$ and PM_{10} levels in Borella, Grandpass and Narahenpita, and the high NOx levels in Grandpass, and Narahenpita, while Fort, Kollupitiya, and Nugegoda are not affected. Fort and Nugegoda are heavily affected by the train emissions while in Kollupitiya high PM_{10} levels were observed due to the settling down of "sea salts."

Highest vehicle counts were observed at Maradana (76573 vehicles in 24 hours and 3829 per hour in average) and second highest was in Fort (62796 vehicles in 24 hours per day and 3140 per hour in average). Lowest vehicle counts were observed at the Kollupitiya (52278 vehicles in 24 hours per day and 2614 per hour in average) and Nugegoda (52954 vehicles in 24 hours per day and 2648 per hour in average). Further, vehicle count results were compared with fuel economy; fuel economy with passenger km for different type of vehicles. Results confirm that dominated vehicle types were three wheelers, motor bikes and cars in all cases. Further results highlights that three-wheelers were actively moving throughout the day.

TVOC results obtained from the PID are as follows; petroleum station is 603.10ppm; direct vehicle exhaust is 1972.9 ppm; vehicles when moving on road is 273.42 ppm; the road side 1ft away from high traffic road is 132.87 ppm; vehicle spray paint area is 78.30 ppm; kerosene using cook stove area is 73.40 ppm. GCMS spectrums of vehicle exhaust samples of different types of vehicles have identified air toxic compounds such as benzoquinoline, naphthalene and benzene derivatives. It could be due to the incomplete combustion of petroleum products mainly arises from vehicle emissions.

1.6 CONCLUSIONS AND FUTURE DIRECTIONS

Chapter 7 enlightens conclusions and future directions of this research. In summary, it could be concluded that there exist two regimes of $NO_X - VOC - O_3$ sensitivity (NO_X-sensitivity and the VOC-sensitivity) among these cities. Study further concluded that the developed urban air-shed model could calculate the steady-state ozone concentration ($O3_{SS}$) that gives the ($O3_{SS}$) concentration values for both regimes. The study further concluded that meteorological parameters such as solar radiation; air temperature; and speed of the wind have a relationship with O_3 production and it is a rising trend. Results of the univariate linear regression model using predicted and observed ozone values confirmed that (O_{3ss}) concentration was significantly correlated with the predicted ozone concentration. Analysis of urban air shed in Colombo also confirms the predicted and observed (O_{3ss}) concentration was significantly correlated. Established Urban air-shed model is essential for Sri Lanka to develop the appropriate interventions for controlling O_3 pollution in each city. It could be concluded that methodology of this research could be used for future researchers to develop relationship among other pollutants to understand the holistic approach. This research

provides a detailed understanding to the air pollution problem in the city of Colombo and its photochemical degradation. High emission sources were identified as power plant emission, train emissions and vehicle emissions. Research further highlighted that cars, three wheelers and motor bikes are the main polluted vehicle types after trains, when considering the number, active vehicle fleet, fuel economy and the passenger km. Study concluded that apart from the domestic on road vehicles train was a major source of air pollution that contributes to vehicle emission in Sri Lanka. It could be further concluded that GCMS spectra of vehicle exhausts contain some of the known carcinogenic compounds.

As future directions, the developed “Urban Air-shed Model” could be used in policy development with appropriate interventions to control O_3 in urban environments of tropical islands. Further continued air quality monitoring at densely urbanized locations in Colombo and countrywide needs to be carried out to improve the accuracy and sensitivity to seasonal variation of the developed “Urban Air Shed Model" which could lead to develop a combined air quality prediction model for Sri Lanka. It is important to identify all possible VOC species and their rection rates in different temparatures through advanced research. This will further improve the developed “Urban Air-shed Model” by improving the k1 and k2 rate constant values in this model development. Study further endorsed developing a district vise complete emission inventory for Sri Lanka. This emission inventory could be linked with the developed model and based on the findings, decisions could be established by the policymakers. A detail research needs to be carried out on train emissions in Sri Lanka that lead to improve the fuel quality of trains and introduction of emission standards and the cleaner technology engines for trains. Finally, it could be mentioned to carry out a detail national level study on VOCs and prepare ambient air quality standards for VOCs in Sri Lanka.

CHAPTER 2

URBAN AIR POLLUTION

2.1 OVERVIEW OF AIR POLLUTION

Air pollution is not a recent phenomenon; it is one of the world's oldest environmental problems that initiated with industrialization and even to date it is a major concern among global scientific and economic sectors [12, 13]. The smoke control ordinances were introduced by a number of cities during the 20^{th}-century. In the United States of America (USA), major 23 urban cities had ordinances mainly targeted at controlling visible smoke from commercial establishments by the year 1912 [14]. Since 18^{th}-century statistics were recorded on deaths that resulted from air pollution in major cities such as London; Meuse Valley, Belgium; Donora, US; New York City, and Japan; Osaka [12,13 and 15]. "London's killer fog" was a reported extreme condition that has lasted for five days in December 1952 and an excess of about 4000 deaths was estimated from the stagnant air of sulfur dioxide, smoke, and fog [12]. Epidemiological studies of air pollution and health essentially began with this episode.

During the 20^{th}-century with emerging scientific evidence, attitudes, and regulations on air pollution slowly developed. Nevertheless, in many wealthy cities, concentrations of air pollution were reduced due to collective effort and cleaner technologies [16]. Furthermore, effective international action was eventually implemented by reputed organizations such as World Health Organization (WHO), United Nations Environment Programme (UNEP) and United States Environmental Protection Agency (USEPA). When the economic development has improved, fast and unplanned

urbanization emerged resulting in urban air pollution, which in turn contributes to regional and global air pollution [17, 18]. With all this understanding of the problems of air pollution, most developing countries do not have statistics to estimate its actual dimension [16]. Although, air pollution synchronizes with other important public health problems, such as malnourishment, low hygiene deficiencies, or vaccination coverage which are given greater importance in situations where cost-effective revenues are limited, has postponed the actions needed to sufficiently evaluate and regulate air pollution in most urban cities in the developing world [5, 15 and 16].

2.2 TYPES AND HEALTH IMPACTS OF AIR POLLUTANTS

Air contains various components. Nitrogen (N_2- 78%) and oxygen (O_2- 21%) constitute approximately 99% of the mixture with the remainder being made up of many components in trace quantities. The USEPA defines an air pollutant as “a substance in the air that, in high enough concentrations, produces a detrimental environmental effect that influences the health of all living beings” [8, 19 and 20]. Air pollutants have been categorized according to different concepts. They can be either primary pollutants or secondary pollutants. Primary air pollutants are released into the atmosphere from a source for example an exhaust pipe, or a factory chimney, or through suspension of contaminated dust by wind. Secondary air pollutants are formed within the atmosphere itself. They arise from chemical reactions of primary pollutants, possibly involving the natural components of the atmosphere, especially oxygen and water. Air pollutants can also be classified by the physical forms of a pollutant. Accordingly, it can be as gaseous form and particulate form.

USEPA has recognized criteria air pollutants (air pollutants with adverse effects on the environment and human health) namely, NO_2, SO_2 , PM, O_3, CO and lead [19]. Furthermore, other air pollutants of concern include VOCs (which is the key pollutant in this research and section 2.3 explains VOCs in detail), poly-nuclear aromatic hydrocarbons, furans, dioxins, and polychlorinated biphenyls (PCBs) emitted by combustion processes [16].

There are three major types of pollutants that result largely from urban transportation [21, 22]:

a. Greenhouse Gases (GHG's) for example methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), chlorofluorocarbons (CFC), carbon monoxide (CO).
b. Aerosols for example oxides of nitrogen (NO_X), volatile organic compounds (VOCs), sulfur dioxide (SO_2), particulate matter (PM).
c. Radiative forcing agents for example- tropospheric ozone (O_3)/ Ozone (O_3).

Although air pollutants are classified based on different concepts, they usually do not appear in separation but in complicated mixtures that produce possible synergistic effects among pollutants [23, 24 and 25]. The composition of air pollutants itself and its associated toxicity are different in different countries, regions, cities, and households. Age, cultural values, life style, and health status may differently influence the health effects resulting from air pollution [26, 27 and 29]. Furthermore, some persons are more sensitive to air pollution such as children, elders, pregnant women, and asthmatic patient and individual sensitivity is an important parameter when reacting to air pollutants [26, 27, 28]. Below Table 1 explained the criteria air pollutants and there health effects in detail.

Table 1: Health effects of criteria air pollutants

Pollutants	Sources	Health effects
Oxides of Nitrogen (NOx)	Complete combustion of fuels: motor vehicles, power generation, industrial processes, [16]. There are two ways of NO_X emissions; N_2 in the atmosphere (ThermalNO_X); N_2 in the fuel itself (Fuel NO_X) [15, 16].	It rises and exacerbate asthma and reduced the growth and development of the lungs of children [34, 35 and 36]. Short-term exposure causes lung edema, damage to lung cells, increasing susceptibility to bronchial infections, acts as a bronchoconstrictor, aggravating asthmatic conditions [5, 36, 37 and 38]. Long-term exposure cause changes in the lung tissues similar to emphysema, irritates the respiratory system and leads to impaired lung functions which would present as an inability of breathing deeply; leads to eye and throat irritations, cough, and lung inflammation [35, 36, 37}.
Ozone (O_3)	O_3 is produced largely from atmospheric chemical reactions between NO_X and VOC in the presence of sunlight [10, 11].	Causes wheezing and shortness of breathe by trapping air in the alveoli [5, 16, 38 and 45]. Causes different respiratory health impacts such as emphysema, asthma, chronic bronchitis [5, 20 and 45]. The respiratory systems becomes more susceptible to infections as well as increasing the chronic respiratory disease such as chronic obstructive pulmonary disease (COPD) [16, 20]. Exposures over a long period would cause permanent lung damage including mal-development of lungs in children [45].

Lead (**Pb**)	Pb is a heavy metal found in paint, contaminated soil, dust, leaded gasoline and emissions from metal smelters and industrial processes.	Causes learning problems, nervous system damage and brain damage, peripheral nerve paralysis, and impairs production of hemoglobin in blood, seizures, mental retardation and behavioural disorders Fetuses, Infants and children are especially susceptible even to low doses, central nervous system damage and retards their intellectual development, causes high blood pressure and heart disease in humans [5, 15, 16, 20]. The human reproductive system is affected with exposure to Pb including the production of abnormal sperm and the reduction of sperm count among males and reduced fertility, miscarriages, and still- birth among women [5, 20].
Carbon Monoxide (**CO**)	Incomplete combustion of fuels: motor vehicles, power generation, industrial processes, wood, natural gases and tobacco combustion [16, 33].	When breathing CO binds with the hemoglobin, replacing O_2 in the blood circulation. Consequently less oxygen transferring to the human brain and heart [5, 30, 31 and 32]. Symptoms including dizziness, headache, nausea, fatigue, memory and visual impairment [26, 27, 32, 33 and 34]. Exposure to higher CO levels can cause damage of visual sensitivity, learning capability, manual dexterity, and performance of difficult tasks are some of the illnesses that can cause due to exposure to very high CO levels [5, 30].

Sulfur dioxide ($\mathbf{SO_2}$)	burning fuels that contain sulfur: mobile sources, stationary sources such as industrial, institutional and utility boilers; petroleum refineries, smelters, paper mills and chemical paints are also involved in SO_2 emissions [16].	Causes breathing difficulties and permanent injury to lungs mostly among those with preexisting respiratory illnesses and asthmatics [5, 34, 39, 40, 41, 42, 43 and 44]. Long term SO_2 exposure leads to poor lung functions and premature deaths from cardiovascular diseases [34, 43].
Particulate matter (PM) (PM_{10})-coarse mode ($PM_{2.5}$)-fine mode	PM_{10} and ($PM_{2.5}$) are generated by motor vehicles, power generation, industrial processes and cook stoves. Sourses of PM_{10} generated by bushfires, sea salts and road soil dust [15, 16, 46, 47, 48, 49 and 50].	PM pollution correlated with a number of adverse health outcomes of children including increased rate of morbidity [61], increasing respiratory illness [15, 51,52, 53, 62, 63 and 64] decreasing lung function [65], aggravation of asthma [61, 66], and cardiovascular diseases [67, 68]. Predominant in more vulnerable groups including children, pregnant women, elderly people as well as individuals with chronic conditions such as asthma [39, 54, 55, 56, 57, 58, 59, 60 and 61]. Nearly ten percent of lung cancer risk of urban non-smokers are due to PM.

2.3 VOLATILE ORGANIC COMPOUNDS (VOCs)

2.3.1 Definitions and classifications of VOCs

There are several definitions and classifications to describe VOCs (Table 2).

Table 2: Definitions and classifications of VOCs

Organization	Definitions and classifications of VOCs		
USEPA	**Outdoor VOCs** – VOCs are any compound of carbon, excluding CO, CO_2, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by USEPA as having negligible photochemical reactivity [9].		
	Indoor VOCs – "VOCs are organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure" [9].		
European Union	A VOC is any organic compound having an initial boiling point less than or equal to 25°C measured at a standard atmospheric pressure of 101.3 kPa" [69].		
WHO	VOCs categorizes based on boiling points as very volatile, volatile, and semi-volatile [70].		
	VVOC	0 to 50 -100°C	Methyl chloride, propane, butane
	VOC	50 -100°C to 240 -260°C	d-Limonene, formaldehyde, toluene, acetone, hexanal, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol)
	SVOC	240 -260 °C to 380 -400°C	Pesticides (DDT), chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB)

2.3.2 Sources of Volatile Organic Compounds

An array of VOCs are produced from biogenic as well as anthropogenic sources [71, 72]. A major portion of VOCs such as pinene, isoprene, and methanol emit from tropical and extra-tropical forests, globally [73]. The typical composition of vegetative VOCs emission is alkenes such as sesquiterpenes, monoterpenes, and isoprene; and oxygenated VOCs such as acetone, methanol, camphor, cis-3-hexen-1-ol, 2-methyl-3-buten-2-ol, and cis-3-hexenyl acetate [73].

Landfills are known to be a great threat to health as well as the environment. Various toxic pollutants emitted from the landfills which includes CH_4 as well as other gaseous pollutants. A study revealed that CH_4 has been detected at 83% of landfills out of 288 landfills [73, 74]. Further, it is a greenhouse gas more powerful than CO_2. Another major source of VOCs is the burning of biomass [74]. This emit different types of VOCs, such as oxygenated species (e.g., multi-functional species, carbonyls, and organic acids), nitriles (e.g., CH_3CN, HCN) and aromatics (e.g, benzene, toluene) [75, 76]. In fact, the burning of biomass is happened in nature such as in forest fires. Further burning of biomass is occurred with the involvement of human activities such as in agricultural activities (e.g., clear the ground). However, a major proportion of VOCs from biogenic sources is mainly from vegetation. Perhaps, the estimated emission from vegetation is 1150 Tg (C) per year [73]; while the anthropogenic sources contribute around 100 Tg (C) per year [77]. Though the contribution of VOCs from biogenic sources greatly exceeds those from the anthropogenic sources by a factor of 11 on a worldwide basis.

Anthropogenic VOCs always dominate in densely populated urban environments. The production, storage, and use of fossil fuels (i.e., motor vehicle exhausts, power plant emissions, and industrial processes) are large anthropogenic sources of VOCs such as alkenes, alkanes, and aromatic hydrocarbons [75, 77]. Although anthropogenic VOCs represent a small proportion in the global context, that can easily predominant on local and regional environments. The key categories of VOCs include aromatic hydrocarbons, oxygenated compounds, alkanes, and alkenes. These anthropogenic VOCs together with increasing NO_X emissions from sources impact local photochemical air pollution.

VOCs removes from the atmosphere either by deposition processes or photochemical reactions and the duration could be varied from seconds to months [10, 11]. Reactions related to photochemical air pollution are mainly from OH in the presence of sunlight and from NO_3 during the nighttime [78]. With these reactions OVOCs are generated and the same series of reactions could occur [79, 80]. Section 3.2 explains the tropospheric chemical reactions in detail. The end product of VOCs produce CO_2 in the atmosphere. Finally, they are deposited on the surface of the earth as dry depositions or uptake in rain droplets as wet deposition [10, 11]. However, the decomposition mechanisms are not fully understood in the present context. When the VOCs undergo photo-oxidation that can produce O_3 and secondary organic aerosols (SOA). Perhaps these by-products have important consequences for air quality status and climate change leading to detrimental effects on human health particularly in the respiratory system.

The VOCs have reported higher concentrations in indoor environments as compared to outdoor environments. The indoor to outdoor ratios can be based on many factors such as construction materials, layout of the building (e.g., garage) [81, 82, 83 and 84]. Indoor VOCs are emitted by a wide array of products. These products comprised of

paints, lacquers, wood preservatives, aerosol sprays, cleansers, disinfectants, moth repellents, and air fresheners, cosmetic products, pesticides, tobacco smoke, stored fuels, and automotive products; building materials and furnishings, office equipment, office stationaries, craft materials, etc [9, 81and 82].

A substantial variation of indoor sources could be seen in tobacco smoke and consumer products proven by personal and indoor concentrations in previous exposure studies [84, 85]. The VOCs can be found in different consumer products. As a few examples, *p*-dichlorobenzene can be found in deodorizers, moth cakes, air fresheners. The naphthalene can be found in pesticides and mothballs. The chloroform can be found in chlorinated water and pesticides. The α- and β-pinene and *d*-limonene can be found in cleaning products and air fresheners [83, 84, 85 and 86]. Acetaldehyde has been shown in tobacco smoke, water-based paint, leakages from combustion stoves (i.e., fireplaces, furnaces, and wood stoves) [83, 84]. Benzene is released from tobacco smoke, coatings, some furnishings, paints, fuel combustions, wood products, etc [81, 83 and 87]. Benzene and styrene are known to have increase concentrations in homes with smokers as well as in urban areas with high traffic due to fuel combustion [88]. Burning incense releases formaldehyde which is a commonly found VOC species in indoor air. Formaldehyde is further found in tobacco smoking; compressed wood products; building materials such as fiberboard, plywood board with urea formaldehyde resin [86, 89 and 90].

2.3.3 Health impacts of Volatile Organic Compounds

The adverse health effects of VOCs could result in a substantial latent period after the exposure or after repeated exposure [9]. Similar to the other pollutants, adverse health effects of VOCs depend on many factors. As an example, duration and the severity of exposure of VOCs is important for the extent of health effects. Health effects could be varied greatly with the toxicity of VOCs. Thus the highly toxic VOCs resulted in more serious health effects [91, 92 and 93]. The VOCs affect many systems (e.g., respiratory system, digestive system, etc.) in the human body. Symptoms and signs of the respiratory system include discomfort of the nose and throat, difficulty in breathing. Symptoms of the nervous system include headache, dizziness visual disorders, and memory impairment. Symptoms of the digestive tract include nausea, epistaxis, fatigue, and dyspnea. Sick building syndrome is a mixture of non-specific symptoms which occurs with exposure to VOCs [91, 92, 94, 95, 96, 97 and 98]. Adverse effects of VOCs are not limited to the symptoms and signs, perhaps result in more serious health outcomes including chronic respiratory diseases (e.g., chronic obstructive pulmonary disease, asthma) and cancer [94, 95 and 96]. However, there is little evidence on more serious health effects of VOCs on the human body specifically on the general population [94, 97 and 98]. Nevertheless, research on animals as well as on special occupational categories emerges evidence of long-term and serious health effects on VOCs. Further, adverse health effects of exposure to mixtures of VOCs are limited; scientific research gives evidence mostly based on specific VOCs [94]. In the modern world, people are exposed to various VOCs emited from newer chemical compounds. However, the adverse consequence by exposing to these VOCs are limited specifically in non-occupational settings [99,100 and 101]. Usually, non-cancerous adverse health effects are reported over cut-off concertation of VOCs. However, for carcinogens it is believed

to have no threshold of exposure. Perhaps, even a lower concentration of some VOCs attributable for the occurrence of cancer [94]. This is proven by research based on animals. The studies on animals show that exposure to VOCs are associated with an elevated risk of cancer [101]. Certain VOCs are listed (e.g., formaldehyde, paradichlorobenzene benzene, acetaldehyde, benzene, naphthalene, chloroform) by the International Agency for Research on Cancer (IARC) as potential carcinogens of humans [94].

2.3.4 Measurement methods used in VOCs

Measurement technique and equipment of VOCs impact on measured composition and quantity. However, measurement technique and equipment are unique and capable of monitoring only a selected number of VOCs. Measuring capability, accuracy and quantification vary according to the selected equipment. The range of measurement methods is shown in Table 3. Generally, used measurement methods of VOCs are proton transfer reaction mass spectrometry (PTR-MS), flame ionization detection (FID), photoionization detection (PID); gas sensor; passive air sampling organic vapour monitors and canisters or airbags follow with Gas Chromatograph Mass Spectrometer (GCMS). The equipment will decide the preferences, selectivity, and sensitivity of the measurements. Currently, none of the measurement methods are capable of capturing all VOCs that is present in the ambient air.

Table 3: Measurements methods of VOCs

No.	Measurements methods	Advantages	Disadvantages	Sensitivity
1	GCMS - Gas Chromatograph Mass Spectrometer collected to the canisters or airbags [102].	*Can identified higher number of VOCs. *One of the best methods available. *Sensitivity is high .	*Cannot capture rapidly variations in the atmospheric conditions. *If the analysis time is higher, then VOCs may react in the container.	0.1 pptv
2.	PTR-MS - Proton transfer reaction mass spectrometry [78, 79 and 103].	*Have a quick-response method, therefore major VOCs can be measured. *A soft ionization method. *hydronium ions (H_3O^+). involves in the proton-transfer reactions.	*Can't recognized Isomers *The mass spectra are complexed with product ions.	10–100 pptv
3.	Flame Ionization Detection (FID) [78].	*Most widely used to detect TVOC levels. *Use a hydrogen flame to ionize the VOC.	*Needs to carry a hydrogen cylinder required to provide fuel and also a calibration gas cylinder.	0-1,000ppm
4.	PID - Photo Ionization Detection [78, 79].	*Easiest and most efficient way to detect TVOC levels. *Provides real time measurements of total VOCs. *CH_4 is not counted when getting the values for total VOCs.	* Sensitivity varies on ultra-violet (UV) light.	MiniRAE Lite PID gives 0 to 5,000 ppm.
5.	Organic Vapour Monitors - Passive air sampling [97, 99, 103, 104, 105]	*Charcoal-based passive air samplers. *Target VOCs can be extracted.	*Sensitivity is lower than active sampling.	-
6.	Gas Sensor [106].	*Provide a single aggregate reading for all of the detectable substances present at any moment.	*Cannot distinguish between the different contaminants.	-

2.4 AIR QUALITY GUIDELINES AND STANDARDS

2.4.1 Air Quality Guidelines

Air Quality Guidelines are guidelines developed to protect community health from the adverse outcomes of air pollution [107]. It moreover proposed to guide decision-makers and deliver suitable goals for a comprehensive selection of policy decisions for managing air quality in different areas in the world [108]. WHO has updated guidelines in 2006 and 2021 (Table 4) with interim targets (IT) [108]. The "interim targets" are introduced by the WHO, to reduce the high air pollution progressively by all the counties in the world.

Table 4: WHO Ambient Air Quality Guidelines

Pollutant	**Air Quality Guideline**	**Averaging Times**	**IT1**	**IT2**	**IT3**	**IT4**
Nitrogen Dioxide (NO_2)	10 µg/m^3	Annual	40	30	20	-
	25 µg/m^3	24-hour	120	50	-	-
Particulate Matter (PM_{10})	15 µg/m^3	Annual	70	50	30	20
	45 µg/m^3	24-hour	150	100	75	50
Particulate Matter ($PM_{2.5}$)	5 µg/m^3	Annual	35	25	15	10
	15 µg/m^3	24-hour	75	50	37.5	25
Ozone (O_3)	100µg/m^3	8-hour	160	120	-	-
Sulfur Dioxides (SO_2)	40µg/m^3	24-hour	125	50	-	-

2.4.2 Air Quality Standards

Standards of ambient air quality are essential to reduce the emissions of air pollutants to the environment [19, 20 and 50]. The first foremost standards for ambient air quality were developed by the USEPA through the "Clean Air Act" for the assessment of health and welfare. After that many counties have developed air quality standards to achieve clean air. According to USEPA, the ambient standards should be renewed with necessary revisions as a minimum of every five years' time period USEPA's latest National Ambient Air Quality Standards are shown in Table 5.

Table 5: USEPA National Ambient Air Quality Standards

Pollutant	**Standards**	**Average duration**
Particulate Matter (PM_{10})	50 µg/m^3 (Primary and secondary)	Annual
	150 µg/m^3 (Primary only)	24-hour
Particulate Matter ($PM_{2.5}$)	15 µg/m^3(Primary and secondary)	Annual
	65 µg/m^3 (Primary only)	24-hour
Ozone (O_3)	0.08 ppm (Primary and secondary)	8-hour
	0.12 ppm (Primary and secondary)	1-hour
Nitrogen Dioxide (NO_x)	100 µg/m^3 (0.053 ppm) (Primary and secondary)	Annual
Sulfur Dioxides (SO_2)	0.03 ppm (Primary only)	Annual
	0.14 ppm (Primary only)	24-hour
	1300 µg/m^3 (0.5 ppm) (Secondary only)	3-hour
Carbon Monoxide (CO)	10mg/m^3 (9 ppm) (Primary only)	8-hour
	40 mg/m^3 (35 ppm) (Primary only)	1-hour
Lead	1.5 µg/m^3 (Primary and secondary)	Quarterly Average

As presented in the Table 5, there are two types of standards namely, primary and secondary derived by USEPA. The limits of the primary standards are arranged to

protect the community health of people and it includes sensitive individuals for example children, the elderly, and asthmatics. The limits of the secondary standards are arranged to protect the welfare, such as damage to flora, crops, and animals; reduced visibility; safeguard constructions [19, 20 and 50].

2.4.3 Sri Lankan Air Quality Standards

Table 6 summarized the ambient air quality standards for Sri Lanka. Sri Lanka initially published the ambient air quality standards in 1994 and revised in 2008. The revisions of the standards have been constructed by the existing air quality monitoring data, current status, and "WHO guidelines in 2006" [108, 109]. Further details are available on the Gazette No 817/6 – 03.05.1994 and Gazette No 1562/22 – 15.08.2008 [109].

Table 6: Sri Lankan Ambient Air Quality Standards

Air pollutant	Average time	Standard ($\mu g/m^3$)	Method of measurement
Carbon monoxide (CO)	8hr	10000	Non-dispersive infrared spectroscopy
	1hr	30000	
	Any time	58000	
Nitrogen dioxide (NO_2)	24hr	100	Colorimetric using Saltzman method or equivalent gas phase chemiluminescence
	8hr	150	
	1hr	250	
Sulfur dioxide (SO_2)	24hr	80	Pararosaniliene method or equivalent Pulse Fluorescent
	8hr	120	
	1hr	200	
Ozone (O_3)	1hr	200	Chemiluminescence method
Lead (Pb)	Annual	0. 5	Hi-volume sampling, wet-ashing /atomic absorption
	24hr	2	
SPM	Annual	100	Hi-volume sampling
	24hr	300	

	8hr	350	
	3hr	450	
	1hr	500	
$\mathbf{PM_{2.5}}$	24hr	50	Hi-volume sampling and Gravimetric or Beta attenuation
	Annual	25	
$\mathbf{PM_{10}}$	24hr	100	Hi-volume sampling and Gravimetric or Beta attenuation
	Annual	50	

2.5 AIR QUALITY MANAGEMENT IN SRI LANKA

2.5.1 National commitment on air quality management in Sri Lanka

The National Environmental Act (NEA) for Sri Lanka was enacted in 1980 [109]. The Central Environmental Authority (CEA) was established in 1981 under this Act [109]. The Ministry of Environment was first formulated in 1991 in Sri Lanka which mainly works on policy formulations for the national environmental issues [110]. Sri Lanka has been actively participating in many regional and global conventions relevant to ozone layer protection. The phasing out of ozone- depleting substances was introduced in 1985 by the Vienna convention and in 1987 by the Montreal Protocol [111].

A national-level policy document on Air Quality Management was formulated in 2000 to bridge the policy gaps in the Clean Air Action Plan 2000 [110, 112]. Recognizing the importance of air resource management, GoSL introduced various measures including the ambient air quality standards at the national level in the year 1994 (by Gazette No. 850/4); phasing -out of petroleum products with Pb in June 2003 (by Gazette No-1295/11); introduction of low sulfur diesel in January 2003 (by Gazette No-1295/11); mobile air emission standards, fuel standards, and vehicle specification standards in 2008 (by Gazette No 1562/22); establishment of Sri Lanka vehicle

emission testing program (SLVET) in 2008 (by Gazette No. 1557/14); amended regulation on improved air emission and vehicle importation standards in 2015 (by Gazette No. 1895/43) and stationary source emission control in June 2019 (by Gazette No. 2126/36) [109]. GoSL has further gazetted banning of importation of two- stroke three-wheelers from the year 2008 (by Gazette No. 1557/14); more stringent standard for fuel sulfur content, i.e. 350 ppm and 150 ppm sulfur content for auto diesel and super diesel (by Gazette No. 1895/43) respectively in 2015; tax concession of importing newer and cleaner vehicles, i.e. 25% on electric vehicles and 50% on hybrid vehicles [109, 113]. Further regulations on polythene and plastic management was introduced in 2017 [109].

There are several national plans recognized by the GoSL for next 20 years. These plans are Western Region Mega Polis Plan (WRMPP) [114], Electricity generation expansion plan [7], and the fuel quality road map. The fuel quality road map including the use of alternative fuels for transport, industrial and power sectors for Sri Lanka, introducing more stringent limits for sulfur content of the fuel quality standards. Currently 50% of the electricity production is provide by burning of the Coal and Petroleum products and the balance 35% is from the Hydropower and the 15% is from Solar and wind renewable resources in Sri Lanka [6, 115]. A long-term electricity generation expansion plan has been developed by the Ceylon Electricity Board (CEB) from 2018 to 2037 [7] considering the climate change mitigation commitment as well.

As explained there are several implementations are on-going towards improving air quality yet, Sri Lanka desires further implementations as identified by the 2025 clean air action plan [116]. Those are formulating and implementing standards for indoor air

quality, stringent revisions of regulations on ambient air quality and emissions of mobile sources (implemented through vehicle emission testing programme), appropriate urban air quality modeling, predictions through local and regional scale computer modeling are highlighted. This study addressed the appropriate urban air quality modeling on NO_x, VOC and O_3 sensitivity through local scale modeling.

2.5.2 Air Quality Monitoring in Sri Lanka

There are several national organizations that are involved in monitoring ambient air quality in the city of Colombo and the country. These organizations are the National Building Research Organization (NBRO); CEA; and Industrial Technology Institute (ITI) [109, 117 and 118]. In 1989 Air Quality Monitoring Program for Colombo was introduced by NBRO as a first attempt [118]. ITI has carried out a survey in major traffic junctions in the city of Colombo, measuring traffic density and pollutant emissions [117]. Automated ambient air quality monitoring in Colombo started with two fixed air quality monitoring stations and one mobile station in December 1996. These two fixed automated stations were originally located at the Fort railway station and at the meteorological station in Colombo. The mobile air quality monitoring station was used to collect air quality data in the rural and suburban settings which was donated by the VET programme and it is currently not in action [109]. CEA has latest two fixed air quality monitoring stations and they are located at CEA premises in Battaramulla and in Kandy for continues air quality monitoring [109]. ITI has also purchased a mobile air quality monitoring station and currently it is available to get the emission measurement on request by making payments [117]. In 2020, March, the Colombo Municipal Council (CMC) in collaboration with the NBRO launched a fixed air quality monitoring station at CMC premises in Colombo. Further NBRO was carrying out

ambient air quality passive sampling measurements in the city of Colombo, Kandy, Gampaha, Kalutara, Galle, Rathnapura, Kurunegala and Anuradhapura from the year 2012 to date [118]. Apart from the above mentioned institutes, organizations such as Atomic Energy Authority, Industrial Services Bureau, Universities, and individual researches monitor the ambient air quality with different objectives.

2.5.3 Previous ambient air pollution status in Colombo

The time-series analysis was conducted using the 24-hour average ambient concentrations of PM_{10}, NO_2, CO, O_3 and SO_2 air pollutants data obtained from fixed air pollution monitoring station located at Fort, Colombo from 1998 to 2008 to describe previous ambient air pollution status in Colombo [109]. According to Figure 2, 24 hour averages of ambient PM_{10} level in Colombo throughout the years have stayed relatively within the 60 to 82 µg/m^3 range with a slight decreasing trend from 2003 to 2008. These values steadily exceeded WHO latest guideline value of 50 µg/m^3 for PM_{10}. However, there is a slight decreasing trend of PM_{10} from 2003 to 2008 (Figure 2) and considerable decreasing trend since 2008 [109]. This could be due to the introduction of vehicle emission testing program and promotion of tax concession on newer cleaner vehicles [110, 113]. 24 hour averages values of ambient NO_2 level in Colombo throughout the years have remained relatively within the 0.030ppm to 0.050 ppm range with a slight decreasing trend from 2003 to 2008 (Figure 2). High pollutant concentration was observed during the months of December to April having dry weather conditions. On the other hand, low pollutant concentration was observed during the months of June to September having wet weather conditions. 24 Hour average values of ambient CO level in Colombo throughout the years have remained relatively within the 1ppm to 2ppm range with a remarkable decreasing trend from 2005 to 2008 (Figure 2). USEPA Standard for CO is 9 ppm (10 mg/m^3) and therefore CO is not a major air pollutant in

Sri Lanka. 24 Hour average values of ambient SO_2 level in Colombo throughout the years have remained relatively within the 0.02ppm to 0.08ppm range with an increasing trend from 2003 to 2008 (Figure 2). USEPA Standard for 24 hour SO_2 is 0.014ppm. Thus city of Colombo was exposed to high SO_2 pollution during this period. 24 Hour average values of ambient O_3 level in Colombo from July 2007 to June 2008 one year period shows that moderate peaks in December and January and prominent high peaks in April and June (Figure 2). This also could be explained as a result of dry weather condition during these four months. Table 7 shows the results of the 1998 to 2008 for the above five pollutant exceedance of the Sri Lankan national standards and the WHO guideline values.

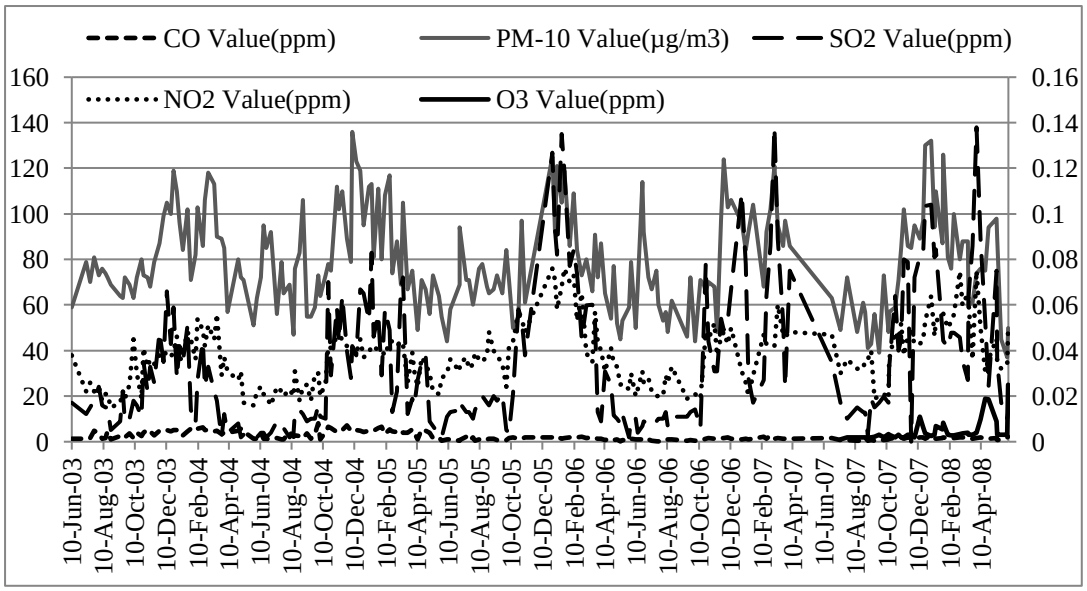


Figure 2: PM_{10}, NO_2, CO, SO_2 and O_3 24 hour average values from 2003 to 2008 at Colombo Fort Air Pollution Monitoring Station

**Concentrations of O_3 and SO_2 are shown in secondary axis*

Table 7: Results of the 1998 to 2008 for the pollutant exceedance of the national standards and the WHO guideline values in Sri Lanka

Year	PM_{10}				NO_2			
	Days of data	Hourly maximum (μgm^{-3})	Total days (%) exceed NAAQS 100μgm^{-3}	Total days (%) exceed WHO 50μgm^{-3}	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS 100μgm^{-3} 0.0494ppm	Total days (%) exceed WHO 40μgm^{-3} (0.0197ppm)
1998	224	101	1 (0.4)	32 (14.3)	224	0.093	4 (1.8)	31 (13.8)
1999	350	132	9 (2.6)	50 (14.3)	343	0.076	13 (3.8)	49 (14.3)
2000	350	145	7 (2.0)	49 (14.0)	350	0.067	16 (4.6)	51 (14.6)
2001	91	103	1 (1.1)	11 (12.1)	112	0.082	8 (7.1)	16 (14.3)
2002	126	120	2 (1.6)	16 (12.7)	147	0.059	7 (4.8)	21 (14.3)
2003	189	119	3 (1.6)	27 (14.3)	203	0.046	0 (0.0)	24 (11.8)
2004	364	136	12 (3.3)	51 (14.0)	371	0.056	5 (1.3)	45 (12.1)
2005	357	126	10 (2.8)	49 (13.7)	343	0.076	7 (2.0)	49 (14.3)
2006	357	124	9 (2.5)	45 (12.6)	357	0.076	11 (3.1)	48 (14.3)
2007	280	132	7 (2.5)	34 (12.1)	182	0.064	3 (1.6)	26 (14.3)
2008	189	126	3 (1.6)	23 (12.2)	140	0.075	9 (6.4)	20 (14.3)
Year	CO				SO_2			
	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS I -hour 30mgm^{-3}	Total days (%) exceed WHO 35ppb (35000ppm)/ 40mgm^{-3}	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS Annual- 0.03 ppm / 24 hour- 0.14 ppm	Total days (%) exceed WHO 20$\mu g/m^3$
1998	224	2.508	0 (0.0)	0 (0.0)	224	0.099	0 (0.0)	0 (0.0)
1999	350	2.27	0 (0.0)	0 (0.0)	350	0.095	0 (0.0)	0 (0.0)
2000	343	2.94	0 (0.0)	0 (0.0)	350	0.166	2 (0.6)	2 (0.6)
2001	105	8.197	0 (0.0)	0 (0.0)	112	0.14	1 (0.9)	1 (0.9)
2002	140	5.536	0 (0.0)	0 (0.0)	133	0.116	0 (0.0)	0 (0.0)
2003	182	5.332	0 (0.0)	0 (0.0)	203	0.066	0 (0.0)	0 (0.0)
2004	364	8.108	0 (0.0)	0 (0.0)	343	0.067	0 (0.0)	0 (0.0)
2005	336	5.981	0 (0.0)	0 (0.0)	308	0.127	0 (0.0)	0 (0.0)
2006	329	2.289	0 (0.0)	0 (0.0)	357	0.135	0 (0.0)	0 (0.0)
2007	252	2.86	0 (0.0)	0 (0.0)	259	0.138	0 (0.0)	0 (0.0)
2008	161	2.31	0 (0.0)	0 (0.0)	77	0.084	0 (0.0)	0 (0.0)
Year	O_3							
	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS 1Hour200μgm^{-3} (0.0946ppm)		Total days (%) exceed WHO 1hour- 0.12ppm 8 hour-0.08ppm			
2007	175	0.011	0 (0.0)		0 (0.0)			
2008	161	0.025	0 (0.0)		0 (0.0)			

2.5.4 Air Quality Research Studies in Sri Lanka

Research on air quality in Sri Lanka are concentrated on monitoring of urban and rural air pollutants, vehicular air pollution, climate change effects, health related research, indoor air pollutants related research, fiscal policies /cost benefit analysis, air quality modeling and approaches on emission inventory. The Air Resource Management Centre (AirMAC) at the Ministry of Environment are conducting "Air that we Breathe" national symposiums on air quality management every two years' time since 2004 with all stakeholders of air resources to gather present research and forward the findings for policy formulation. Apart from the national commitment several universities, institutes and individual researches are involves in inclusive research studies on air pollution. Several research studies have been conducted to assess numerous methods of air quality monitoring and existing air quality trand patterns in Colombo [119,120, 121 and 122]. Methods of analyzing the particulate matter PM_{10} and $PM_{2.5}$ and elemental analysis in Sri Lanka had described in detail by AEA [123]. Trends of air pollutants in outdoor air (NO_2, SO_2 and $PM_{2.5}$) in major cities from year 2012 to 2018 of Sri Lanka [124, 125] and in Kandy [126] has been studied using passive sampling techniques. Further applicability of passive air samplers to monitor outdoors and indoors air quality have been studied by them [124, 125]. Source apportionment of fine particulate pollution has been conducted for 18 elements by energy dispersive X-ray fluorescence (ED-XRF) [127]. These elements (Black carbon, Pb, Al, Si, Cl, Fe, Na, Zn, Mg, Ni, Cu, V, S, Br, Cr, K, Ti, and Ca) were analyzed by positive matrix factorization technique to explore the possible sources of atmospheric aerosols in Colombo [127]. Similar research has been conducted in Kandy and EAP PMF of wide-ranging sources for domestic and community areas were created as smoke burning, sea salt, soil, traffic, biomass and industry sources [128]. Researchers have studied on the atmospheric deposition of

polycyclic aromatic hydrocarbon and heavy metals in Kandy [129]. Toxic gas emissions and dispersion of solid waste disposal site were studied by NBRO [130]. Several researchers have studied the association with air pollution and human exposure of different urban and rural populations in Sri Lanka [131, 132, 133]. Among them human exposure to aerosol pollution of city dwellers [134], police officers [135], children [136], bus drivers [137] have been studied in detail. Passenger exposure to black carbon and fine particulate matter in city of Colombo has been measured [138]. In this study nearly 150km distance was considered when monitoring personal exposure of black carbon and $PM_{2.5}$ over 800 minutes commuting in the public buses travel in city of Colombo. Results showed that median personal exposure of black carbon concentration and $PM_{2.5}$ was 13.58 $\mu g/m^3$ and 108.39 $\mu g/m^3$. Effects related to the phase-out of the lead in gasoline has been studied by comparing the blood lead levels of child respondents [139]. Results confirmed concentrations of Pb in blood have indicated potential toxic levels in traffic policemen and children in Sri Lanka. Further, based on these research findings, in the year 2002, the removal of leaded petrol was taken place. Another study was conducted six months later to see the effect of the phase-out of Pb in petrol. Findings indicated that lead concentrations in ambient air had rapidly decreased [140]. The contamination of diesel and petrol fuels in Sri Lanka also has been studied [141].

Some researchers have studies on the epidemiological and exposure effects of air pollution [139, 142, 143, 144, 145, 146, 147, 148 and 149]. Most of the reported indoor air quality research are “descriptive observational” research work and exposure levels have been evaluated using proxies such as number of windows in the house, having a separate room for sleeping, type of cooking fuel, presence of smokers, , etc… [144, 145, 146, 147 and 148]. Concentrations of particulate matter fractions and kitchen

characteristics among solid fuel and LPG using households in Sri Lanka also has been studied and the study was focus on size of different PM produced in wood and LPG usage [149]. Further different chemicals released from indoor combustion sources have been described [150]. Relation between biomass usage as a cooking fuel and indoor air pollution has been studied extensively and several research approaches been done to identify its dimension and impacts on, women (especially during pregnancy), children [148, 149 and 152, 153], sensitive groups [48 and 154] and experimental mitigation approaches also has been studied [155]. Furthermore, personal exposure on children and effects of indoor air pollution on children has been studied by few researchers [143, 144, 147 and 148]. In-depth description on indoor environmental quality and health risk has been written by Nandasena et al in Chapter 12 on Combustion and Cook stoves [156]. Exposures to air toxics, polycyclic aromatic hydrocarbons from environmental tobacco smoke have been studied by several researchers [157, 158 and 159]. Exposure to cigarette smoke and exposure to other indoor smokes such as mosquito coils, joss sticks; long-term exposure at work place; in houses and in indoor public places also has been studied [158, 159, 160 and 161].

Further to above mentioned research work, initial work on effects of indoor air quality in office buildings on occupant illness symptoms (Sick building Syndrome) [162] and indicating indoor air pollutant parameters to evaluate ventilation conditions in commercial and office buildings [163] has been studied. Effects of outdoor air pollutants on the road-side workplace interiors with air conditioners has been studied as an exposure assessment [164]. Research on impact of airborne biological pollutants on pulmonary health of preschool children in rural and urban sites has been studied [165], and identification of specific bacteria in Kandy air using real-time PCR technique was

carried out [166,167]. Further assessment of air quality using Lichens [168, 169] has also been highlighted. Several research approaches have been considered on the effects of air pollution on Agriculture crops [170, 171].

Project related to urban air quality management in Sri Lanka has been developed in 2004 and programme comprised on institutional development vehicle emission reduction fuel quality improvement and reviewing of fiscal policies on fuels and vehicles [172]. The implantation of ongoing vehicle emission testing programme in 2008, improvement of fuel quality Euro IV were important achievements of this programme. Best practices and effectiveness of the vehicle emission testing programme has been studied with the experience from Hong Kong [173]. Future improvements of the vehicle emission testing programme have been studied using methods for developing driving cycle [174]. Attitude survey has been conducted by using structured questioner aiming vehicle owners, technical staff of the VET centers [175]. Evaluation of economic, financial, social and environment impacts on introducing a tax concession for electrical powered, liquid petroleum (LPG), compact natural gas (CNG) and hybrid vehicles were studied [113] and implemented in the budget in year 2010. This decision was affected to increase the number of hybrid and electric vehicle fleet in Sri Lanka. Assessment of net impact by changes of fiscal policy on rolling stocks and fossil fuel from 2010 to date in Sri Lanka and marginal increase of air pollution result on those policies and policy intervention on AQM [176] have been studied. Hospital admission air pollution and health impact of auto-diesel emissions has been studied using adjusted cost of illness approach [177].

Other areas of concern research are mitigation of climate change and GHG emissions; development of an inventory for atmospheric emission; development of air quality index; transboundary air pollution and air quality modeling approaches in Sri Lanka. Concept of Sri Lankan industry and challenges in facing of "climate change mitigation" [178]. To secure energy crisis, an alternative for LPG, biogas technology related research has been carried out [179]. Sri Lankan Green House Gas (GHG) Emission inventory and policies to control GHG emissions has been studied [180]. Another research has been studied on control of GHG emissions in Aviation industries [181]. Researches have looked at the possible effects of transboundary air pollution in Kandy [182] and Anuradhapura [183]. Several researches have carried out research on developing of atmospheric emission inventory in Sri Lanka [184, 185]. However, thus far a complete atmospheric emission inventory has not been developed. The diversity of lichens in the Horton Plains National Park with the correlation of atmospheric purity index has been studied [186]. To provide the general public with air quality information and health concerns attributed to different levels of air pollution, Air Quality Index (SLAQI) for Sri Lanka has been developed [187]. Fewer review articles were also available which covers the various aspects of environmental pollution relevant to Sri Lanka [146, 188].

Below explains some of the air quality modeling approaches in Sri Lanka. US-EPA SCREEN -3- model and AUSPLUME (Australian Plume) model have been used to study the contribution of major thermal power plants emissions in Western province as a tool for urban planning approach [189]. Further AUSPLUME model has recommended for air pollution regulatory purposes [189]. Furthermore AUSPLUME dispersion model has been used for stack emission modeling in the process industry. It

has been used to predict the downwind concentrations of a substance in the stack emission of a cement plant in Sri Lanka [190]. Further findings of this research have showed the criticalness of the industrial stack emissions and recommended the model for process of Environmental Impact Assessment (EIA). Hybrid mesoscale wind model which simulating the wind flow in three dimensional spaces has been applied to Sri Lanka under different synoptic flows in order to check the performance of the models [191]. The model consists of two sub models namely the predictive surface wind model and diagnostic mass consistent model. Both sub models have been worked well for simulating locally induced thermally driven circulations over Sri Lanka. Further Hybrid mesoscale wind model has predicted pollutant concentration and wind behavior [191]. Application of Geographical Information Systems (GIS) to identify the air pollution potential areas in the city of Colombo was another air quality modeling approach [192]. The spatial variations of monthly exposure levels of ambient NO_2 levels in Colombo city and neighboring areas during the period of North East monsoon has been analyzed using the spatial interpolation technique and compared against spatial distribution of positive and negative factors [192]. Results have found that land transport was highly correlated with ambient NO_2 concentrations and population densities, housing and underserved settlements were significantly correlated [192]. Researchers have looked at the possibility of using CFD computer modeling tools on urban design and planning [22, 193, 194]. ENVI-met, a CFD model has been used to estimate planning and land use variables related to air quality effects [22, 193, 194]. Several ENVI-met simulations has been conducted such as change of street vegetation, building geometry, change of soil condition (bare soil vs. paved sidewalks) increase and decrease of mobile sources, in order to estimate the effects of urban planning variables and land use [22, 193, 194].

CHAPTER 3

AIR QUALITY MODELS FOR PHOTOCHEMICAL DEGRADATION

3.1 CHEMISTRY OF THE TROPOSPHERE

Photochemical degradation that lead to ground level ozone formation is taking place in the troposphere which is the lowest layer of the atmosphere of the Earth. It has a series of layers based on temperature, and moving upward from the ground level, there are five layers. These layers are in the order of troposphere; stratosphere; mesosphere; thermosphere and exosphere [195, 196]. Troposphere has a large content of water vapour, the bulk of clouds, local and global scale weather. [195, 196]. The upper boundary layer of the troposphere is known as the tropopause. It varies on time of the year as well as on latitude ranging from 10 km (at high latitudes) to 15 km (at the equator) [195]. In the troposphere, air temperature linearly decreases with altitude [196]. Therefore, in the troposphere strong vertical mixing is taking place with the negative temperature gradient. This will further allow fast chemical movements [196]. The free troposphere (FT) and the planetary boundary layer (PBL) are the subdivision of the troposphere [197]. The depth of the PBL is around 1km and it varies significantly according to the time of day and meteorological conditions [197]. The troposphere contains about 90% of the atmospheric mass and though its bulk composition is around 78% of N_2, 21% of O_2. The remaining 1% is made up of noble gases, CO_2, and other trace constituents made up of a various gases in the atmosphere [77, 198]. Even though N_2, and O_2 are in bulk composition, important role in the atmospheric interactions are governed by the minor gases. Out of these minor gases, VOCs are the most important

trace constituent in the progression of photochemical air pollution. They are generated from different biogenic and anthropogenic sources [199, 200]. In section 2.3, VOC's are explained in detail.

3.2 TROPOSPHERIC CHEMICAL REACTIONS

Ozone (O_3) is produced in the presence oxides of nitrogen (NOx) and volatile organic compounds (VOCs) in troposphere and the interaction among NO_x, VOC and O_3 are determined by the complex nonlinear photochemistry [10, 11]. The key removal process for VOC's in the troposphere are the physical loss processes of dry deposition, wet deposition and the chemical transformation procedures of photolysis reaction with nitrate (NO_3) radical, reaction with O_3 and hydroxyl (OH) radicals [202]. These chemical cycles involve in the dispersion process of VOCs are described below.

3.2.1 $NO_X - O_3$ Cycle

The majority of NO_X (NO and NO_2) is emitted as NO in the troposphere. Fossil fuel combustion and biomass burning are the major sources of NO. The key source of NO_2 is the response of NO with O_3. As shown in the reactions 1, 2, 3; NO, NO_2 and O_3 are interconnected as a cycle. The photolysis of NO_2 forms NO and O ($3P$) which gives O_3. NO_2 is then regenerated through the reaction of NO and O_3 [10, 11].

$$NO_2 + hv \rightarrow NO + O(3P)\ (\lambda < 420nm) \qquad 1$$

$$O(3P) + O_2 + M \rightarrow O_3 + M \qquad 2$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad 3$$

Since the inter conversion between these species is so fast, a steady state is reached within a few minutes.

This photo stationary state relation determines the O_3 concentration. The O_{3ss} concentration is proportional to the $[NO_2]/[NO]$ ratio [10, 11].

3.2.2 Tropospheric VOCs transformation processes

Figure 3 shows VOCs role in atmospheric chemistry in summary.

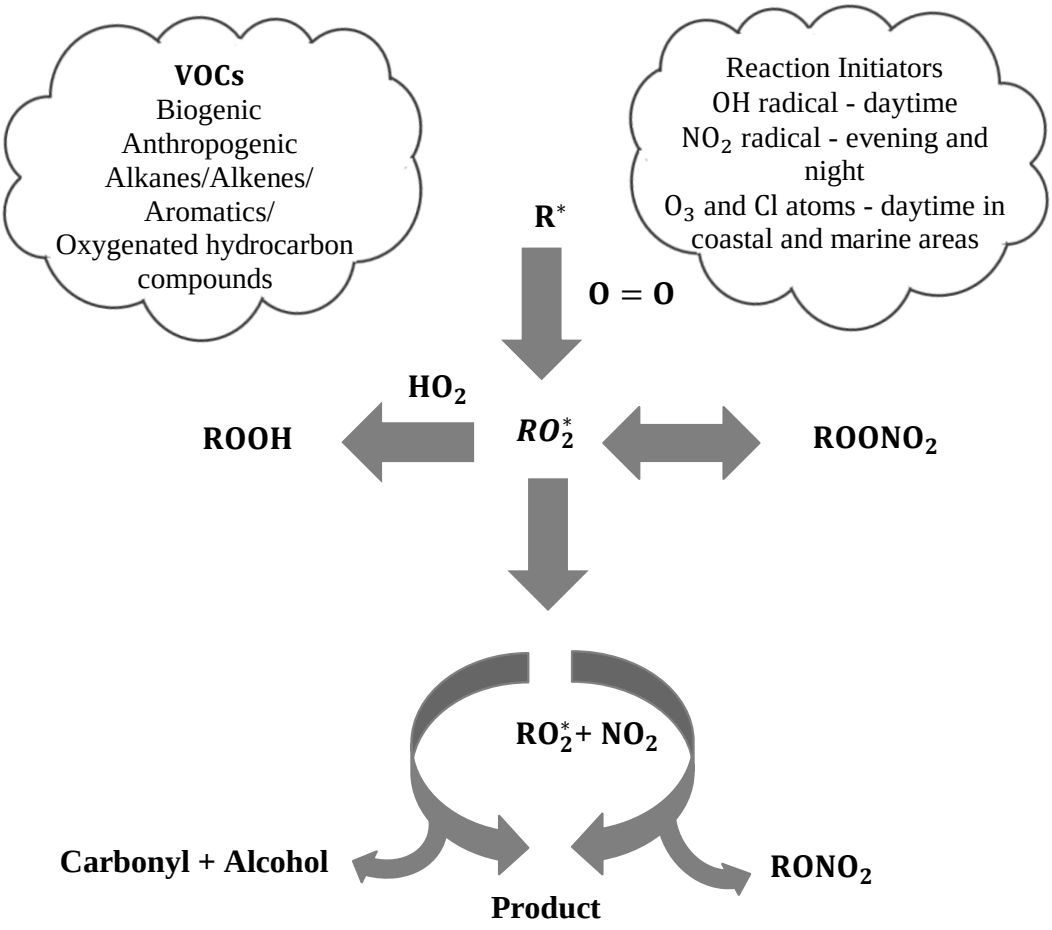


Figure 3: $VOCs$ role in atmospheric chemistry [10]

There are several rection initiators, for the transformation process of VOCs. One mechanism is OH radical reaction with VOCs, during daytime hours (explain in the below sections). Another mechanism is reaction during night time and evening hours with the NO_2 radical (explain in section 3.2.3). Further mechanisms are reaction with

O_3 and reaction with Cl atoms, during daytime hours, in coastal and marine areas and explain in section 3.2.4 [11].

a. **OH Reaction with VOCs**

OH Chemistry is the most important process in the troposphere because of reactivity and relatively high concentration. It reacts in catalytic cycles and acts as a scavenger for a many of organic compounds in the troposphere. Therefore, the OH radical controls the tropospheric concentration of many trace gases. The concentration of OH is maintained in the order of 106 molecule cm^{-3} [77]. In terms of reactivity, the OH radical initiates radical-chain oxidation. In the presence of water vapour, the main source of OH is photolysis of O_3 by ultraviolet light (reaction 4).

$$O_3 + h\nu \rightarrow O(1D) + O_2 \ (290\text{nm} \leq \lambda \leq 335\text{nm}) \qquad 4$$

The bulk of the formed excited oxygen, $O(1D)$ atoms is quenched to ground state oxygen, $O(3P)$ atoms (reaction 5 and 6).

$$O(1D) + M \rightarrow M + O(3P) \ (M = N_2, O_2) \qquad 5$$

$$M + O(3P) + O_2 \rightarrow O_3 + M \qquad 6$$

A fraction of $O(1D)$ atoms react with water vapour to generate 2 OH radicals (reaction 7).

$$O(1D) + H_2O \rightarrow 2OH \qquad 7$$

Approximately, OH radicals of 0.2 are produced per $O(1D)$ formed at 298 K, 50% atmospheric pressure and relative humidity [11]. CH_4 and CO are the two major sinks of OH in the troposphere.

OH radical and the peroxy radicals HO_2 and RO_2

The reaction with OH radicals is the leading scavenger for the bulk of the gas-phase VOCs existing in the troposphere. Oxidation of CH_4 is similar to that of other VOCs and proceeds via the concept of a H to form R, (an alkyl radical where R denotes a generalized organic fragment).

Peroxy radicals (RO_2) are formed in reaction 8 and 9 respectively.

$$OH + RH \rightarrow H_2O + R \quad (8)$$

$$M + O_2 + R \rightarrow M + RO_2 \quad (9)$$

The fate of RO_2 is determined by the NO_X concentration. At high NO_X conditions, peroxy radicals react with NO to give an alkoxy radical (RO) and NO_2 (reaction10). Then the photolysis of NO_2 occurs resulting in the formation of one O_3 molecule (reaction 11 and 12).

$$RO_2 + NO \rightarrow RO + NO_2 \quad (10)$$

$$NO_2 + h\nu \rightarrow O(3P) + NO \ (\lambda < 420 \text{ nm}) \quad (11)$$

$$M + O(3P) + O_2 \rightarrow M + O_3 \quad (12)$$

The reaction of the alkoxy radicals with O_2 to form oxygenated species ($R'CHO$) is the most common completion of this cycle (reaction 13).

$$RO + O_2 \rightarrow R'CHO + HO_2 \quad (13)$$

Then, the hydroperoxy radicals HO_2 can react with NO and regenerate OH to complete the cycle (reaction 14).

$$HO_2 + NO \rightarrow NO_2 + OH \quad (14)$$

The overall reaction (reaction 15) of this cycle is:

$$OH + RH + 2NO + 2O_2 \rightarrow OH + R'CHO + H_2O + 2NO_2 \quad (14)$$

For instance, two molecules of O_3 are formed from NO_2 photolysis; and, the oxygenated hydrocarbon species is also formed. In low NO_X conditions, the peroxy radicals will react with HO_2 or with other peroxy radicals instead, forming radical and non-radical species (reaction 16, 17, 18 and 19).

$$RO_2 + RO_2 \rightarrow RO + RO + O_2 \quad (15)$$

$$RO_2 + RO_2 \rightarrow ROH + ROH + O_2 \quad (16)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \quad (17)$$

$$RO_2 + HO_2 \rightarrow ROH + H_2O + O_2 \quad (18)$$

The oxidation process is more complicated for larger hydrocarbons and other classes of VOCs. Innovative research has been conducted in this area [202] to understand the VOCs oxidation in the troposphere [10] and their potential in forming O_3 through photochemistry [203, 204, and 205]. Thus far, rate constants have been measured for nealy 700 VOCs for OH radical reaction [10]. However, rate constants for number of VOCs are not experimentally calculated Hence, new methods have been proposed to estimate the OH radical reaction with VOCs. Most often-used method is the structure-activity relationship developed, extended and tested by Atkinson [206, 207, 208] and updated in 1995 [209].

OH reaction with CO

OH radical reacts with CO producing CO_2 and an H atom which reacts fast with O_2 to form the hydroperoxy radical (HO_2) which is shown in reaction 20 and 21[10, 11].

$$OH + CO \rightarrow H + CO_2 \quad (19)$$

$$H + O_2 + M \rightarrow M + HO_2 \quad (20)$$

"HO_2" is a key peroxy radical in the troposphere which exist for 1 min in pure air and less than that in impure air [210]. The major source of HO_2 is the reaction of OH with CO, H_2, O_3 and by the reaction with O_2 and the decomposition of the alkoxy radicals (reactions 20 and 21). $HCHO$ is another major source of HO_2. It can either photolysis or react with OH to form the CHO radical (reaction 22 and 24). The CHO radical then reacts with $O_2$to form HO_2 and CO. Besides, the photolysis of $HCHO$ has a non- radical channel (reaction 24) forming CO. Eventually, the CO formed from reactions 23 and 25 will produce HO_2 through reactions 20 and 21. Similar atmospheric process can be envisaged in other carbonyl species, e.g. acetaldehyde [10, 11].

$$HCHO + h\nu \rightarrow H + CHO \ (\lambda < 370 \text{ nm}) \qquad 21$$

$$HCHO + h\nu \rightarrow CO + H_2 \qquad 22$$

$$HCHO + OH \rightarrow H_2O + CHO \qquad 23$$

$$CHO + O_2 \rightarrow HO_2 + CO \qquad 24$$

The O_3 initiation reaction with alkenes is another source of HO_X radicals. This reaction forms a carbonyl compound and a Criegee biradical. The Criegee biradical can be collisionally stabilised or undergo unimolecular decomposition. Unimolecular decomposition of Criegee biradicals leads to the production of HO_X (OH and HO_2) radicals. This radical can form OH radicals at changing concentration based on the alkene structure. Despite the O_3 initiated reaction with alkenes being relatively slower than NO_3 and OH and initiated reactions with alkenes, it has been proven that this is an important route for HO_X formation [211].

OH is regenerated in the atmosphere mainly by the oxidation of CO and hydrocarbons to produce HO_2. HO_2 reacts with NO at high [NO_X] (reaction 26) or O_3 at low [NO_X]

(reaction 27) to produce OH. At low [NO_X], HO_2 can also react with itself producing hydrogen peroxide H_2O_2 and removing HO_2 radicals from the system (reaction 28) [10, 11].

$$HO_2 + NO \rightarrow OH + NO_2 \quad 25$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad 26$$

$$HO_2 + HO_2 \rightarrow H_2O_2 \quad 27$$

As above, the OH radical initiates the formation of RO_2, RO and HO_2 radicals. As OH and hydroperoxy radical (HO_2), O_3, NO_X (NO and NO_2) and are interacting in one system, OH radical cannot be treated alone [10, 11].

3.2.3 NO_3 initiated reaction

In contrast to daytime chemistry, nighttime chemistry leads to removal of O_3. Nevertheless, it can form secondary pollutants. Nitrate radical (NO_3) is the major nighttime radical and this is produced by oxidation of NO_2 via O_3 gradual process.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad 28$$

Another source includes the decomposition of dinitrogen pentoxide (N_2O_5) which is a reversible reaction.

$$N_2O_5 + M \leftrightarrow NO_3 + NO_2 + M \quad 29$$

NO_3 absorbs visible wavelengths strongly and rapidly photolyed during daytime [10, 11

$$NO_3 + h\nu \rightarrow NO + O_2\ (585 < \lambda < 640\ \text{nm}) \quad 30$$

$$NO_3 + h\nu \rightarrow NO_2 + O(3P)\ (\lambda < 640\ \text{nm}) \quad 31$$

NO_3 also reacts rapidly with NO which has a significant daytime concentration compared to the night-time.

In general, the NO_3 radical will abstract the H-atom from the alkyl group of a saturated organic compound. The alkyl radical will then react with oxygen under atmospheric conditions [10, 11].

$$NO_3 + RH \rightarrow HNO_3 + R \qquad 32$$

In contrast, the NO_3 initiated reaction with alkenes forms an supplement mechanism. Consider the effect of NO_3 with propene as an example. The preliminary addition of NO_3 can added to the double bond at whichever end as shown in reactions 33 and 34.

$$CH_2 + NO_3 = CHCH_2 + M \rightarrow M + CH_2CHCH_2(ONO_2) \qquad 33$$

$$CH_2 + NO_3 = CHCH_2 + M \rightarrow M + CH_2CH(ONO_2)CH_2 \qquad 34$$

Once the alkyl radicals have been generated, they go on to react in an analogue manner, as the alkyl radicals formed by OH reaction in the daytime [10, 11].

3.2.4 O_3 initiated reactions

Criegee first suggested the mechanism of the O_3 reaction with the alkenes in the late 1940s. O_3 initiated reactions are only important for unsaturated compounds, such as alkenes. When the addition of O_3 undergo with the alkenes double bond, it forms an ozonide. This is an energy-rich initial component, that then undergo fast decays through two pathways to form a vibrationally excited carbonyl oxide which is known as Criegee intermediate and carbonyl products [212]. The branching ratio of the ozonide decomposition varies according to the alkene structure [10, 11, 212]. The stability of

Criegee intermediates can be achieved either unimolecular decomposition of the products or collisionally stabilized by a third body.

The stabilized form of this intermediate will react with H_2O, NO_2, SO_2, NO, and CO to give a carbonyl compound and SO_3, CO_2, NO_2, NO_3 and H_2O_2 respectively assuming that the leading reaction is with water vapour under tropospheric conditions [212]. For alkyl-substituted Criegee intermediate, an important decomposition pathway is through a vibrationally heated hydro-peroxide intermediate to produce a substituted alkyl radical and an OH radical (Figure 4).

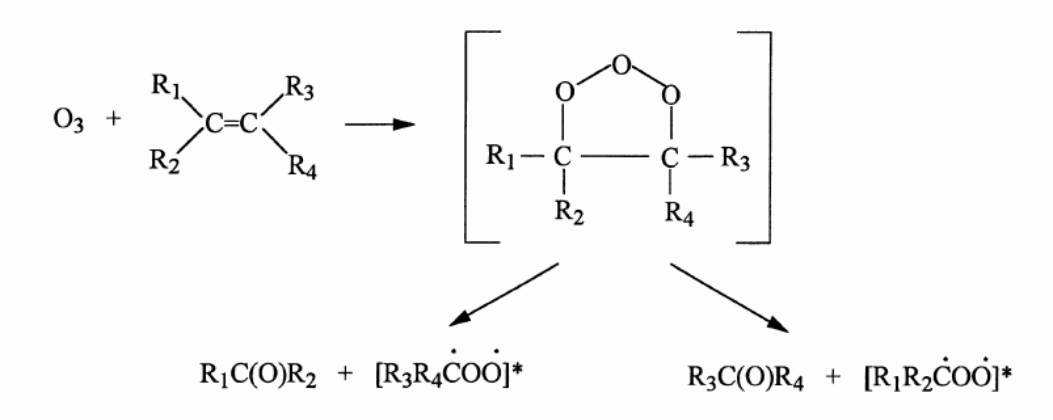


Figure 4: O_3 reactivity with alkenes [11]

3.3 FACTORS AFFECTING THE PHOTOLYSIS

O_3 isopleth diagram (Figure 5) represented the formation of O_3. This is a contour plot of maximum O_3 concentrations as a function of initial NO_X and VOCs [10, 11, 213]. t is created by contour plotting the predicted O_3 maxima achieved from an enormous number of simulations. To achieve this diagram, a large number of initial variable concentrations of VOCs and NO_X data needs to incorporate keeping all other variables set as constants [213, 214, 215, 216].

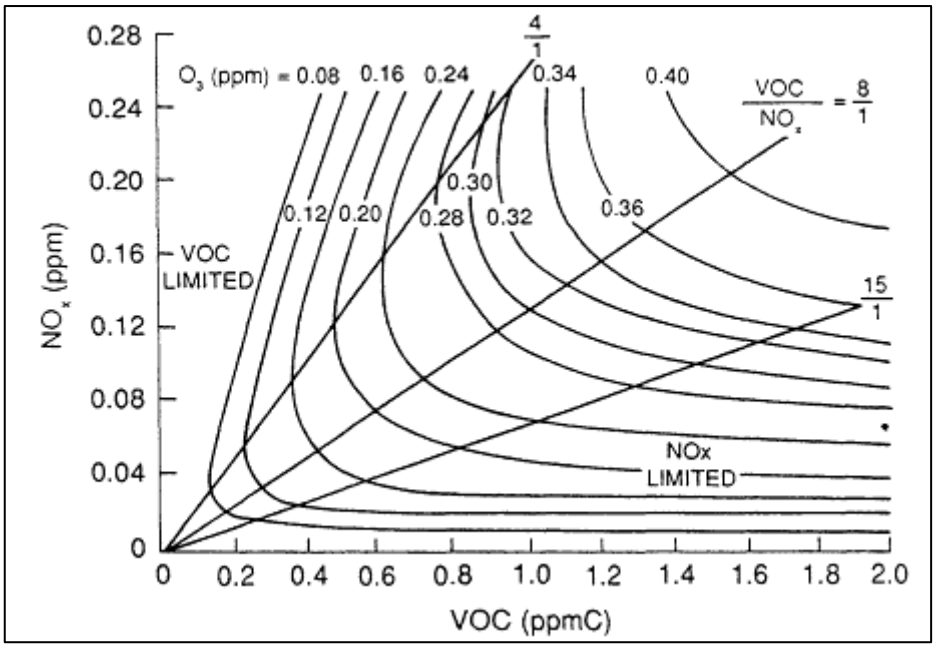


Figure 5: Typical Ozone isopleth plot [213]

Figure 5 represents the NO_X, VOCs and O_3 relationship and it further highlights critical policy development problems related to controlling O_3. O_3 and other related oxidants cannot build up without the combined action of NO_X and VOCs. Thus, controlling photochemical air pollution requires reducing both VOCs and NO_X [213]. Other possible relationships also are looked at to understand the process. Many chemical reactions are

active by radiation of the sun, directly or indirectly. The photolysis is a chemical decomposition caused by light or other electromagnetic radiation. Photolysis has to be taken into account for all the compounds that are photo- labile at the wavelengths in the troposphere. The rate of photolysis (j) for a particular compound is defined by the following equation [10, 11 and 217]:

$$j = \int \sigma \cdot \varphi \cdot I d\lambda$$

Where;

σ = the absorption cross section

φ = the quantum yield, i.e. the probability that an absorbed photon of a given wavelength will cause photodissocation

I = solar photon flux at a given wavelength (λ)

σ and φ are both λ dependent. Also, temperature dependency is associated with "σ"; while pressure dependency is associated with φ. To calculate the solar photon flux, accurate measurements for all photolysis channels are required to be available as a function of λ to determine the rate of photolysis of a particular compound [10, 11 and 217]. The chemistry described in sections 3.2 is generalized and a simplification of the degradation of any VOCs that is present in the atmosphere, however it provides an overview of the chemistry that needs to be included in the chemical mechanism component of any atmospheric model. There are several atmospheric models available, and the chemical mechanism used can be understood using such modeling explained in section 3.4.

3.4 EVOLUTION OF THE PHOTOCHEMICAL MODELING

To predict O_3 concentration, it is necessary to know, how O_3 concentration change in response to NO_X and VOCs. The existing chemical models are serving as a connection between the available laboratory studies and the development of chemical mechanisms. The First chemical model was developed by Hecht, Dodge and Seinfeld [214, 215]. Second model was Dodge mechanism which was introduced in 1977. This model was known as "Ozone Isopleth Plotting Program (OZIPP)" and smog chamber data was simulated with the ozone isopleths [216]. Later USEPA has developed the "Empirical Kinetic Modeling Approach (EKMA)" and foundation for this modelling was based on the Dodge mechanism. EKMA is a "Lagrangian box-model" which associated with NMHC and NO_X (O_3 precursors) and O_3 maximum concentration of a particular city [216, 217]. The base of the O_3 isopleth diagram (Figure 5) has been used in this mechanism and the effects of peak ozone concentrations was achieved by reducing initial concentrations of the NMHC and NO_X [218]. This model was used for longer period aiming at quantitatively reduction of O_3 and for regulatory policies in USEPA [216, 218].

There was a long gap of the development of new models because economical computer hardware was required to run for large models and the technology improvements. The next development of modelling was three-dimension Eulerian-formulated models [217]. These models were involes with the combination of many paramters such as air emissions, meteorological effects and chemical reactions. In late 80's, with the improvements of the computer hardware many chemical models were developed [219]. During this period, widely accepted chemical mechanisms were CB4 & CB5 mechanism [219, 220 and 221], CAL mechanism [222, 223] and the regional acid

deposition model (RADM) [224, 225]. CB4 mechanism was appropriate for the previously used models by the USEPA, namely EKMA, OZIPP and and Eulerian-formulated models [215, 218 and 219]. It has been pointed out that, as a result of above developed models having the similar evaluations, same mechanistic data base and kinetic may affects the accuracy of the model [226]. Then the development of three dimensional regional or global Eulerian atmospheric chemistry models was occurred. These models consist of tens of thousands of grid boxes in which the concentrations of model chemical species are calculated [227]. There are several regional models avialble and extensively used models are Weather Research and Forecasting Model (WRF/ Chem) [228]; the Comprehensive Air Quality Model with extensions (CAMx) [229]; the Community Multi- Scale Air Quality Model (CMAQ) [227]; and the global atmospheric chemistry and transport model (GEOS-Chem) [230]; Typically, these types of models are run with configurations that consist of 10^5 or more grid boxes and required high computational power.

The next step in modeling was the development of explicit mechanisms that needs millions of reactions including every known emitted compound [231]. However available laboratory kinetics data do not support this level of detail. Therefore, there are significant gaps in laboratory kinetics data that prevent the development of explicit chemical mechanisms based only on laboratory measures [232]. Very detailed explicit mechanisms have been developed without very large scale automation. They are namely, Master Chemical Mechanism (MCM) [234, 235 and 236] and National Center for Atmospheric Research Master Mechanism (ARMM) [233].

National Center ARMM has nearly 800 organic species and 2,200 reactions [233]. Various versions of the MCM exist (MCMv3.1, MCMv3.2) and range in size from

about 5,000 to a few tens of thousands of reactions that treat the reaction of 10 to more than 100 emitted organic compounds, their reactive intermediate, and their products [234, 235 and 236]. This model has been verified well with the field measurements and environmental chamber [237, 238]. However, it is too large for routine use. Considering all these factors, commonly used models are the Carbon Bond (CB) Mechanism [221]; the Regional Atmospheric Chemistry Mechanism (RACM) [225, 239, 240 and 241]; Statewide Air Pollution Research Centre Mechanism (SAPRCM) [242] and Master Chemical Mechanism (MCM) [234, 235 and 236]. Summary of the comparison of extensively used chemical models are in Table 8.

Table 8: Comparison of widely used photochemical models

Chemical Mechanisms/ Models		No. of chemical species	No. of Reactions	Ref.	Advantages	Disadvantages
Carbon Bond Mechanism	**CB4**	33 chemical species	82 reactions	[218, 219, 220, 221]	Relatively condensed mechanism; Widely used in U.K., Europe, U.S., Korea, Japan, China, Brazil, Chile, and Australia Has high computational efficiency. NO_X recycling reactions has been added. Expanded inorganic reaction. Presence of updated rate constants Urban to rural conditions have a better representation.	Neither CB4 nor CB5 has a satisfactory performance in simulating aromatic chamber data. Many of the reactions have not been studied experimentally. Not used in policy applications.
	CB5	54 chemical species	156 reactions			
	CB6	92 chemical species	218 reactions			
RACM mechanisms	**RACM 1**	77 chemical species	237 reactions 23 photolysis reactions and 214 chemical reactions	[225, 239, 240, 241]	Moderately condensed mechanism. Detailed description of biogenic O_3 precursors Represent formation of OH and nitrate radical in the forest covers.	Many of the reactions have not been studied experimentally. Not used in policy applications

	RACM 2	119 chemical species	363 reactions			
SAPRC mechanism	**SAPRC**	124 model species	347 reactions	[242]	Shows good consistency with the available laboratory data. Provide precise forecasts of produced VOC on atmospheric impacts.	
	SAPRC-99	76 chemical species	214 reactions			
	SAPRC-07C	118 chemical species	599 reactions			
Master Chemical Mechanism	**MCMv3.2**	5900 species	approximately 13,500	[234, 235, 236]	Mechanism is near explicit. Widely used in supporting field measurements. Selected to design and interpret both chamber and laboratory experiments. A benchmark mechanism to provide support for general modeling. Analyzing the mechanism of SOA. Used in research and policy applications.	Many of the reactions have not been studied experimentally. Too large for routine use. .
	MCMv3.1	4, 647	13,586			
	NCAR Master Mechanism	800	2,200			

3.5 IDENTIFIED RESEARCH GAPS IN AIR QUALITY MODELING IN PHOTOCHEMICAL DEGRADATION

There are many thousands of VOCs emitted in to the atmosphere. Each of these VOCs has its own decomposing mechanism depending on which the O_3 production varies. Therefore the models explained in section 3.4 does not demonstrate all VOC reactions and many of the reactions that have identified also have not been studied experimentally to provide the rate constants on the governing relationships. Further above mentioned chemical models developed by the researchers focus on developed countries where more attention is paid for maintaining air quality, fuel quality and industrial standards. Furthermore, since, photochemical reactions largly depend on the climatic and the

geographical conditions, having different wheather conditions associated with seasonal variations and large land areas in those countries, the photochemical reactions could be considerably different to that of Sri Lanka, a tropical island. Therefore, its own observations on the photochemical degradation combined with numerical modeling in different urban air sheds are essential for decision making.

Several studies have been investigated the relation among NO_X, O_3 and VOC reactivity and $NO_X - VOC - O_3$ sensitivity [243 to 255]. In urban areas this can be affect the design of control strategies to reduce ambient O_3 levels. If $NO_X - VOC - O_3$ sensitivity to certain measurable species could be introduced which have different values to calculate this phenomenon, it will greatly help to identify the interventions required to reduce the O_3 concentration in urban environments. Therefore, the comprehensive analysis of $NO_X - VOC - O_3$ sensitivity is an urgent need for effective ozone control. A true understanding of the relation among O_3, NO_X and VOC is especially important because it suggests the possible role for developing national air quality management plan. Lack of clear understanding on physical phenomenon among O_3, NO_X and VOC interactions has hindered in developing air quality modeling tools with sufficient accuracy. Consequently, development of interventions for the control of O_3 has become a challenging task for the policy makers and regulatory agencies in Sri Lanka.

CHAPTER 4

METHODOLOGY

4.1. BASIC APPROACH IN PRESENT METHODOLOGY

Over-role framework of the Methodology is presented in Figure 6.

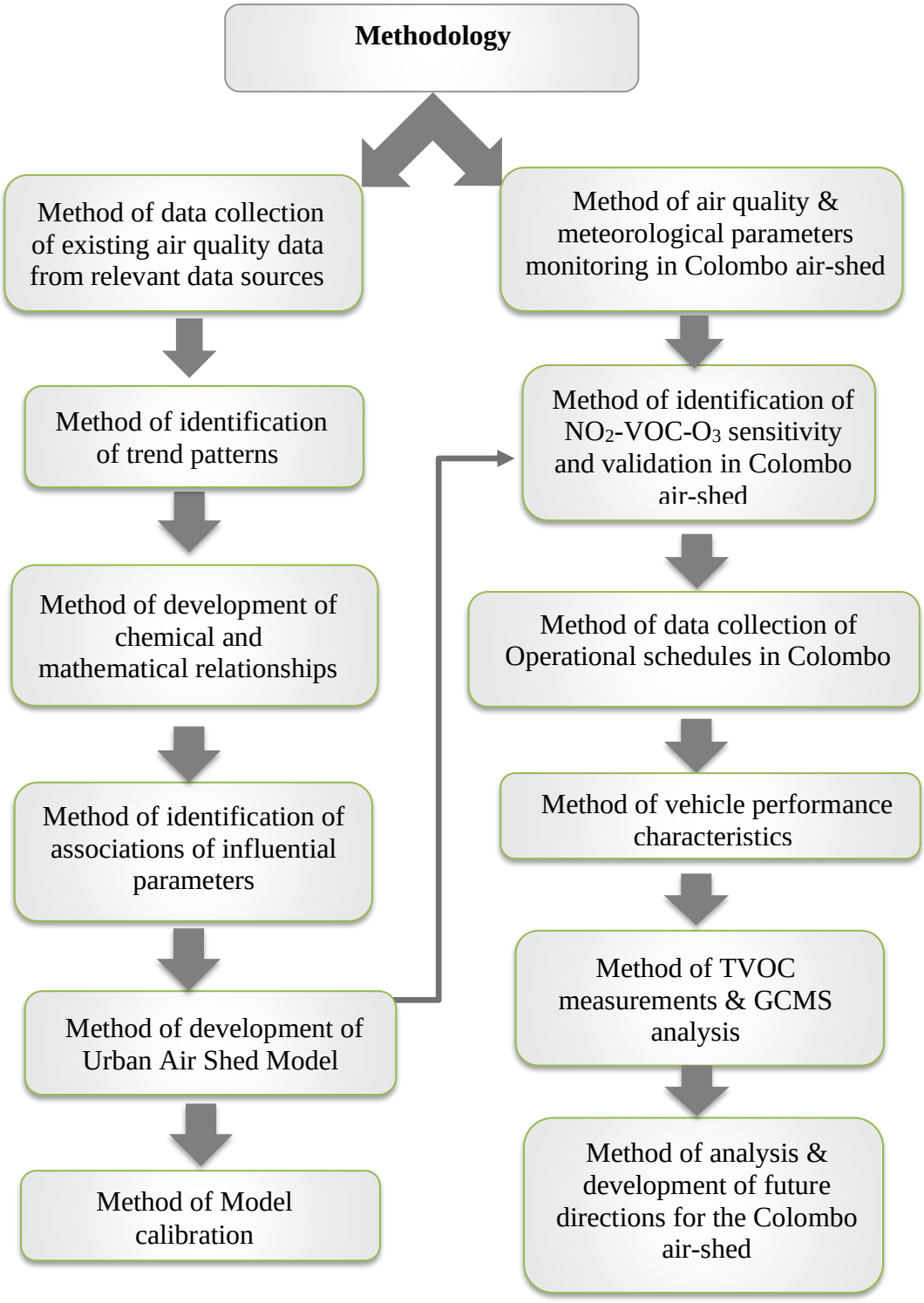


Figure 6: Over-role framework of the Methodology

The study consists of two phases and the flow of the Methodology sections are presented as shown in Figure 7.

Phase I - Method of development of the Urban Air-shed Model

Phase II - Method of analysis of Colombo Air-shed

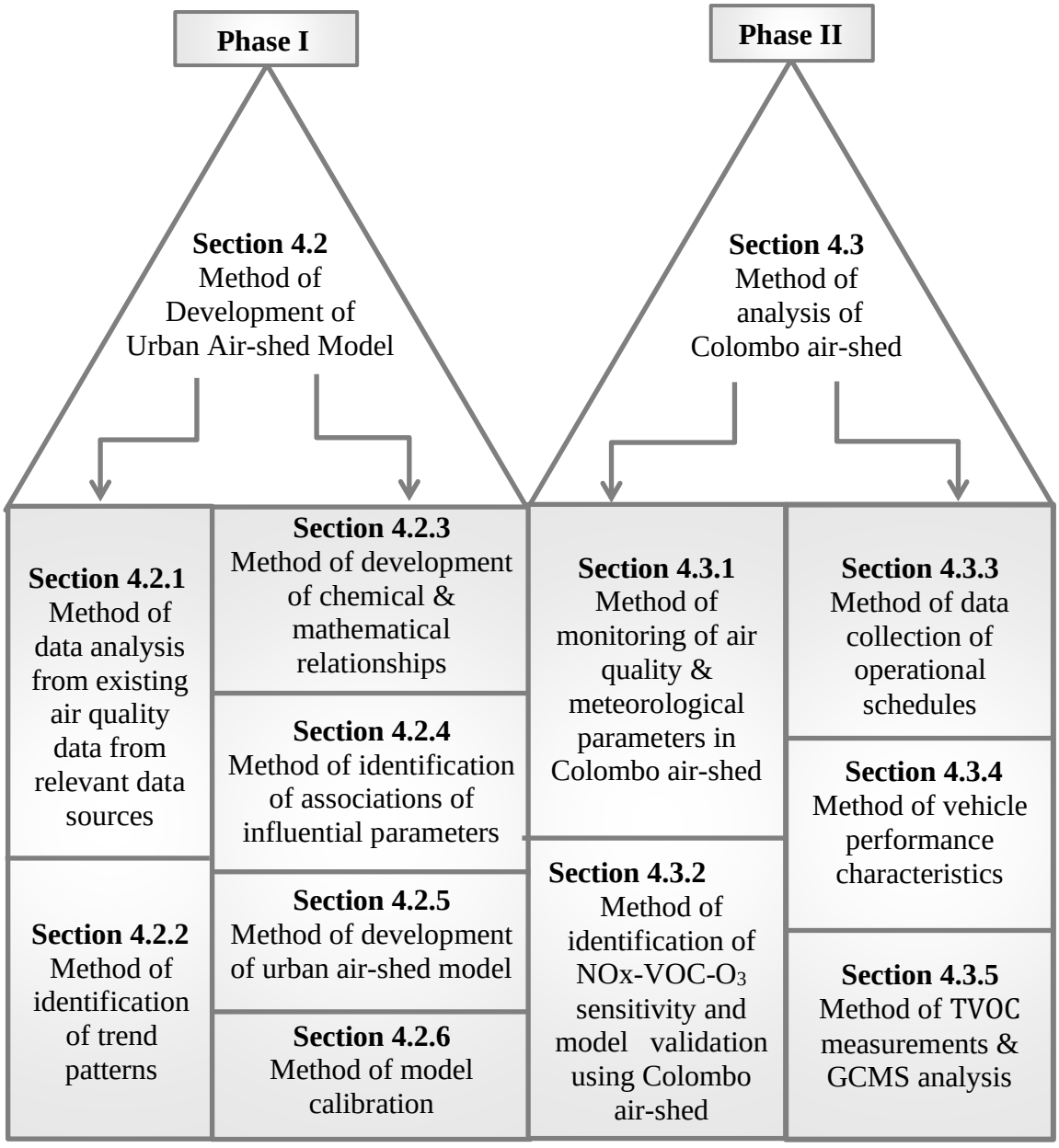


Figure 7: Flow of the of Methodology Sections

4.2 PHASE I- METHOD OF DEVELOPMENT OF URBAN AIR SHED MODEL

4.2.1 Overview of urban air-shed model

Flow chart of the development of urban air-shed model is presented in Figure 8.

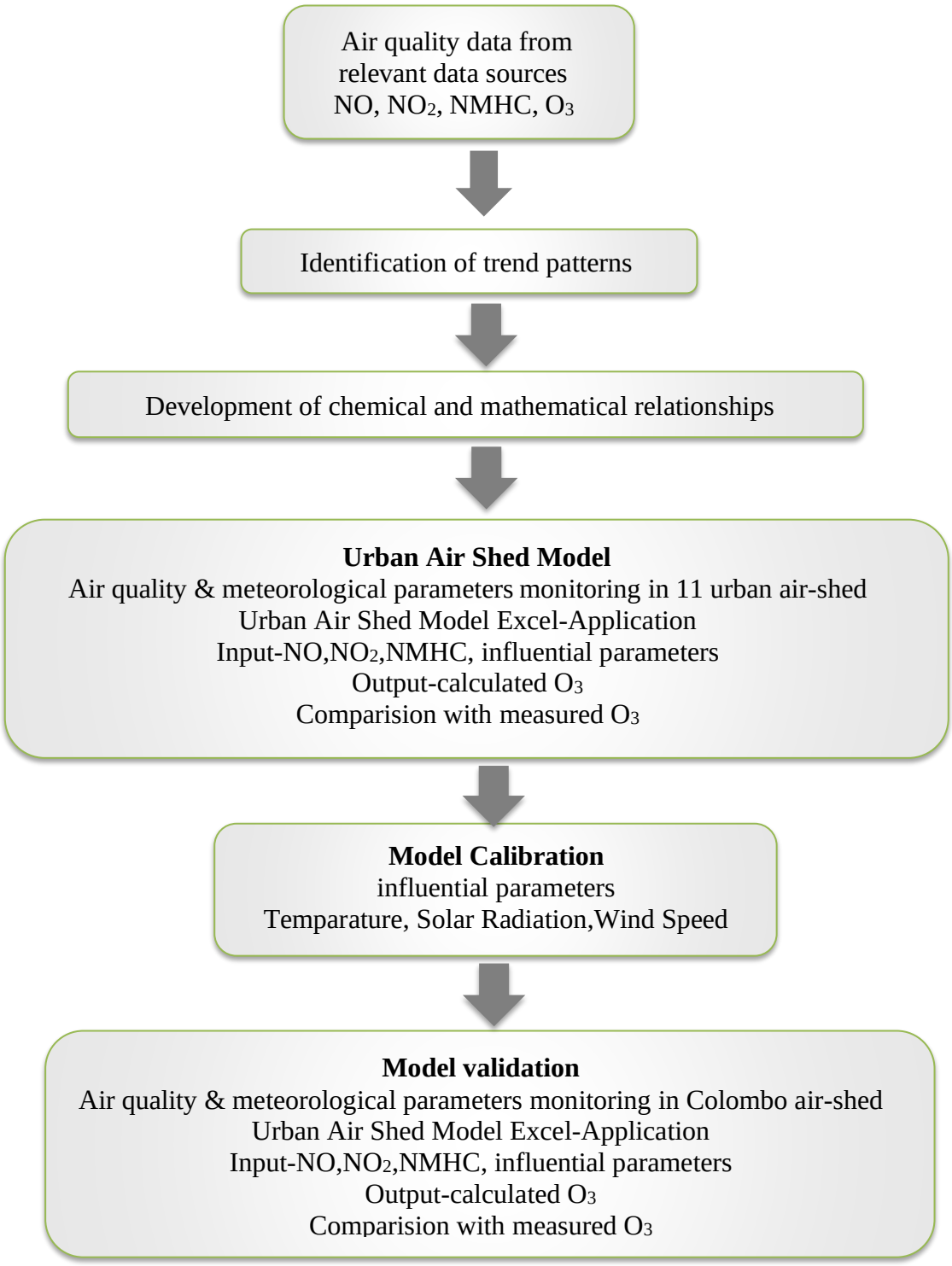


Figure 8: Flow chart of the development of urban air-shed model

4.2.2 Method of data analysis from existing air quality data from relevant data sources

The ambient real time air quality monitoring data obtained from year 2013, 2014 and 2015 were analyzed from the mobile automated monitoring station for eleven cities in Sri Lanka. The eleven cities are Jaffna, Anuradhapura, Colombo, Ratnapura, Kurunegala, Gampaha, Matara, Badulla, Kandy, Nuwaraelliya and Pollonnaruwa that located within eight provinces of the country. Ambient air quality monitoring measurements had been conducted from the mobile monitoring station of CEA (Figure 9) using USEPA standard procedures. Ambient concentration data was obtained for pollutants namely $PM_{2.5}$, PM_{10}, THC (total hydro-carbon), CH_4 (methane), NMHC (non-methanic hydro-carbon), NO_2, NO, CO, SO_2 and O_3 with subsequent meteorological parameters of air temperature, relative humidity, solar radiation, wind speed, and wind directions with their distribution patterns (wind-rows) for the eleven different cities. Data was obtained as every hourly averaged for a period of 7 days covering five week days and the two weekend days.

Figure 9: Equipment's of the mobile monitoring station of CEA

4.2.3 Method of identification of trend patterns

The data in five out of eleven cities were selected for identification of major trend patterns/ outliers/ regimes as initial analysis, while the data of remaining cities were used for validation of the identified outliers/ regimes (Figure 10). The locations of the mobile automated monitoring stations considered for the initial analysis are resided in the cities of Jaffna, Anuradhapura, Colombo, Rathnapura and Kurunegala covering five different provinces in the country (Figure 10). The 24-hour average data of above mentioned pollutants and meteorological parameters at these five different locations was compared with each other to assess air pollution status in different cities. Further similarities and differences of the trend patterns were analyzed to develop the inter-relationships of VOC, NO_2, NO and O_3 pollutants, and the $NO_X - VOC - O_3$ sensitivity. The ambient real time air quality data of all air pollutants and meteorological parameters were presented in weekly basis for the detailed analysis. Validation was carried out for the $NO_X - VOC - O_3$ sensitivity for developed regimes using ambient real time air quality monitoring data collected in weekly based for the rest of the six cities (Matara, Badulla, Pollonnaruwa, Gampaha, Kandy, and Nuwaraelliya) for the above mentioned pollutants and the trends were compared to confirm the proposed $NO_X - VOC - O_3$ sensitivity for Sri Lankan cities.

4.2.4 Method of development of chemical & mathematical relationships

Chemical relation-ship was developed from the gathered literature and related to the air quality data obtained in section 4.2.2 to identify two regimes with $NO_X - VOC - O_3$ sensitivity. Chemical reactions were explained in details for both NO_X sensitivity and VOC sensitivity. Mathematical equations were developed for the identified two regimes with $NO_X - VOC - O_3$ sensitivity.

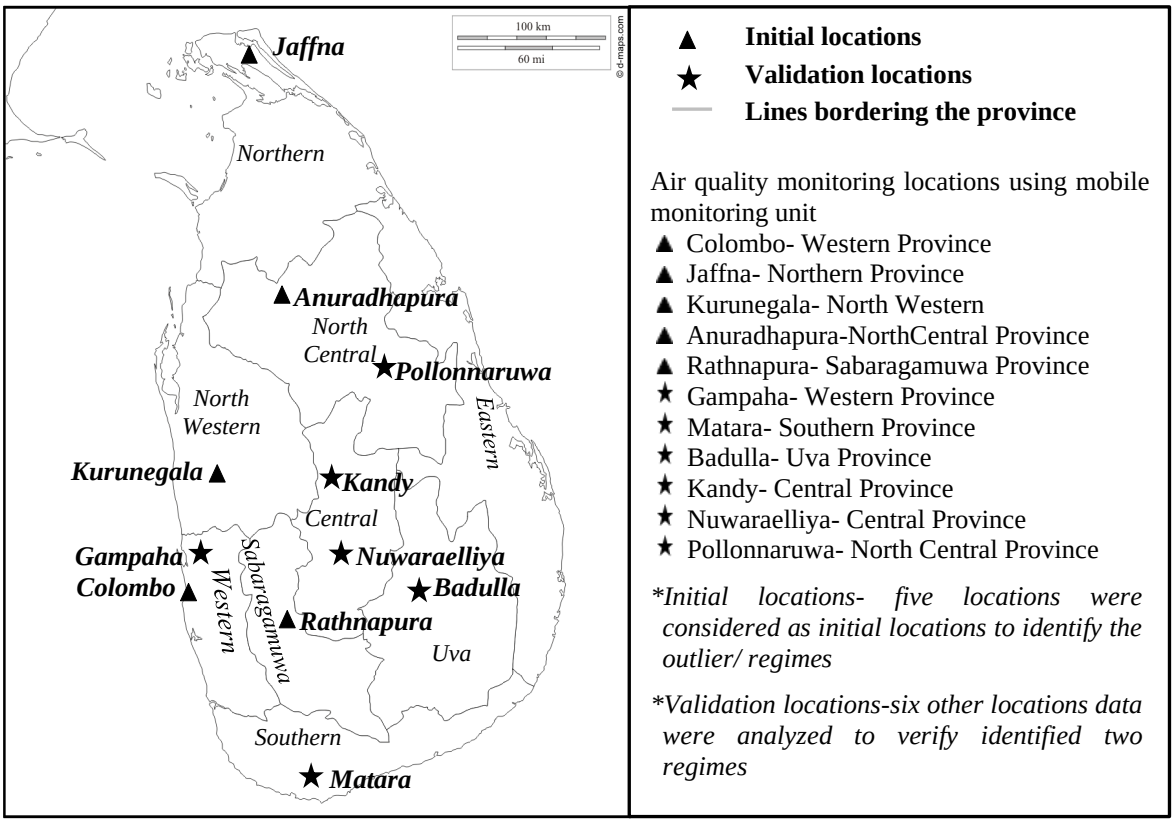


Figure 10: Selected air quality monitoring locations in Sri Lanka

4.2.5 Method of identification of associations of influential parameters

Using the MATLAB version 2015 software, NO_X, VOC (NMHC) and O_3 pollutant parameters and their distribution patterns are extensively studied and visualized as 2D and 3D. Further, relationship of the pollutants and other influential parameters such as temperature, solar radiation and wind speed, were studied using SPSS version 16 software and visualized as 2D figures.

a. Relationship of NO_X, VOC (NMHC) and O_3 air pollutants

i. Relationship of $\mathbf{NO_X}$ and **VOC**

ii. Relationship of NO_X and O_3

iii. Relationship of VOC and O_3

iv. Relationship of $\mathbf{NO_X}$, VOC and $\mathbf{O_3}$

b. Relationships of meteorological parameters

i. Relationship of $\mathbf{O_3}$ and temperature

ii. Relationship of $\mathbf{O_3}$ and solar radiation

iii. Relationship of $\mathbf{O_3}$ and wind speed

4.2.6 Method of urban air-shed model development

Variations of the influential parameters were incorporated to the developed chemical and mathematical relationship and urban air shed model was developed. Weekly air quality monitoring of selected five locations namely; Anuradhapura, Colombo, Ratnapura, Jaffna and Kurunegala covering five different provinces in the country were considered for the comparison. O_{3ss} concentrations were calculated in each city separately using the measured data of NO, NO_2 and NMHC concentration obtained from respective city weekly data. These calculated O_{3ss} concentrations of each city were compared with the measured O_{3ss} concentrations in respective city. Further total five cities calculated O_{3ss} concentration was compared with the measured O_{3ss} concentration. Difference of measured O_{3ss} concentration and calculated O_{3ss} concentration were considered in weekly air quality monitoring of selected five locations data in each case with the measured wind speed data to see the relationship.

4.2.7 Method of model calibration

Model calibration was carried out using the univariate linear regression mode using predicted and observed ozone values. Further multivariate regression model using wind speed as an additional independent variable also has been carried out. Furthermore, multivariate regression adding wind speeds as a variable which could interact with O_3 level was also analyzed. Model validation is expined in Phase II, section 4.3.2, Method of identification of NOx-VOC-O_3 sensitivity and model validation in Colombo air-shed.

4.3 PHASE II- METHOD OF ANALYSIS IN COLOMBO AIR-SHED

4.3.1 Method of monitoring of air quality & meteorological parameters in Colombo air-shed

a. Method of data collection of roadside & on-road TVOC monitoring

Suitable study settings were selected representing the sources including road transportation, population density, area demand for petroleum products and high air pollution exposure in the Colombo urban setting. The seven high traffic locations were selected based on the traffic details of Department of Transport and Logistic Management at the University of Moratuwa, namely Dehiwala, Kollupitiya, Fort, Maradana, Boralla, Narahenpita and Grandpass (Figure 11).

Figure 11: Selected locations of this research in Colombo

Hourly spot measurements were conducted beside the road during 10.00 am to 11.00 am at the seven locations in Colombo using MiniRAE Lite TVOC monitor (Figure 12a)

during weekdays of month of May 2014. Monitor was fixed at 150cm above the ground (approximate breathing zone of an adult with average height) and 1m away from the side of the road. Further TVOC levels were measured on road by fixing TVOC monitor inside a moving vehicle keeping air flow tube outside the vehicle window (Figure 12b) to understand concentration variations in between the locations. Figure 13 (a-f) shows the directions of six on road TVOC measurements path ways between the junctions in Colombo.

(a) **(b)**

Figure 12: Measurements from MiniRAE Lite portable VOC monitor

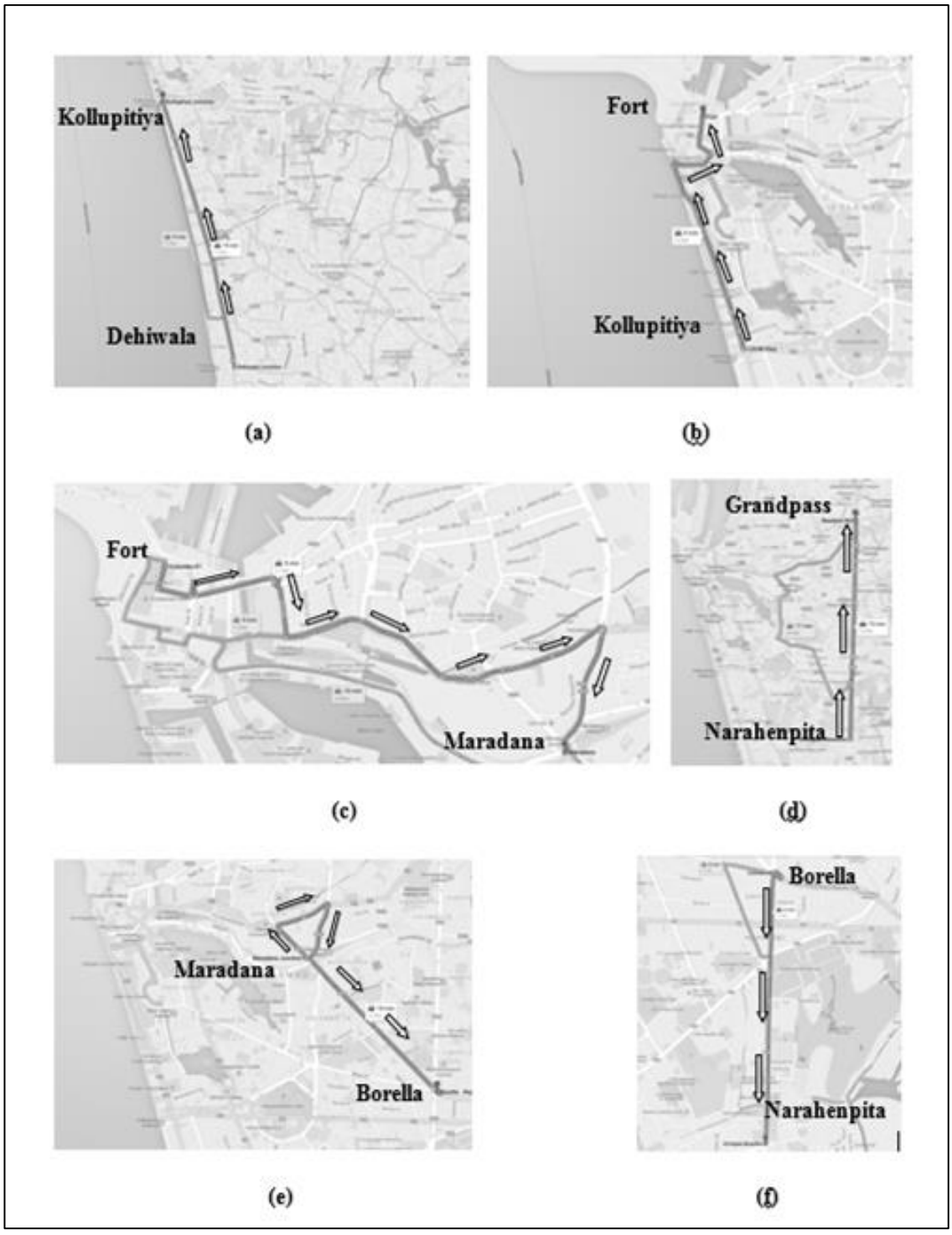


Figure 13: Directions of on road $TVOC$ measurements path ways in Colombo

b Method of data collection of 24 hour air quality monitoring

Based on the hourly spot measurement results, detail 24 hour outdoor measurements were carried out at the six major traffic junction sites with subsequent vehicle counts for consecutive three days covering two working days and one weekend days in year 2018 and 2019. Equipment's of the mobile monitoring station belongs to ITI were used for the ambient air quality monitoring measurements (Figure 14) and USEPA standard procedures have been followed for the ambient roadside air pollutant monitoring. Ambient concentration data was obtained for pollutant $PM_{2.5}$, PM_{10}, HC (methane HC and non-methane HC), NO_2, NO and O_3 pollutant with subsequent meteorological parameters of air temperature, relative humidity, solar radiation, wind speed, and wind directions with their distribution patterns (wind-rows) for the six major traffic junction sites. Data was obtained as every hourly averaged for 24 hour measurement.

Figure 14: 24 hour ambient air quality monitoring in Colombo

4.3.2 Method of identification of NOx-VOC-O_3 sensitivity and model validation using Colombo air-shed

Based on the 24 hour air quality monitoring data O_3, THC, CH_4, NMCH, NO, NO_2 and NO_X trend patterns were drew to understand the $NO_X - VOC - O_3$ sensitivity Model validation was carried out using the data obtained from Colombo urban locations namely, Borella, Grandpass, Narahenpita, Fort, Kollupitiya and Nugegoda. Obtained trend patterns were compared with the identified NO_X sensitive regime and VOC sensitive regime. O_{3ss} concentrations were calculated in each city separately using the measured data of NO, NO_2 and NMHC concentration obtained from respective city weekly data. These calculated O_{3ss} concentrations of each city were compared with the measured O_{3ss} concentrations in respective city. Further total six Colombo location calculated O_{3ss} concentration was compared with the measured O_{3ss} concentration. Model validation was carried out for the data obtained from Colombo using using the calculated and measured O_3 concentration

4.3.3 Method of data collection of operational schedules

Operational schedules of emission sources such as vehicle count data, train scheduled data, and working hours of power plants were conducted in the year 2018 and 2019 during the measurements of air quality monitoring in Colombo.

a. <u>Method of data collection of vehicle counts in Colombo</u>

Vehicle counts were conducted for 24 hours for 3 days (two week days and one weekend day) at the seven major traffic locations in Colombo. Vehicle counts were collected separately for vehicle types and total vehicles (Figure 15). Vehicle types are; motor

bicycles, three wheelers, motor cars, vans, jeeps/ SUV, motor coach/ buses, dual purpose vehicles, lorries and containers.

Figure 15: Taking vehicle counts at Colombo

b. Method of data collection of train scheduled data

Data was obtained from the Fort railway station for every minuted, incoming and outgoing trains in all railway tracks during 24 hour day. Based on the data obtained, numbers of trains passing the Fort railway station within an hour were counted for 24 hour (one day). The data was graphically presented with the air pollution data within a day.

c. Method of data collection of power plant scheduled data

Operational schedules data was obtained from the Kelanithissa power stations based on the working hours of the power plants on the subsequent air quality measurements days. Working hours of the power stations were compared with the air pollution data.

4.3.4. Method of vehicle performance characteristics

a. Method of analysis of Fuel Economy values with different type of vehicles

Fuel Economy of different type of vehicles was compared with the measured vehicle counts in the city of Colombo. Further fuel economy with passenger km of different

type of vehicles was compared with the measured vehicle counts at the city of Colombo. Necessary trend patterns were drew to understand the highly polluted vehicle types.

b. Method of analysis of the vehicle exhaust hydrocarbon data

A representative random sample (434,497 vehicles) of vehicle exhaust hydrocarbon data in the year 2013 of the VET programme of DMT was analyzed to find out the relationship of accelerated and idle HC concentration with the variables: year of manufacture, current mileage, number of strokes, and number of cylinders.

4.3.5 Method of TVOC measurements & GCMS analysis

a. Method of data collection of TVOC monitoring in different sources

Source identification was carried out with visual observations with in 1km diameter area of all eleven ambient air quality monitoring locations mentioned in section 4.2.2 and selected locations in Colombo for this research in Section 4.3.2 targeting the VOC sources of that particular area. Based on the source identification in all locations fourteen different TVOC monitoring sites were identified for detailed measurements. Real time TVOC measurements for 10 minutes (reporting every minuted data) from all fourteen sites were carried out using Photo Ionization Detectors (PID), *EW technologies*, *USA* (Figure 16a). PID has a range of 0 to 1 ppm and commonly used for indoor research. Fourteen TVOC measurements sites are: wood using cook stove area; LPG using cook stove area; petroleum station (Figure 16b); vehicle spray paint area; tobacco smoking area; incent sticks burning area; outdoor polythine/ and other garbage burning area; vehicle service area; mosquito coil burning area; kerosene using cook stove area and kerosene lamp burning area, vehicle exhausts, road side (heavy traffic), and on road measurements (heavy traffic).

(a) Photo Ionization Detector (b) TVOC measurements at a petroleum station

Figure 16: $TVOC$ measurements using Photo Ionization Detector

b. Method of GCMS analysis

GCMS analysis was carried out for the air collected from the exhaust line of the 50 randomly selected ongoing vehicles in the western province using Teflon air bags. Figure 17 shows air bag measurement of a vehicle from the exhaust line. Type of vehicles selected were cars, three wheelers, motor bikes, vans and lorries. The inlet tube of air pump was fixed to an exhaust pipe of the vehicle and the other end was connected to the to the Teflon air bag. Air pump was switched on when the vehicle was run on road for 10 minutes. Collected samples were kept in-side a black bag to minimize the photochemical reactions. Air-conditioned vehicle was used to transport the samples of air bags immediately (minimize further reactions) to the laboratory for GCMS analysis (Figure 18) at the Department of Chemistry in the University of Colombo. USEPA Method (EPA TO-14A/TO-15 mod- VOC by GC-MS) was followed for the analysis to identify the detail VOC compounds at each location. Methodology followed and temperature programme used for the GCMS analysis is annexed in Annexure I.

Figure 17: Preparation of air bag measurement of a vehicle

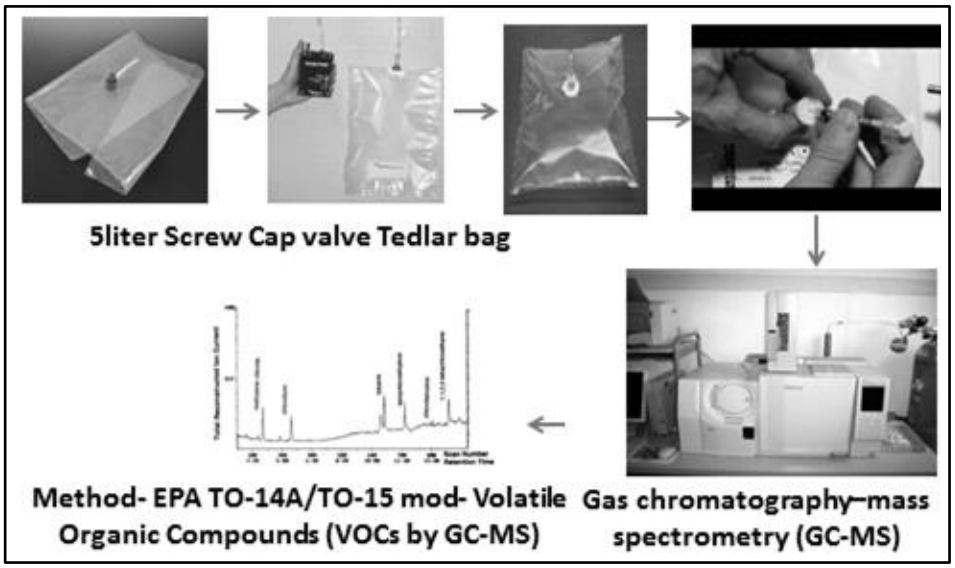


Figure 18: Air bag measurement procedure

CHAPTER 5

ANALYSIS OF DEVELOPMENT OF URBAN AIR - SHED MODEL

5.1. BASIC APPROACH IN ANALYSIS OF DEVELOPMENT OF URBAN AIR-SHED MODEL

Over-role frame-work of analysis of development of urban air-shed model is presented in Figure19:

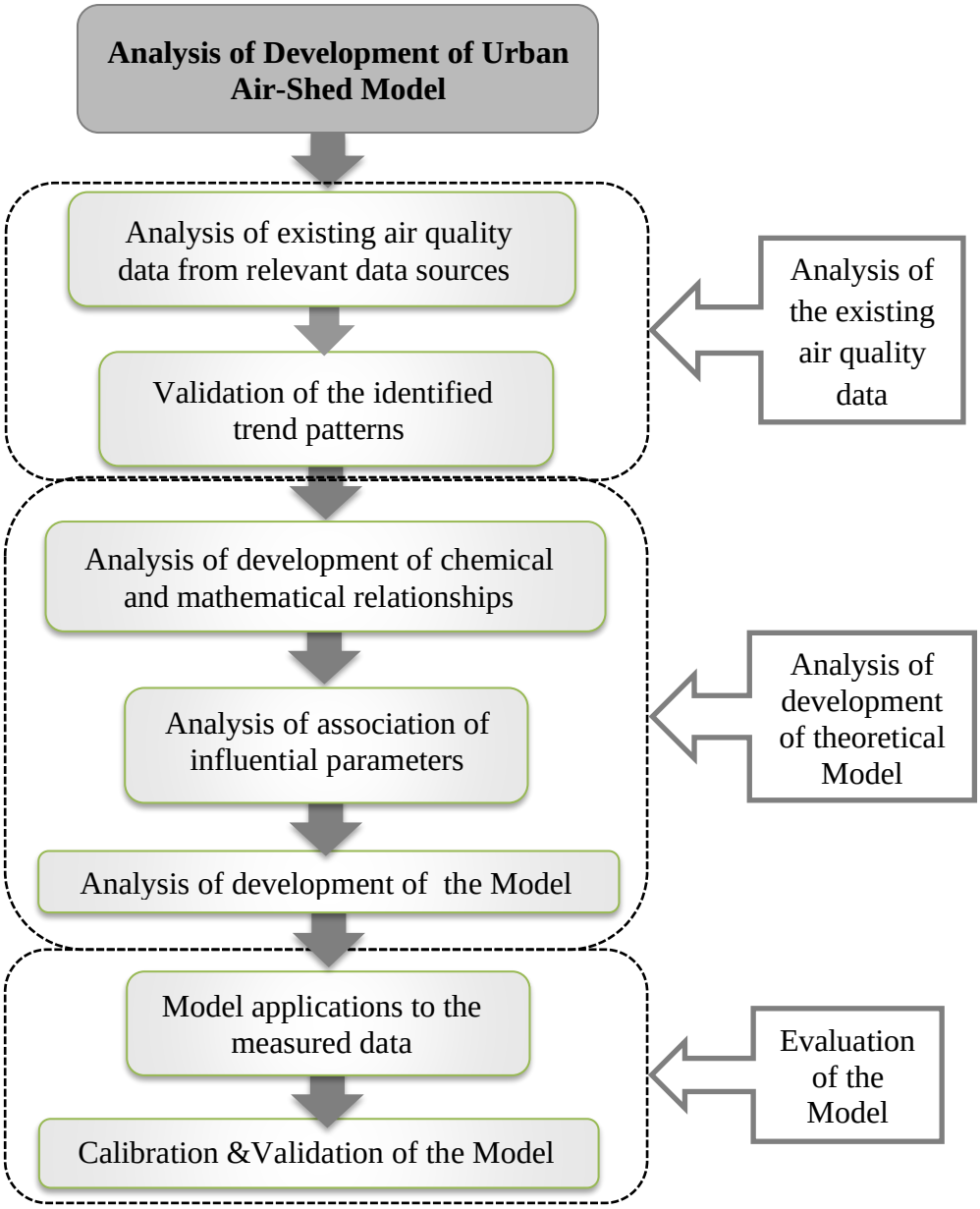


Figure 19: Over-role frame-work of analysis of development of Urban Air-shed Model

Chapter 5 presents the Phase I of Results and Discussion of analysis of development of urban air shed model. Flow of the analysis of development of urban air shed model sections are presented in Figure 20.

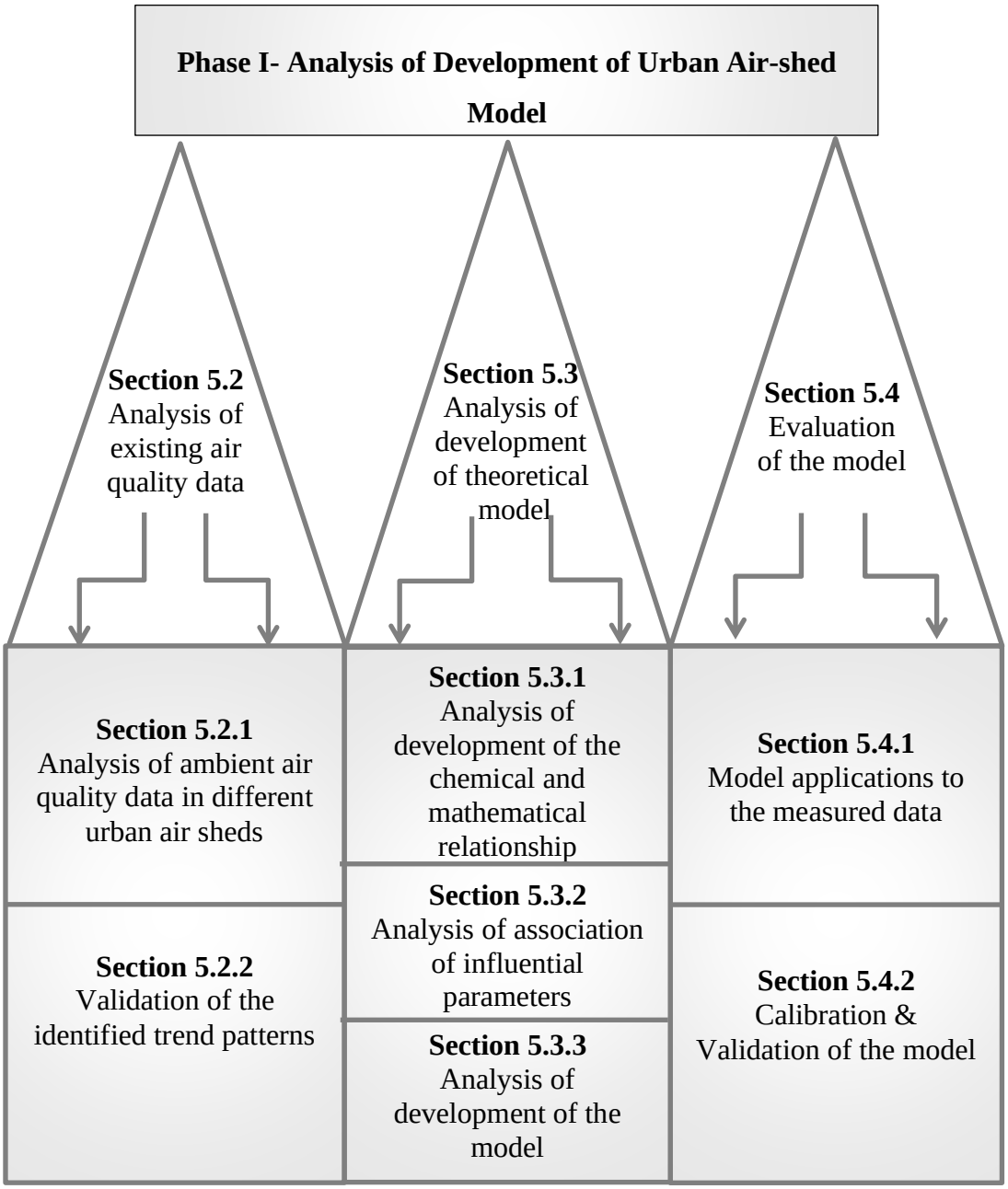


Figure 20: Flow of the analysis of development of urban air shed model sections

5.2 ANALYSIS OF EXISTING AIR QUALITY DATA FROM RELEVANT DATA SOURCES

5.2.1 Analysis of ambient air quality data in different urban air-sheds

In this section, analysis of the ambient real time air quality monitoring data in five locations in Sri Lanka has carried out. Table 9 shows the comparison of 24-hour average values of pollutant at five different locations in Sri Lanka. It shows that high level of air pollutants have shown in different location base on the pollutant source.

Owing the industrial air pollution at Ratnapura highest particulate pollution (PM_{10}-64µgm^3, $PM_{2,5}$- 40µgm^{-3} where in both cases WHO guideline value has exceeded), high oxides of nitrogen (0.125ppm), and high non-methane hydrocarbon (NMHC-0.997ppm) was observed. Colombo (Nugegoda) has high air pollutant levels mainly coming from vehicular emission [22]. In Colombo (Nugegoda) high particulate pollution was observed for both PM_{10} and $PM_{2,5}$ (PM_{10}-55µgm^{-3}, $PM_{2.5}$- 28µgm^{-3}, ppm where in both cases WHO guideline value has exceeded), high oxides of nitrogen both NO and NO_2 (NO-0044ppm and NO_2-0.026ppm), and high non-methane hydrocarbon (NMHC-0.669ppm) was observed. Jaffna and Anuradhapura have comparatively low air pollutant concentration. Low concentration of air pollutants at Jaffna could be due to the high sea breeze in the area. At Anuradhapura having higher paddy fields high CH_4 (CH_4-1.828ppm) concentration was observed. With the favorable temperature (28.4°C) in Anuradhapura, production of O_3 (0.017ppm) was also higher.

Table 9: Comparison of 24-hour average concentration of air pollutants at five locations in Sri Lanka

Pollutant/ Parameters	Colombo	Anuradhapura	Jaffna	Ratnapura	Kurunegala	Standard/ Guideline [163]
$PM_{2.5}$ (μgm^{-3})	28	16	15	40	25	$PM_{2.5}$ SL Standard-50μgm^{-3}, $PM_{2.5}$ WHO Guideline-25μgm^{-3}
PM_{10} (μgm^{-3})	55	30	39	64	51	PM_{10} SL Standard-100μgm^{-3}, PM_{10} WHO Guideline-50μgm^{-3}
THC (ppm)	2.344	2.254	1.678	2.672	2.243	No standard has been developed yet
CH_4 (ppm)	1.674	1.828	1.259	1.675	1.440	
NMHC (ppm)	0.669	0.426	0.419	0.997	0.803	
CO (ppm)	0.769	0.556	0.503	1.017	0.747	CO I -hour SL Standard-30mgm^{-3}, CO 1-hour USEPA Standard-35ppb (35000ppm)/ 40mgm^{-3}
NO (ppm)	0.044	0.048	0.005	0.114	0.031	NO_2 SL Standard 100μgm^{-3} (0.0494ppm) NO_2 WHO Guideline-40μgm^{-3} (0.0197ppm)
NO_2 (ppm)	0.026	0.005	0.011	0.011	0.011	
NO_X (ppm)	0.070	0.053	0.016	0.125	0.042	
O_3 (ppm)	0.005	0.007	0.017	0.013	0.003	O_3 1-hour SL Standard--200μgm^{-3} (0.0946ppm) O_3 1-hour USEPA Standard-0.12ppm
Temperature °C	28.21	26.05	28.62	26.95	27.02	
Relative-Humidity %	76.43	82.67	77.08	73.25	75.94	
wind speed m/s	0.694	0.328	1.908	0.620	0.953	
wind direction degree	223.64	109.82	157.70	232.89	180.35	

5.2.2 $NO_X - VOC - O_3$ Sensitivity in five locations in Sri Lanka

Data signifies that two concepts exist for $NO_X - VOC - O_3$ sensitivity (i.e., NO_X-sensitivity and VOC-sensitivity). In certain environments, the course of O_3 formation is dominated entirely by NO_X concentration and is mainly independent of VOC concentration. This condition is considered as NO_X-sensitive regime. On the other hand, in certain other environments, the course of O_3 formation rises with rising VOC. Further, the course of O_3 formation rises or occasionally even reduces with rising NO_X.

a. NO_X-Sensitive Regime

NO_X-sensitive regime has comparatively low NO_X and high VOC concentrations and O_3 concentration rises with rising NO_X concentration. As an example, Figure 21 shows that this phenomenon occurs in Colombo (Nugegoda). The city is located in the wet zone. The average high temperature is around 31°C (Figure 22) from March to April. Instruments are located down wind. At the Colombo (Nugegoda) site, wind direction is mainly from West and Southwest (Figure 23). Similarly, NO_X-sensitive regime occurs in Kurunegala and Jaffna as well. Further, it was observed the trend patterns of NO, NO_2 and NO_X in these cities in Sri Lanka. This city is with high traffic congestion and witnessed trends are probably due to traffic related emissions [22, 132]. The Sri Lanka vehicle emission testing program (SLVET) was established in 2008. Sri Lanka has attempt to reduce air pollution by vehicle emission reduction methods including promotion of cleaner fuels and technologies (such as shifting to electric vehicles, fixing catalytic converters at the exhausts line), tax concession of importing newer and cleaner vehicles, i.e. 25% on electric vehicles and 50% on hybrid vehicles [113], reduction of traffic by transport demand management, etc.

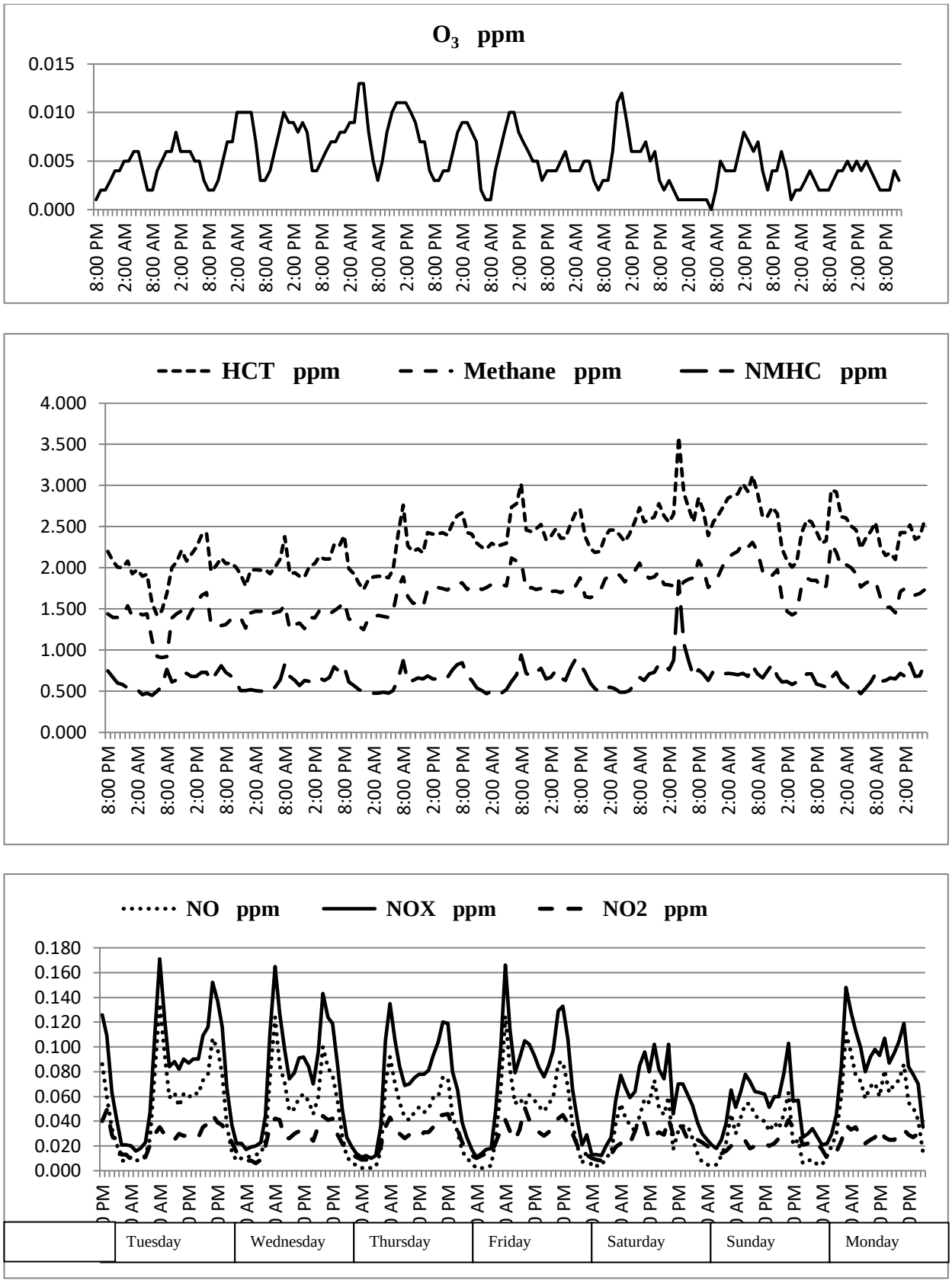


Figure 21: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_2 concentration variation within the week at Colombo

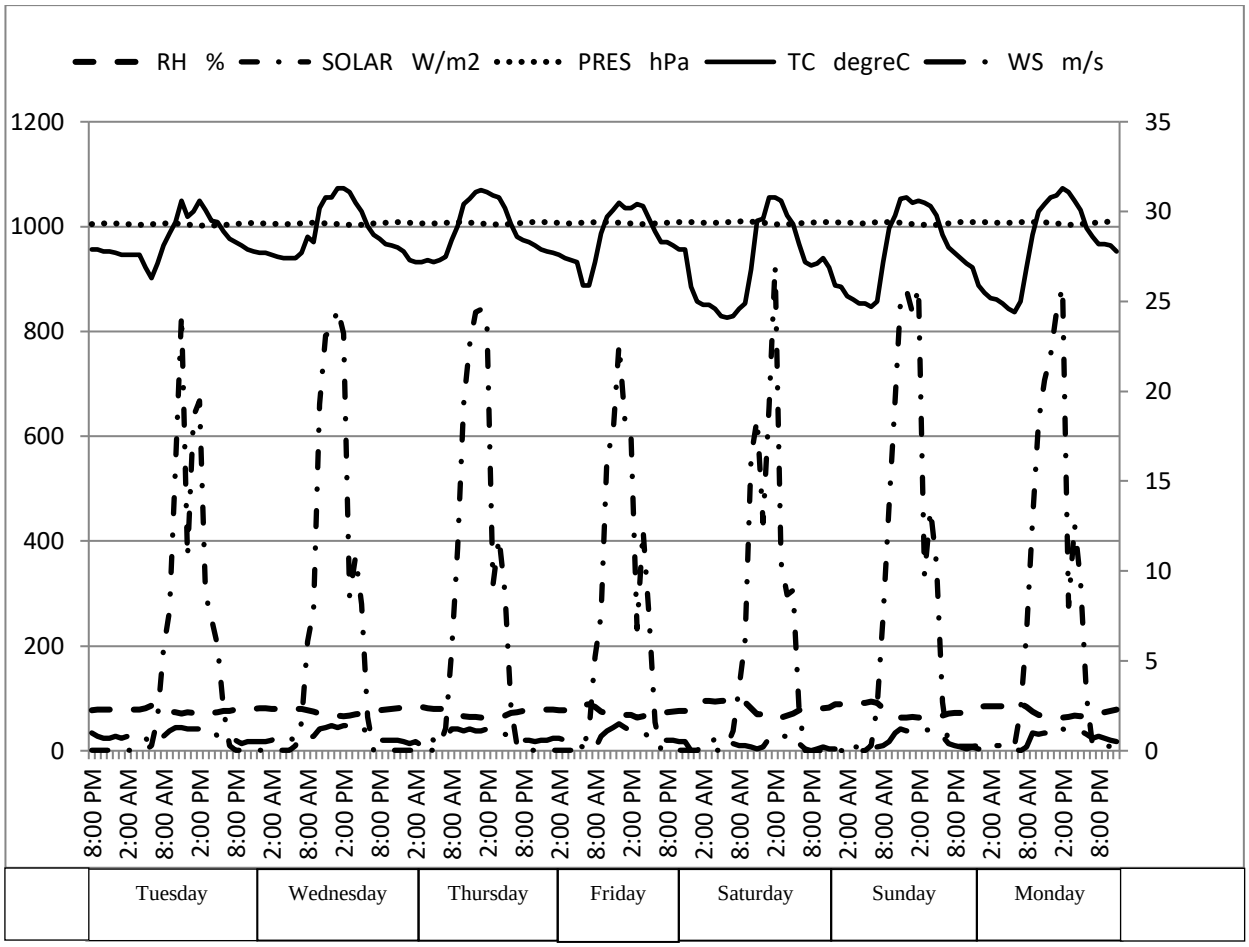


Figure 22: Temperature, solar radiation, pressure, relative humidity and the wind speed during the week at Colombo

**Wind speed and the temperature values are represented in the secondary (right hand side) axis.*

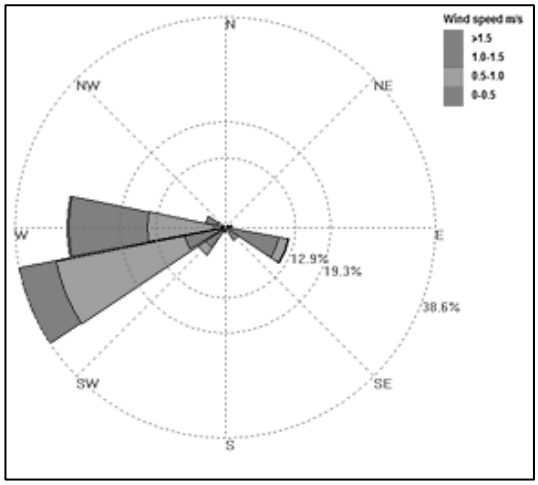


Figure 23: Wind Rose at Colombo (Nugegoda)

Monsoon seasons are from;

- May to August
- October to January

and heavy rains can be expected.

Wind direction is mainly from West and South-west.

b. VOC-sensitive regime

In the NO_X saturated or VOC sensitive regime O_3 decreases with rising NO_X and rises with rising VOC, which is predominant in city of Ratnapura (Figure 24). In Ratnapura the average temperature is in the range of 24 to 35°C with high humidity levels (Figure 25). NO concentration vs wind direction at the Ratnapura location shown that the source or the industry may placed in 60^o to 80^o direction (Figure 26). Ratnapura is located in the wet zone. The town receives rainfall mainly from south-western monsoons from May to September. At the Ratnapura site, wind direction is mainly from North West directions (Figure 27).

In the presence of low NO concentration, marked O_3 concentration is seen in Figure 21. However, with very high NO concentration, O_3 concentration has reduced. This is due to the removal of O_3 through reaction with NO as described in the introduction section. Further NO concentration vs wind direction at Rathnapura shows that pollutants are coming from the direction of 60°- 80° implying that a point emission source such as industry is located in that particular direction. Further, high peaks of NO concentration were observed when the industrial actions are involved. This type of condition needs to handle carefully as reduction in NO concentration may result in high production of O_3. Therefore, it is essential to reduce both pollutants NO and VOC simultaneously to mitigate formation of O_3.

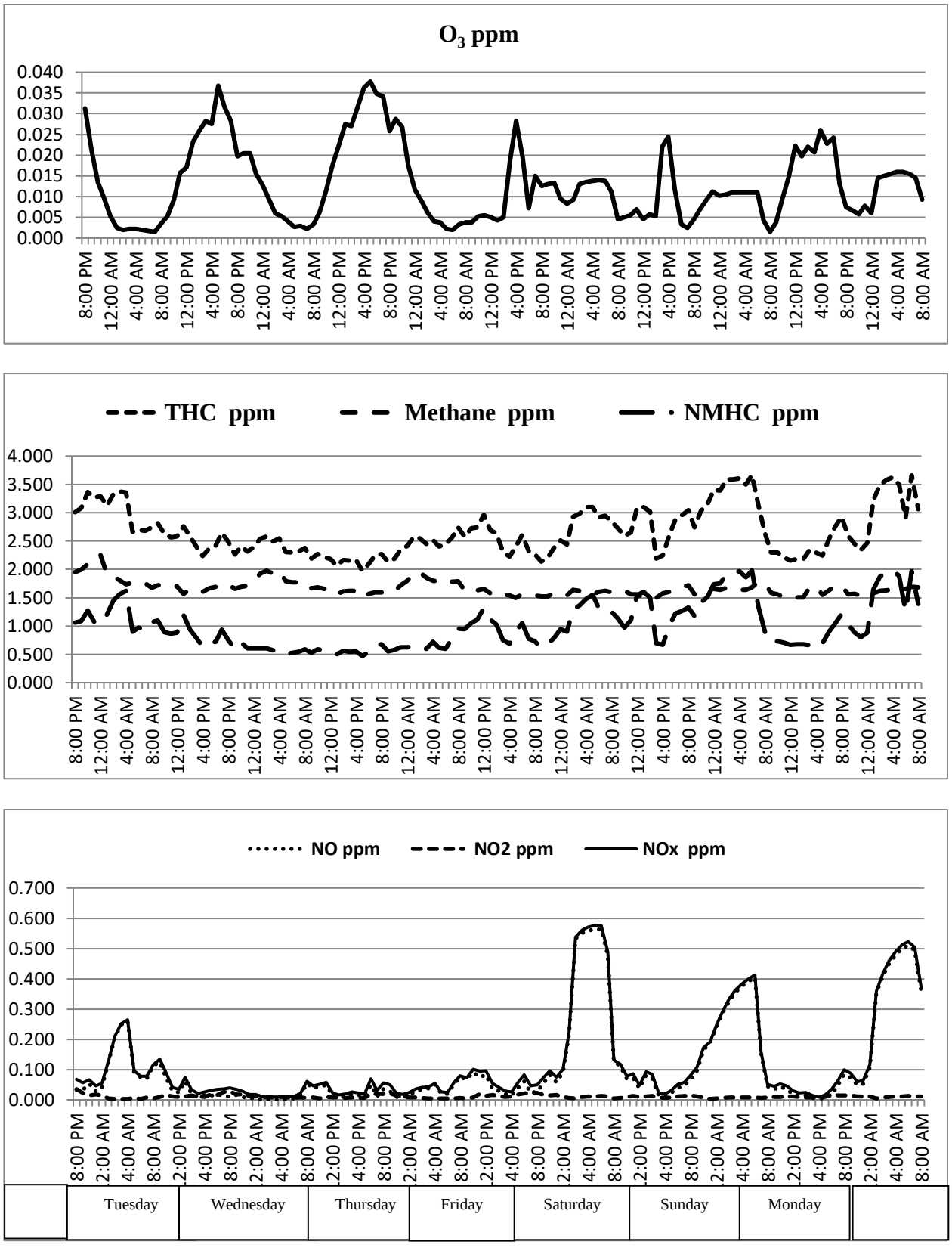
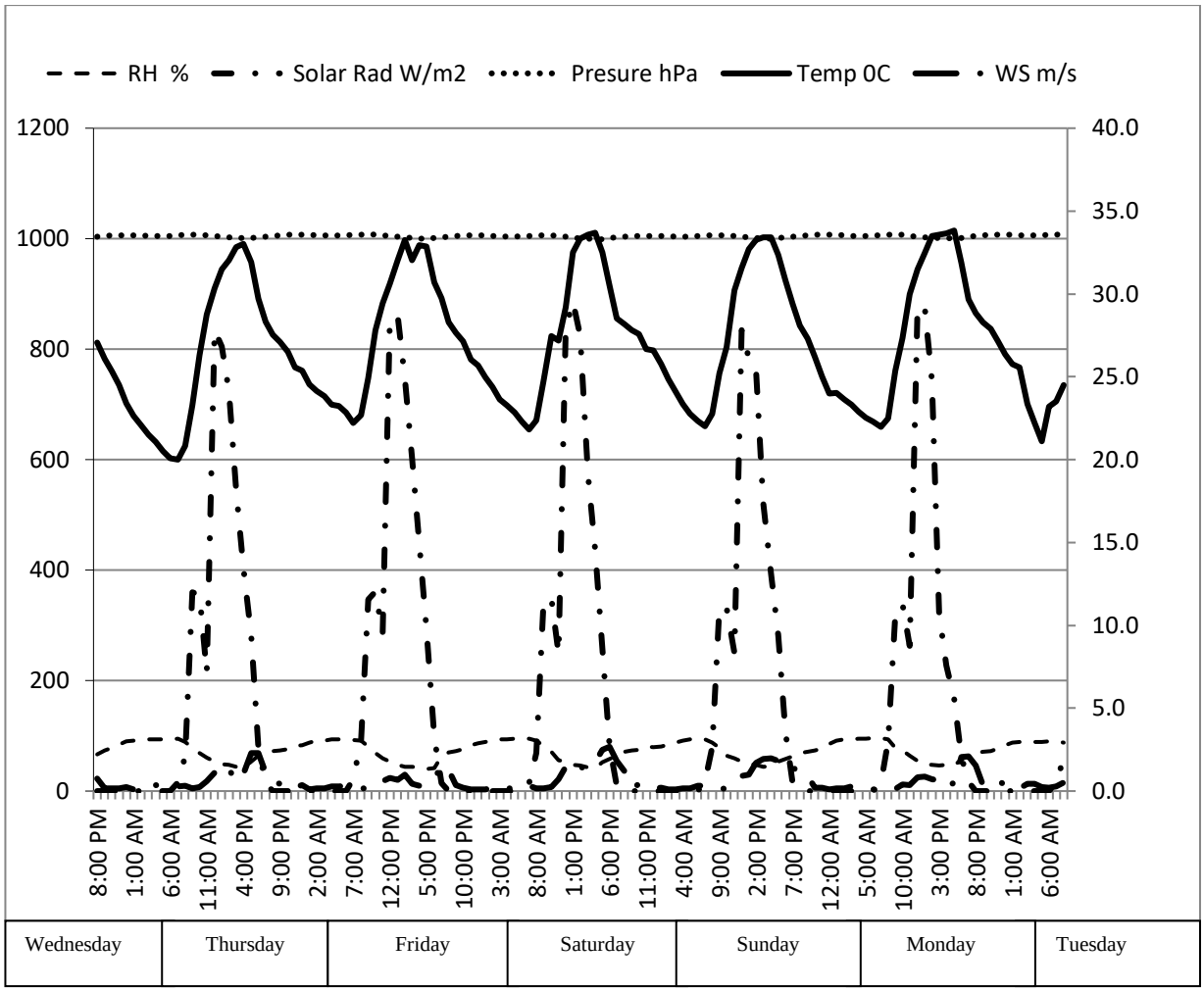


Figure 24: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_2 concentration variation within the week at Ratnapura



*Wind speed and the temperature values are represented in the secondary (right hand side) axis.

Figure 25: Temperature, solar radiation, pressure, relative humidity and the wind speed during the week at Ratnapura

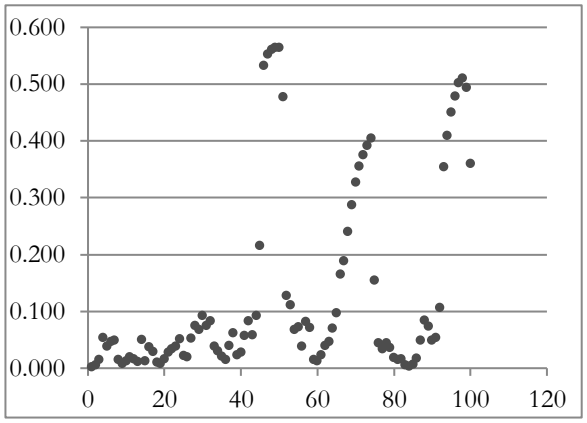


Figure 26: [NO] vs wind direction at Ratnapura

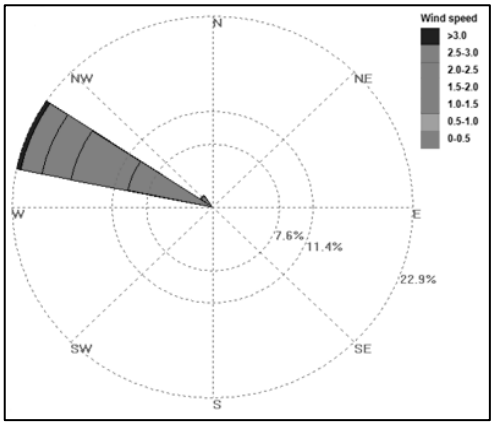


Figure 27: Wind Rose at Ratnapura

Intermediate of this high O_3 production and how the titration of produced O_3 concentration suddenly reduced could be clearly showed in Figure 28 at the Anuradhapura site. Anuradhapura is usually hot and humid throughout the year and the average temperature remains 25°C - 30°C (Figure 29). The town receives rainfall mainly from Southwest monsoon season begins in mid-May to October. At the Anuradhapura site, wind direction is mainly from North-west and South-east (Figure 30).

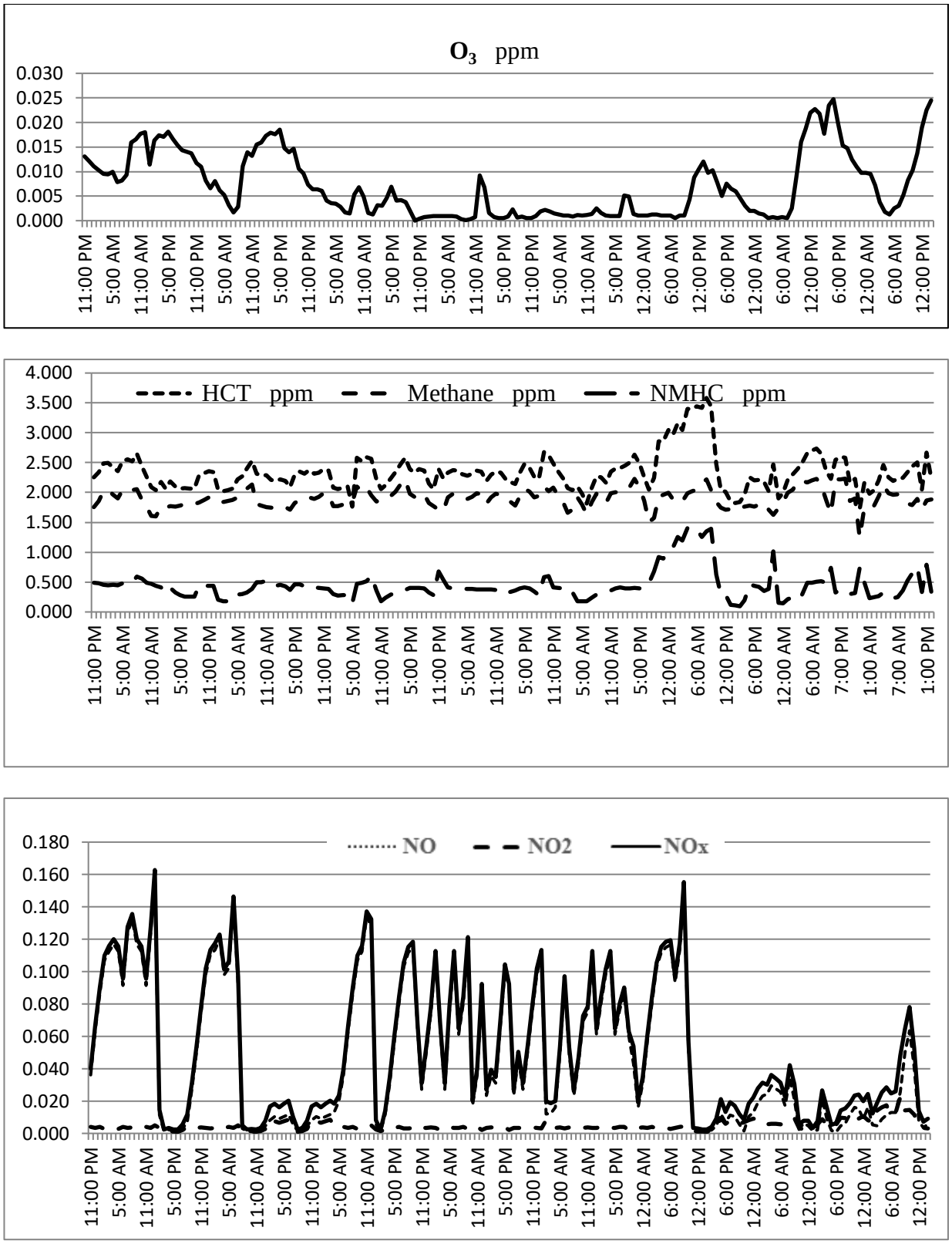
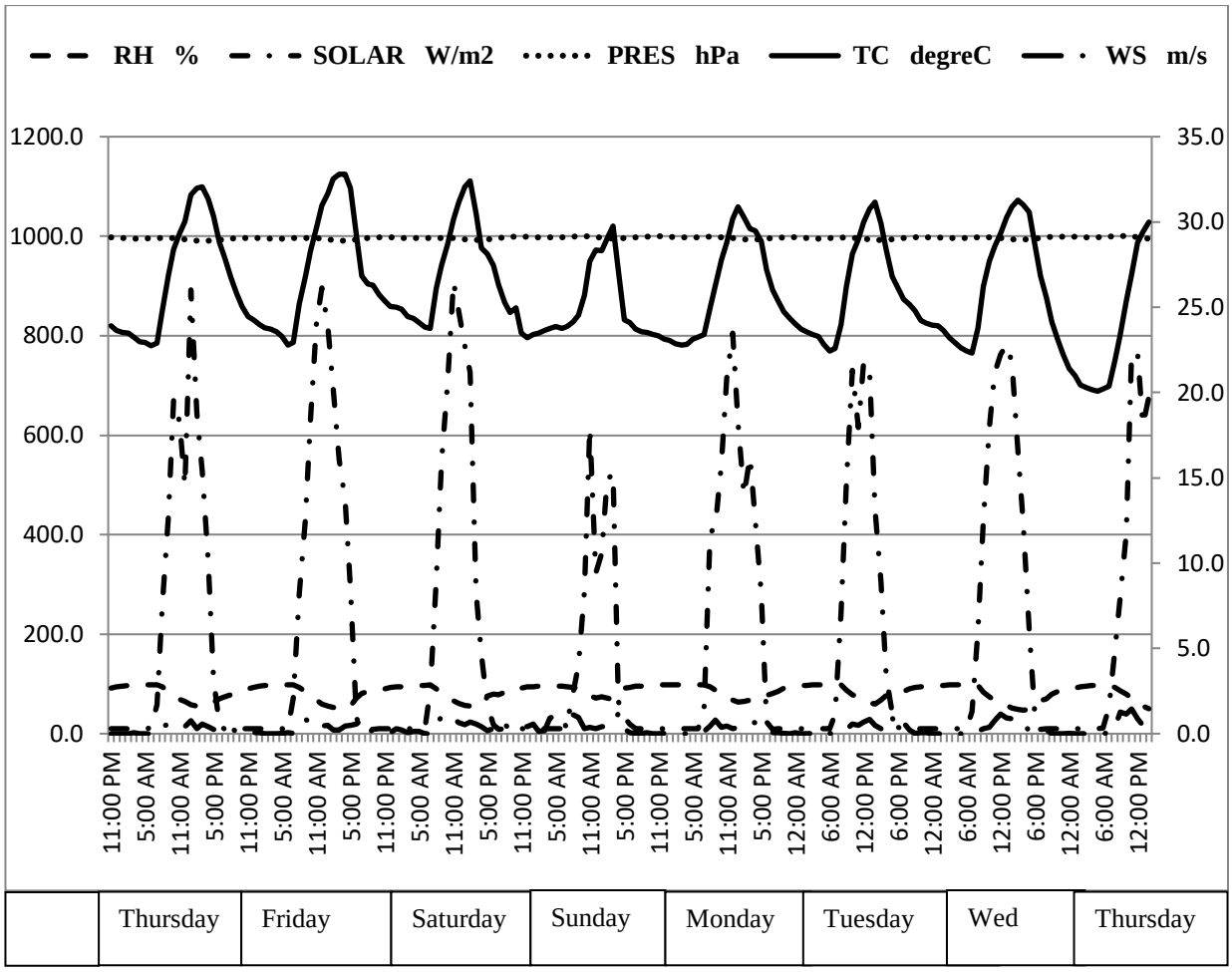


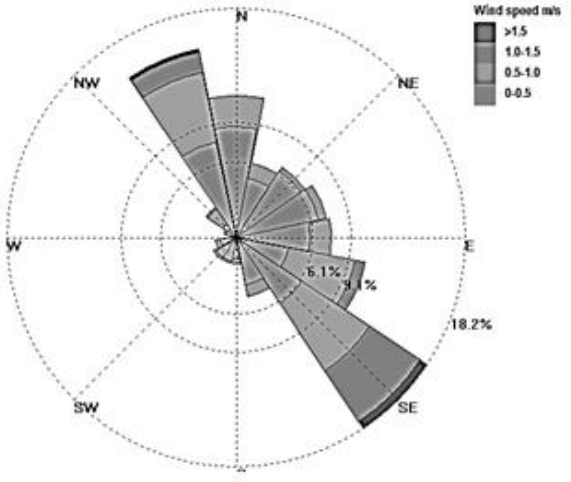
Figure 28: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_2 concentration variation within the week at Anuradhapura



*Wind speed and the temperature values are represented in the secondary

(right hand side) axis.

Figure 29: Temperature, solar radiation, pressure, relative humidity and the wind speed during the week at Anuradhapura.



- Southwest monsoon season begins in mid-May to October.
- April is the warmest month of the year in Anuradhapura.
- Wind direction is mainly from North-west and South- east.
- Hot and humid throughout the year.

Figure 30: Wind Rose at Anuradhapura

5.2.3 Validation of the identified trand patterns

In Figure 31 shows the NO_X-sensitive regime at Matara location and in Figure 32 shows the VOC-sensitive regime at Nuwara Eliya location. Further, validation results confirm the two regimes of $NO_X - VOC - O_3$ sensitivity. Accordingly in Matara, Badulla, Pollonnaruwa, and Gampaha show the NO_X-sensitive regime. In Kandy and Nuwaraelliya shows the VOC-sensitive regime. Therefore results confirm the proposed $NO_X - VOC - O_3$ sensitivity for Sri Lankan cities.

a. NO_X-Sensitive Regime

In the NO_X-sensitive regime (with relatively low NO_X and high VOC), O_3 concentration rises when the NO_X concentrations is rising and change slightly in response to rising VOC. This regime was observed in Colombo, Kurunegala, and Jaffna.

b. VOC-SensitiveRegime

In the VOC-sensitive regime O_3 reduces with rising NO_X, and rises with rising VOC. This regime was observed in Ratnapura and Anuradhapura. In the immediate vicinity of very large emissions of NO, O_3 concentrations were depressed through the process of NOx titration. This consists of removal of O_3 through reaction with NO.

According to the findings and as shown in Figure 33, out of eleven cities results confirm that NO_X-sensitive regime was observed in Colombo, Jaffna, Kurunegala, Matara, Badulla, Polonnaruwa, Gampaha, and VOC-sensitive regime was observed at Rathnapura, Anuradhapura, Kandy and Nuwara Eliya. The large thermal power plants such as Norocholai Coal Power plant and Sapugaskanda Oil Power plant are away from the eleven measurement sites. Accordingly, emissions of these power plants could be excluded in the present study.

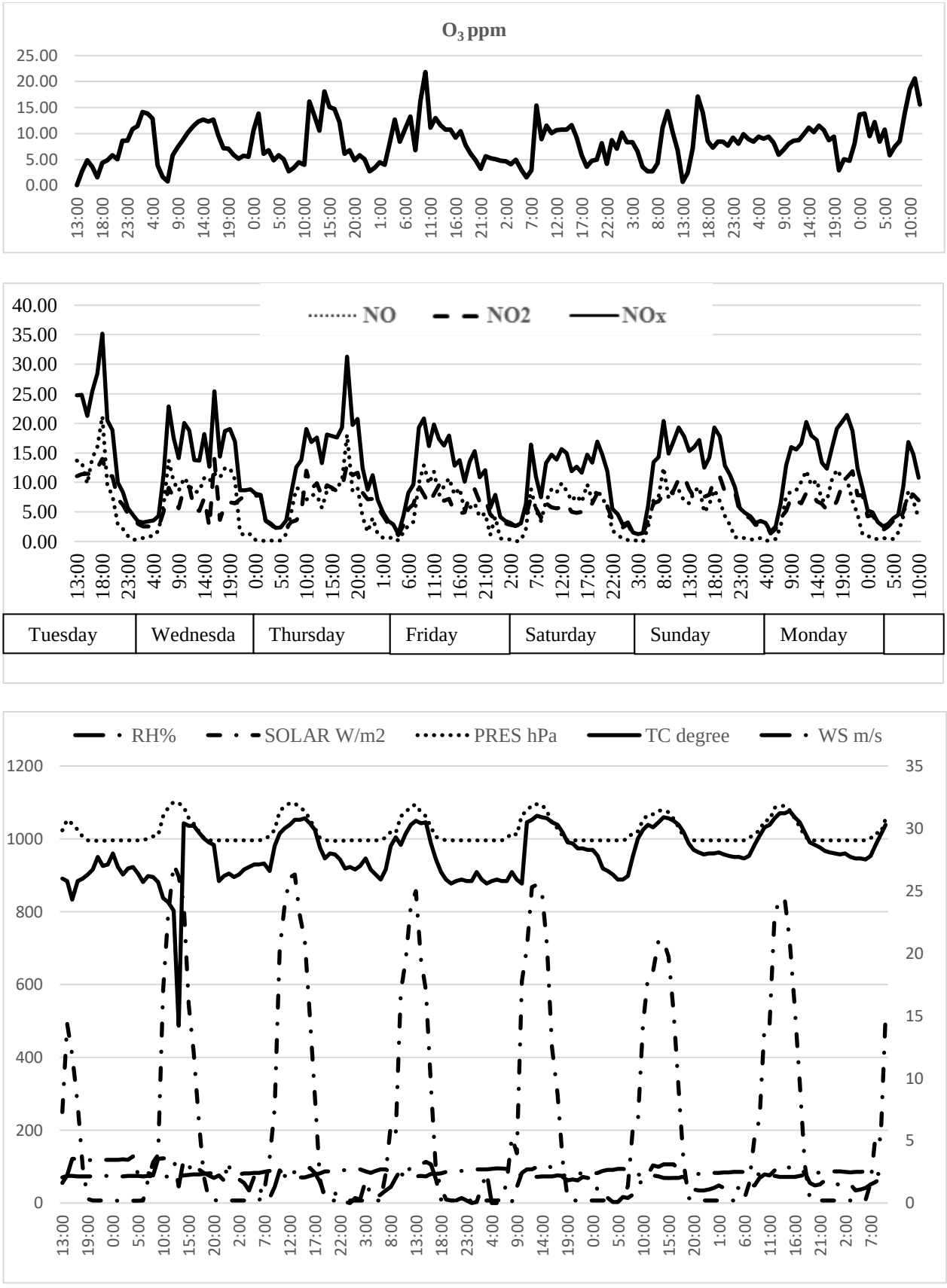


Figure 31: O_3, , NO, NO_2 and NO_X concentration and meteorological parameter variation within the week at Matara

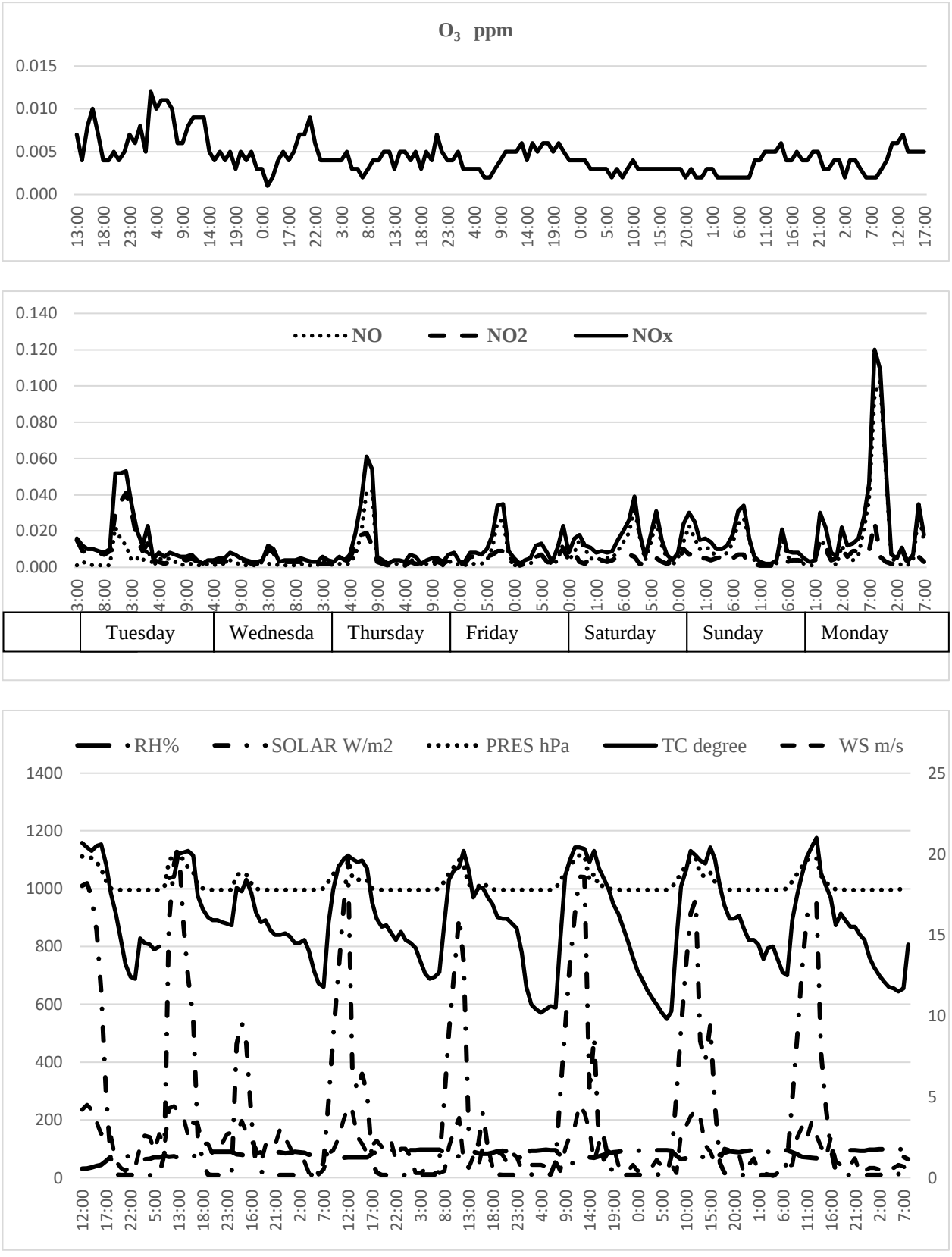


Figure 32: O_3, NO, NO_2 and NO_X concentration and meteorological parameter variation within the week at Nuwara Eliya

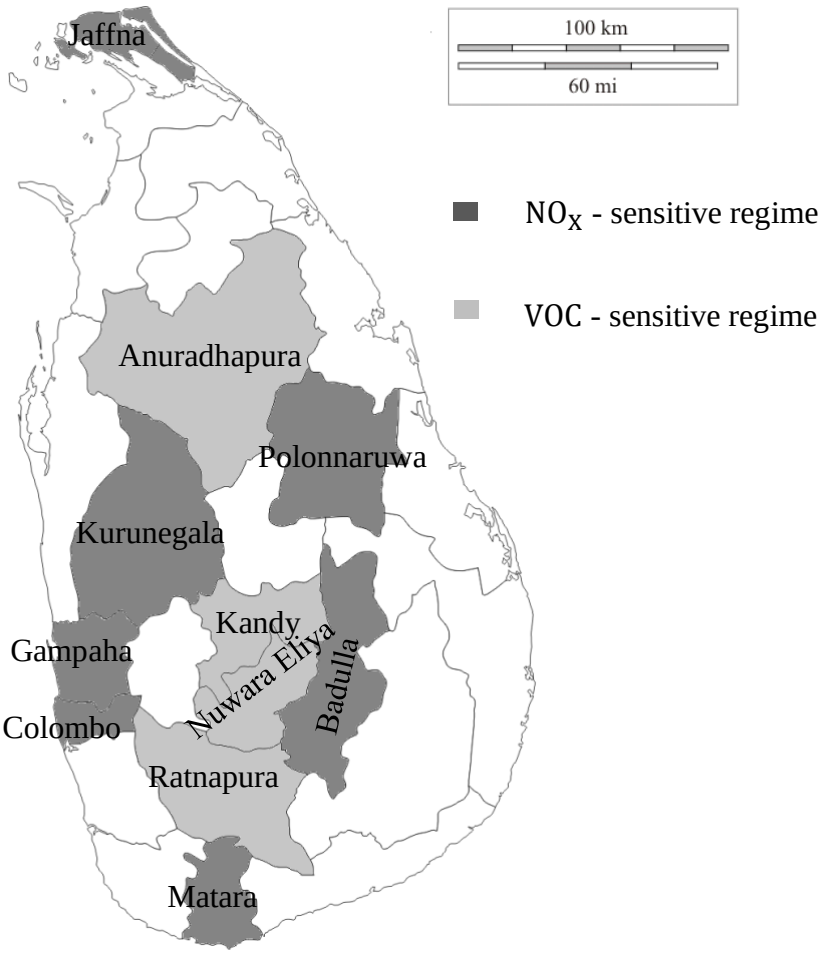


Figure 33: District vise $NO_X - VOC - O_3$ sensitivity for Sri Lankan cities

5.3 ANALYSIS OF DEVELOPMENT OF THEORETICAL MODEL

5.3.1 Analysis of Development of a Chemical and Mathematical Relationship

Following are the chemical reactions that determines the O_3 generations;

$NO_2 + h\nu \rightarrow O(3P) + NO \ (\lambda < 420 \text{ nm})$ *1*

$M + O_2 + O \rightarrow M + O_3$ *2*

$NO + O_3 \rightarrow O_2 + NO_2$ *3*

$OH + VOC \xrightarrow{O_2} H_2O + RO_2$ *4*

$OH + CO \xrightarrow{O_2} CO_2 + HO_2$ *5*

$NO + RO_2 \xrightarrow{O_2} HO_2 + NO_2 + VOC$ *6*

$NO + HO_2 \rightarrow NO_2 + OH$ *7*

a. NOx-sensitive regime

By considering the chemical reactions 1, 2 and 3, mathematical relationship could be developed to calculate O_{3SS} in the NO_X- sensitive regime as [10, 11] Since the inter conversion between these species is so fast, a steady state is reached within a few minutes. This photo stationary state relation determines the O_3 concentration. The NO_X sensitive O_3ss concentration is proportional to the $[NO_2]/[NO]$ ratio and it is defined as:

$$[O_3]_{NO_x \text{ sensitivity}} = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]}$$

Where;k –depends on Temperature; Ω 0.4 ppm^{-1} s^{-1}, j–depends on solar radiation; at night= 0; at full sunlight= 0.4 min^{-1} [10].

b. VOC-sensitive regime

By considering the chemical reactions of $NO_X - VOC$, split mathematical relationship could be developed to calculate O_{3SS} in the VOC- sensitive regime. O_3 formation occurs through the above sequence of reactions. The sequence is almost always initiated by the reaction of various VOC or CO with the OH radical (reaction 4 and 5). This is followed by the conversion of NO to NO_2 (through reaction with HO_2or RO_2 radicals), which also regenerates OH (see reaction 6 and 7). NO_2 is photolyed to produce atomic oxygen, which associate with O_2 to create O_3, as given in reaction 1 and 2 [253].

Here, RO_2 represents any of a number of chains of organics with an O_2 attached (replacing H in the original chain). This reacts with NO (reaction 6) and H (which combines with O_2 to form HO_2). The initial reaction of VOC with OH controls O_3 formation rate.

At the nighttime and in the immediate vicinity of very large emissions of NO, deterioration of O_3 takeplace in the atmosphere as given in reaction 3. This process is known as NO_X titration [253, 256].

Concentrations of odd-H radicals were assessed with a radical steady state approximation (SSA) [256, 257]. Odd hydrogen = OH + HO_2 + RO_2, where RO $_2$stands for any organic peroxy radicals.

$$\frac{d[OH]}{dt} = P_{OH} - [OH]\sum_{i} K_i[S_i] = 0$$

$$\frac{d[HO_2]}{dt} = P_{HO_2} - [HO_2]\sum_{j} K_j[S_j] - 2K_{peroxid}[HO_2]^2 = 0$$

$$\frac{d[RO_2]}{dt} = P_{RO_2} - [HO_2]\sum_{j^1} K_{j^1}[S_{J^1}] - 2K_{o_{peroxid}}[RO_2]^2 = 0$$

where P_{OH}, P_{HO2}, and P_{RO2} are the production rates of OH, HO_2, and RO_2, respectively. S_i, S_j, and S_j' represent (radical or non-radical) types that act as reaction associates in sink reactions of OH, HO_2, and RO_2, individually. Reaction 7 and 8 have k_1 and k_2 reaction rate constants which are available in literature [256, 257].

$$NO + HO_2 \xrightarrow{k_1} NO_2 + HO \qquad 7$$

$$NO + RO_2 \xrightarrow{k_2} NO_2 + RO \qquad 8$$

k_1= 8.5 × 10^{-12}.; k_2= 7.7 × 10^{-12} ; Rate constants at 298 K in cm^3 $molecule^{-1}$ s^{-1} for bimolecular reactions and in s^{-1} for photolysis reactions [258]. Since subsequent NO_2 photolysis and the reaction of O(3P) atoms with oxygen are reasonably fast. With the peroxy radical concentrations obtained from the steady state approximation (SSA), O_{3SS} in the VOC- sensitive regime is thus calculated as;

$$[O_3]_{VOC\ sensitivity} = [NO](k_1[HO_2] + k_2[RO_2])$$

b. Steady State Ozone Concentration

Therefore, steady state Ozone concentration (O_{3SS})in both regimes could be calculated as below;

$$[O_3]_{ss} = [O_3]_{NO_x sensitivity} + [O_3]_{VOC\ sensitivity}$$

$$[O_3]_{ss} = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]} + [NO](k_1[HO_2] + k_2[RO_2])$$

$$[O_3]_{ss} = \frac{0.4\ \text{min}^{-1}[NO_2]}{24\ \text{ppm}^{-1}\ \text{min}^{-1}[NO]} + [NO]\{(8.5\times10^{-12}[HO_2] + 7.7\times10^{-12}[RO_2]\}$$

In the ambient air hydrocarbon concentrations are equal to the volatile organic compounds concentration. As all ambient hydrocarbons are volatile, $[RO_2]$ concentration could be replaced by the measured [NMHC]. Further Input data of NO, NO_2, NMHC, were combined with the j, k factors, k1 and k2 rate constants and Figure 34 shows the calculation of the steady state Ozone concentration (O_{3SS}) in both regimes. Further each stepwise calculation has been shown in Figure 34.

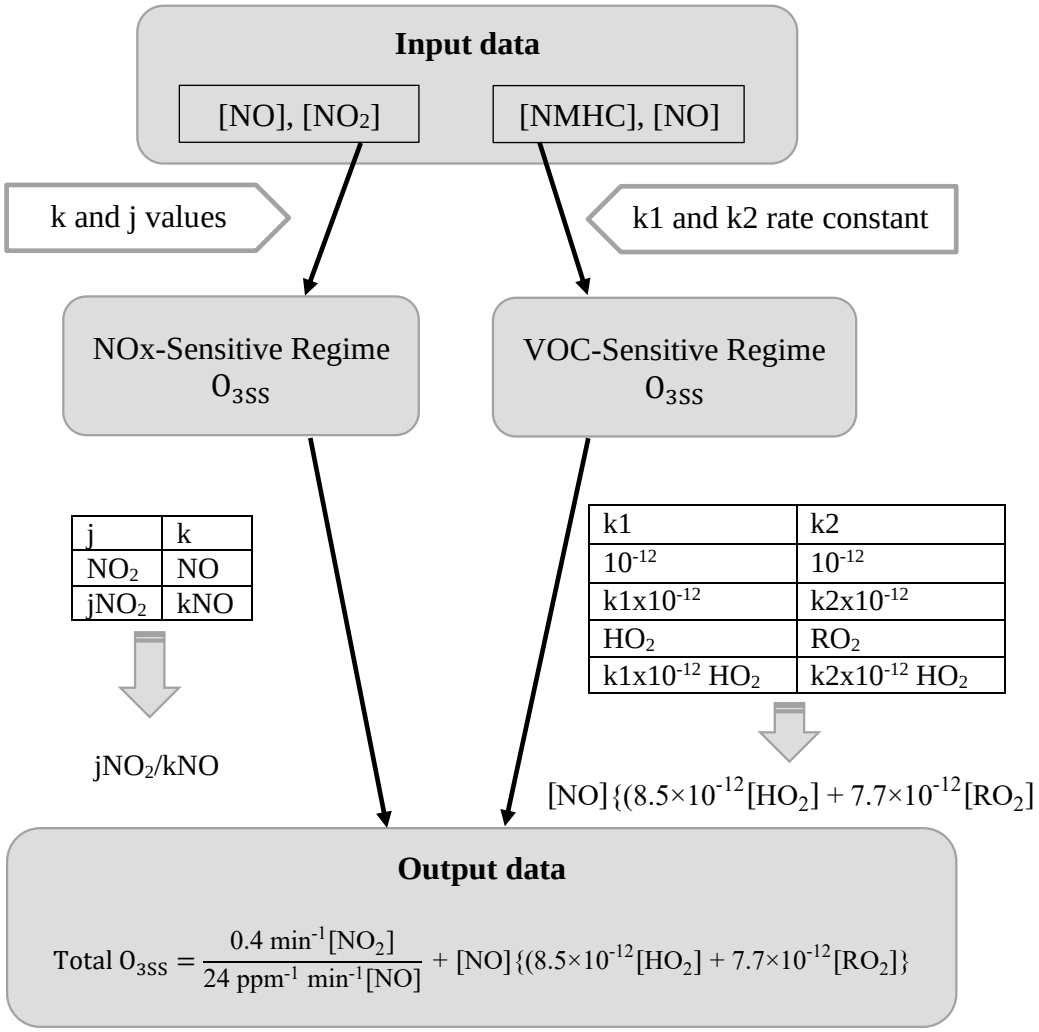


Figure 34: Calculation of the steady state Ozone concentration (O_{3SS}) in both regimes

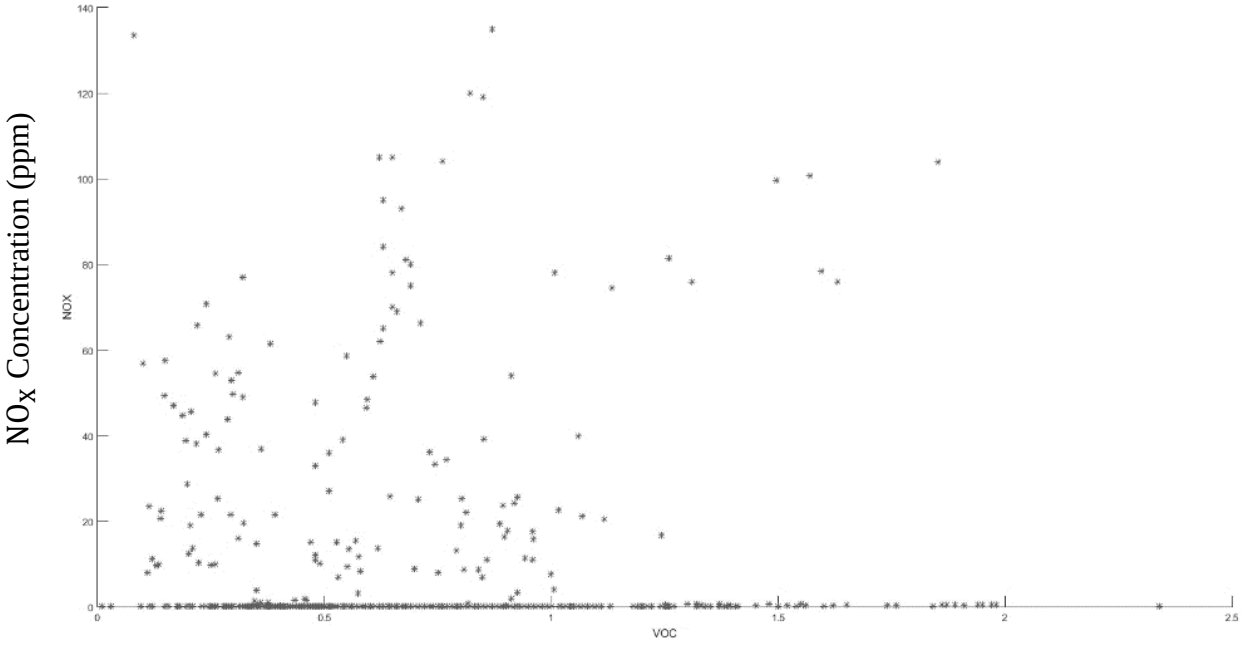
5.3.2 Analysis of association of influential parameters

a. Relationship of NO_X, VOC (NMHC) and O_3 air pollutants

NO_X, VOC (NMHC) and O_3 pollutant parameters and their distribution patterns are extensively studied and visualized as 2D and 3D in this section. According to the Figure 35, 36, 37, 38; 2D and 3D visualization of measured NO_X, VOC (NMCH) and O_3 concentration variation shows the relationship between NO_X, VOC (NMHC) and O_3.

Accordingly, by reducing VOC concentration, O_3 concentration can be effectively reduced only when VOC-sensitive regime reactions dominates. Further by reducing NO_X concentration, O_3 concentration can be effectively reduced only when NO_X- sensitive reactions dominate; while the reductions in NO_X might increase O_3 in VOC- sensitive areas. O_3 and other related oxidants cannot build up without the combined action of NO_X and VOCs. Thus, controlling photochemical air pollution requires reducing both VOCs and NO_X concentations. This explanation could be recognized as explained in typical O_3 isopleth plot diagram [213] in section 3.3.

i *Relationship of* $\boldsymbol{NO_X}$ *and* $\boldsymbol{VOC}$ ($\boldsymbol{NMHC}$) *concentration variation*

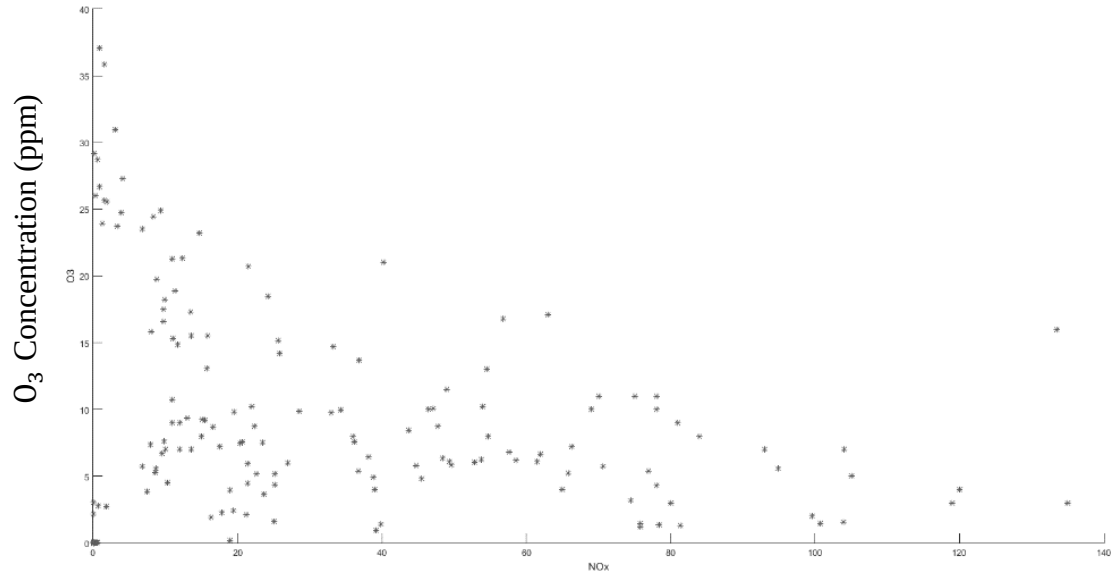


NO_X Concentration (ppm)

VOC Concentration (ppm)

Figure 35: 2D Visualization of measured NO_X and VOC concentration variation

ii *Relationship of* $\boldsymbol{NO_X}$ *and* $\boldsymbol{O_3}$ *concentration variation*



O_3 Concentration (ppm)

NO_X Concentration (ppm)

Figure 36: 2D Visualization of measured O_3 and NO_X concentration variation

iii Relationship of O_3 and VOC concentration variation

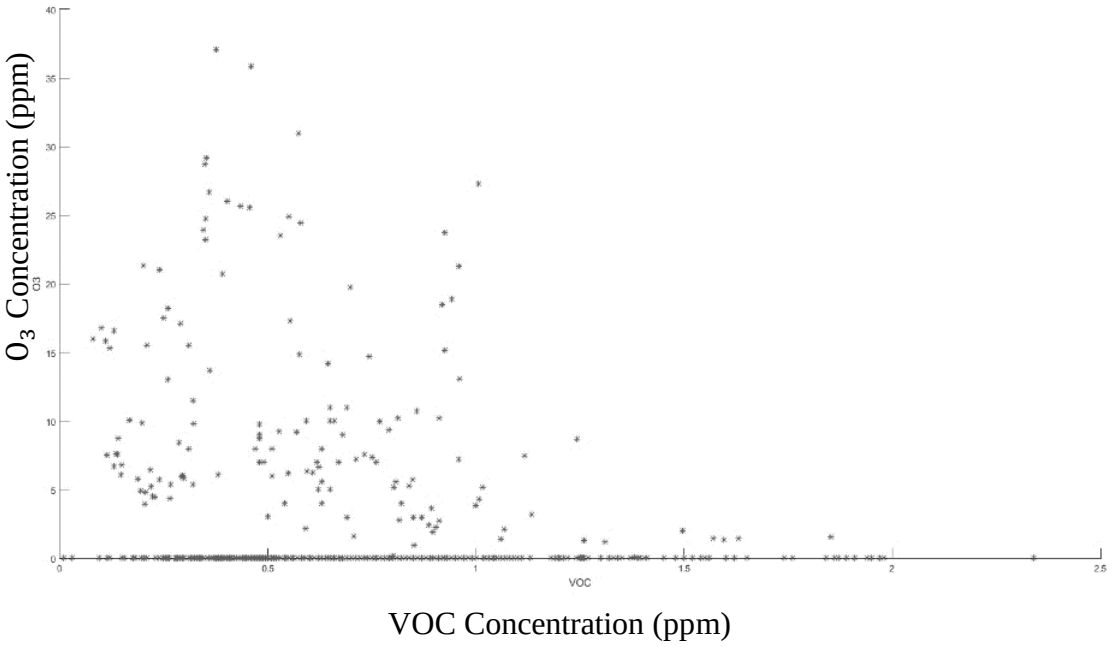


Figure 37: 2D Visualization of measured VOC and O_3 concentration variation

iv. Relationship of the NO_X, $NMCH$ and O_3 concentration variation

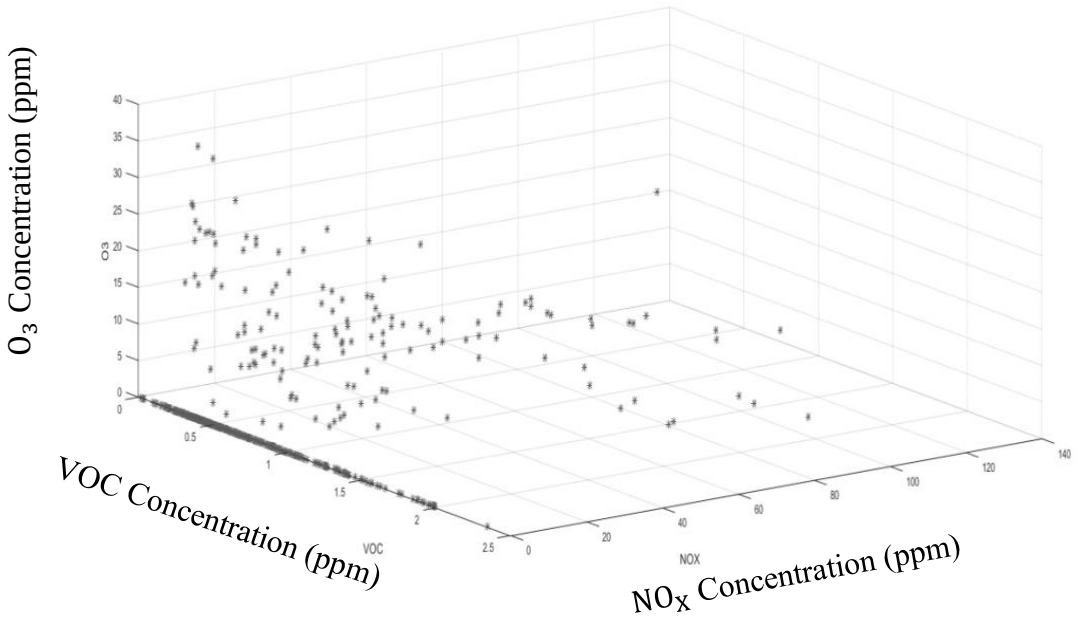


Figure 38: 3D Visualization of measured NO_X, NMCH and O_3 concentration variation

b. Relationships of Meteorological Parameters

Possible relationships of meteorological parameters such as air temperature, solar radiation and wind speed, and their distribution patterns are extensively studied in this section. According to the Figure 39, O_3 production is high, when the temperature is in the range of 25 to 35° C. As shown in Table 10 and Table 11, mean O_3 concentration is two folds higher when the temperature is within the range of 30 to 35° C. Therefore, O_3 production increases when the temperature increased particularly above 30° C.

According to Figure 40, production of O_3 has taken place even the solar radiation value is zero. This further explains the VOC sensitive regime dominate in such cases than NO_X sensitive regime. Highest mean O_3 concentration was observed with solar radiation above 600 W/m^2 as shown in Table 12 and Table 13 Therefore, O_3 production increases when the solar radiation increased.

According to Figure 41, O_3 concentration has an increasing trend with increasing wind speed. When the wind speed increases probability is getting higher for the molecules to collide with each other. As explained in Table 14 and Table 15, O_3 concentration was high when the wind speed value was within 2 to 3.9 m/s. Therefore, meteorological parameters; air temperature, wind speed and solar radiation have a relationship with O_3 production and it is an increasing trend.

i. Relationship of O_3 and Temperature

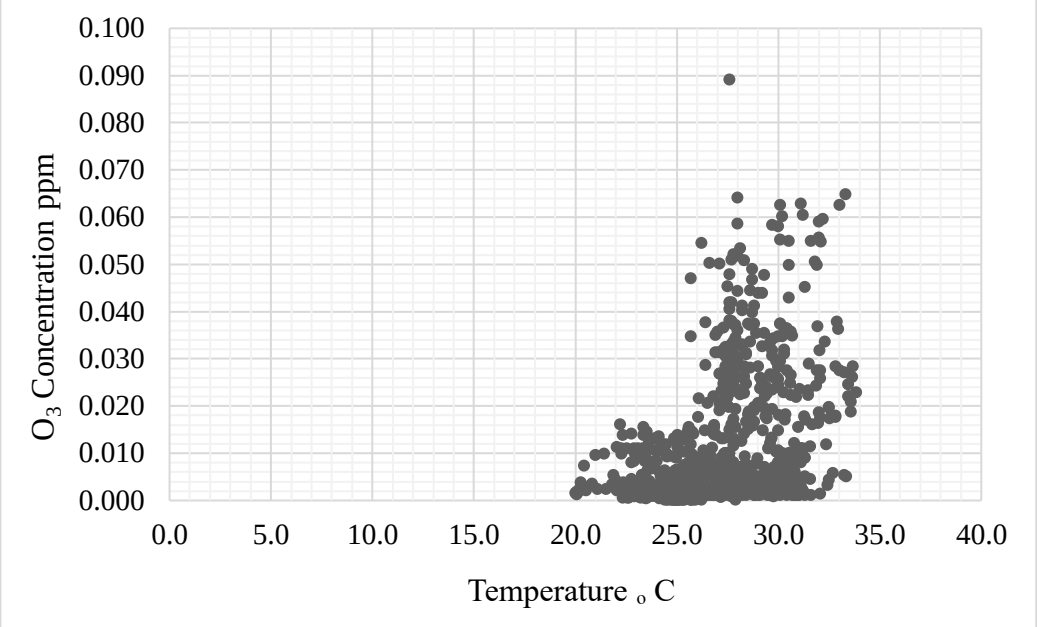


Figure 39: 2D Visualization of measured O_3 concentration and Temperature

Table 10: O_3 Concentration variation with different categories of Temperature

Temperature category (° C)	**Mean O_3 Concentration (ppm)**	**Number of data points**	**Std. Deviation**
1 [20 – 24.99]	0.004	152	0.004
2. [25 – 29.99]	0.005	455	0.007
3. [30 – 34.99]	0.008	187	0.009
Total	0.005	794	0.007

Table 11: ANOVA test of O_3 concentration variation with different categories of Temperature

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	0.002	2	0.001	17.899	0.000
Within Groups	0.044	791	0.000		
Total	0.046	793			

ii. Relationship of O_3 and Solar Radiation

Table 12: O_3 concentration variation with different categories of Solar Radiation

Solar Radiation Category (W/m^2)	Mean O_3 Concentration (ppm)	Number of data points	Std. Deviation
1. [0 - 0.299]	0.004	369	0.006
2. [300 - 599]	0.007	119	0.012
3. [600- 1199]	0.008	109	0.008
Total	0.006	597	0.008

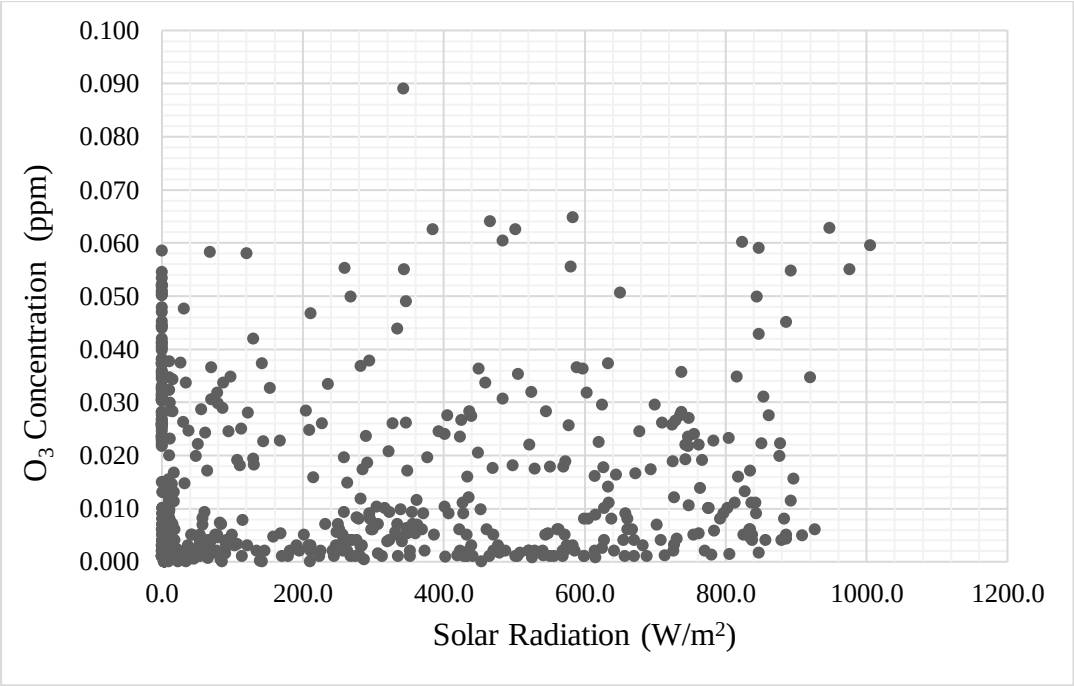


Figure 40: 2D Visualization of measured O_3 concentration and Solar Radiation

Table 13: ANOVA test of O_3 concentration variation with different categories of Solar Radiation

	Sum of Squares	**Df**	**Mean Square**	**F**	**Sig.**
Between Groups	0.002	2	0.001	12.241	0.000
Within Groups	0.037	594	0.000		
Total	0.039	596			

iii. Relationship of O_3, Wind speed

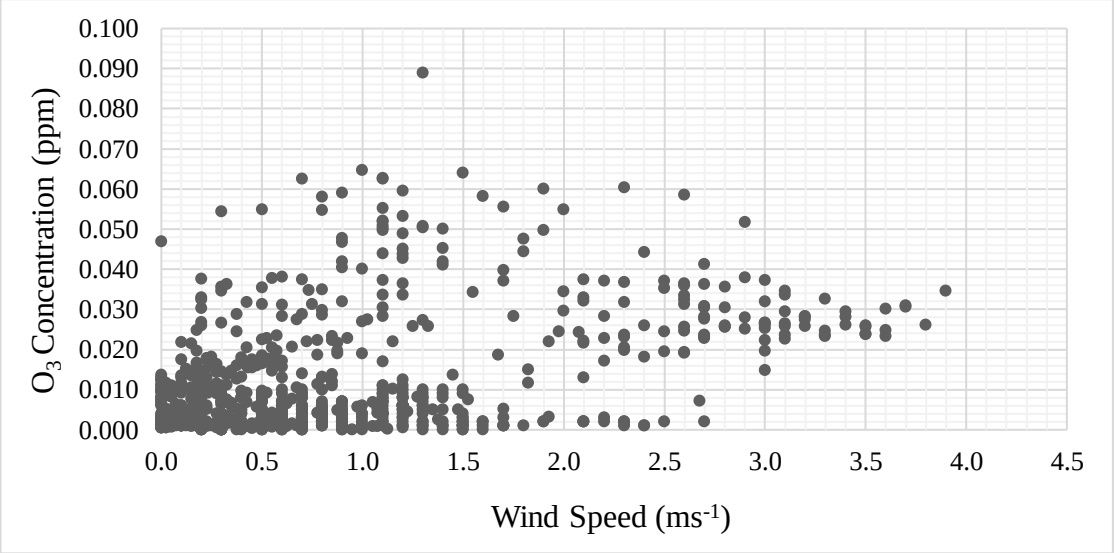


Figure 41: 2D Visualization of measured O_3 concentration and Wind Speed

Table 14: O_3 concentration variation with different categories of Wind Speed

Wind speed category (m/s)	**Number of data points**	**Mean O_3 Concentration (ppm)**	**Std. Deviation**
1. [0 - 0.99]	789	0.009	0.011
2. [1 - 1.99]	288	0.018	0.019
3. [2 - 2.99]	126	0.027	0.012
4. [3 – 3.99]	76	0.026	0.004
Total	1279	0.014	0.015

Table 15: ANOVA test of O_3 concentration variation with different categories of Wind Speed

	Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Between Groups	0.059	3	0.020	106.9	0.000
Within Groups	0.233	1275	0.000		
Total	0.291	1278			

5.3.3 Analysis of development of the Model

Steady state Ozone concentration (O_{3SS}) in both regimes could be calculated as below;

$$[O_3]_{ss} = [O_3]_{NO_x sensitivity} + [O_3]_{VOC\ sensitivity}$$

$$[O_3]_{ss} = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]} + [NO](k_1[HO_2] + k_2[RO_2])$$

$$= \frac{0.4\ min^{-1}[NO_2]}{24\ ppm^{-1}\ min^{-1}[NO]} + [NO]\{(8.5\times10^{-12}[HO_2] + 7.7\times10^{-12}[RO_2]\}$$

Where;

k –depends on Temperature; Ω 0.4 ppm-1 s-1

j–depends on solar radiation; at night= 0; at full sunlight= 0.4 min-1 [10]

k1= 8.5 × 10-12.; k2= 7.7 × 10-12 ; Rate constants at 298 K in cm3 molecule-1 s-1 for bimolecular reactions and in s-1 for photolysis reactions [258].

The above developed equation already includes [NO], [NO_2], [VOC] and [O_3] air pollutant concentrations and the meteorological parameters of Temperature, Solar radiation and Wind parameters. Below explains the relationship of the meteorological parameters with the rate constant.

a. <u>Rate Constant (k):</u>

k = A *e*^(*Ea*/*RT*)

A- Frequency Factor

Ea- Activation Energy

T- Temperature

Increasing Temperature (T) and the activation energy (Ea) increases the Rate Constant. Temperature is signified with the rate constant in the urban air-shed model.

b. Collision Theory and the Rate Constant

Rate Constant: $\mathbf{k = PZ}e^{\wedge}(\boldsymbol{Ea}/\boldsymbol{RT})$

Where A=PZ

Z- Collision Frequency- the average rate of the collision of two reactions in a system (reaction mixture)

P- Steric factor- the orientation of the molecules that collide

Therefore, wind parameter is signified as Collision Frequency and Steric factor in the urban air-shed model.

5.4 EVALUATION OF THE MODEL

5.4.1 Model applications to the measured data

Measured steady state $O_{3_{ss}}$ concentration was compared with the calculated steady state $O_{3_{ss}}$by application to the developed theoretical Urban Air-shed Model in section 5.3.3. Graphs were drew for each location at Anuradhapura, Kurunegala, Nugegoda, Ratnapura and Jaffna and the total five locations selected and results are presented in Figure 42 to 47.

a. Anuradhapura

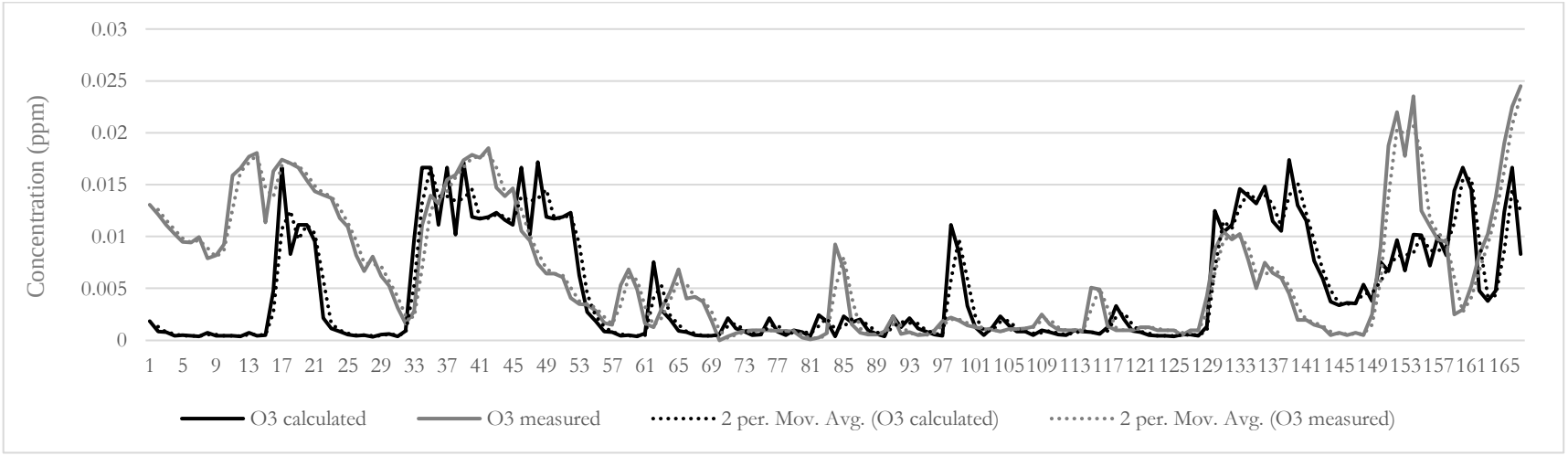


Figure 42: Comparison of measured steady state $O_{3_{ss}}$ concentration with the calculated steady state $O_{3_{ss}}$concentration in Anuradhapura

b. Kurunegala

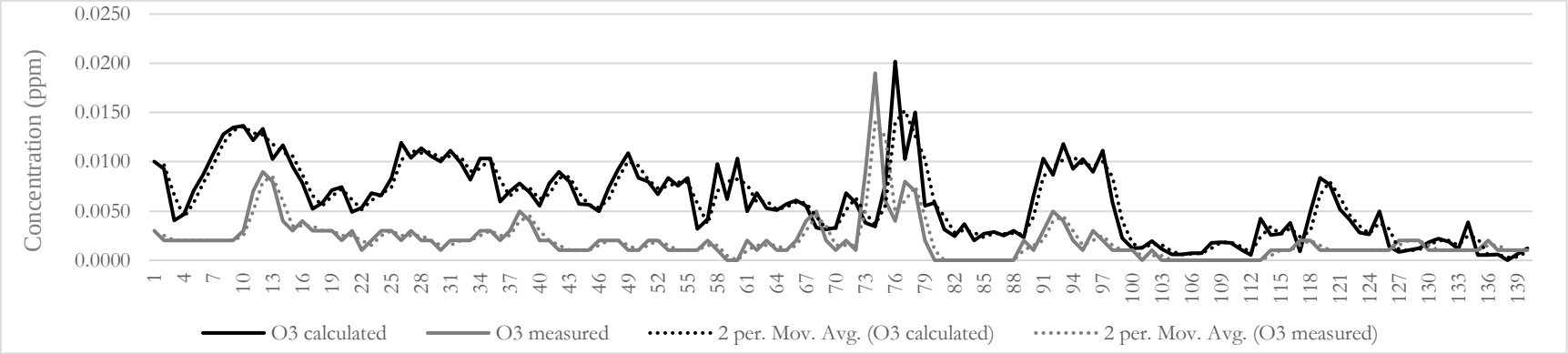


Figure 43: Comparison of measured steady state $O_{3_{ss}}$ concentration with the calculated steady state $O_{3_{ss}}$concentration in Kurunegala

c. Colombo – (Nugegoda)

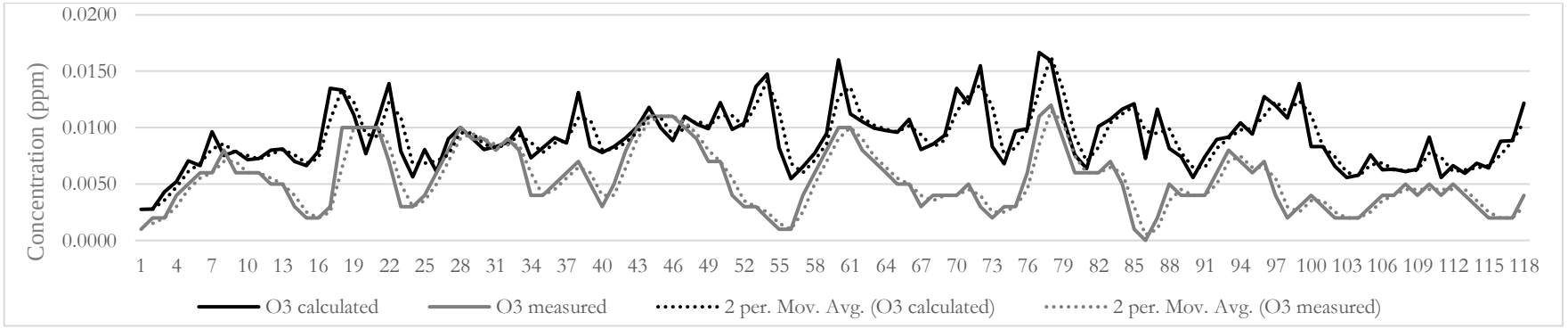


Figure 44: Comparison of measured steady state $O_{3_{ss}}$ concentration with the calculated steady state $O_{3_{ss}}$concentration in Colombo

d. Ratnapura

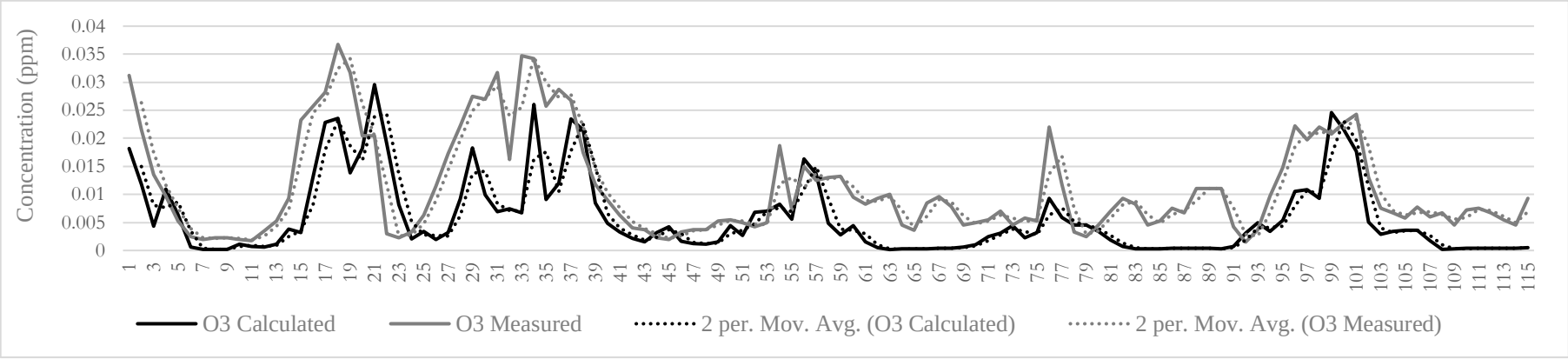


Figure 45: Comparison of measured steady state $O_{3_{ss}}$ concentration with the calculated steady state $O_{3_{ss}}$concentration in Ratnapura

e. Jaffna

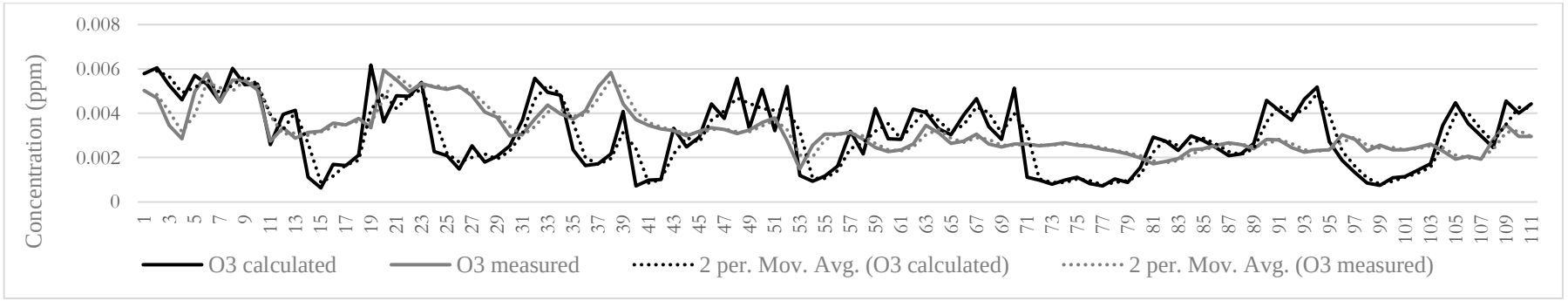


Figure 46: Comparison of measured steady state $O_{3_{SS}}$ concentration with the calculated steady state $O_{3_{SS}}$concentration in Jaffna

f. Combination of five city data

According to the Figure 47, measured steady state $O_{3_{SS}}$ concentration has close relationship with the calculated steady state $O_{3_{SS}}$ concentration. However, small deviation was observed between the two trend patters. This variation could be due to the wind speeds and their directions in the locations. Therefore, to identify this deviation, wind speed trend pattern were drew in the same graph with measured steady state $O_{3_{SS}}$ concentration and calculated steady state $O_{3_{SS}}$ concentration as shown in Figure 48.

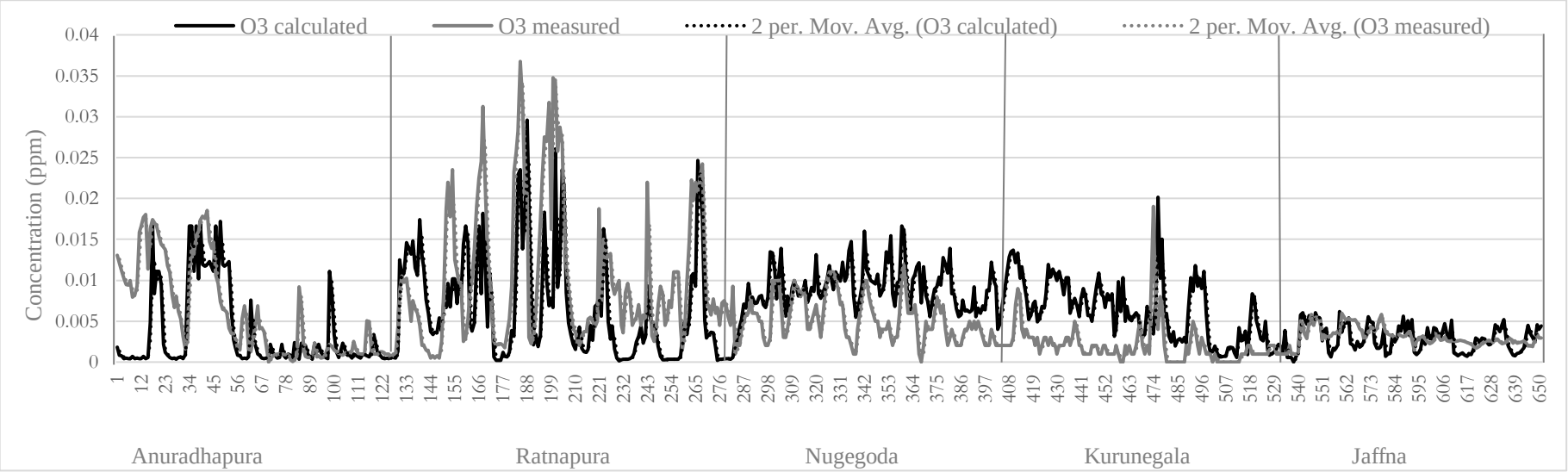


Figure 47: Comparison of measured steady state $O_{3_{ss}}$ concentration with the calculated steady state $O_{3_{ss}}$concentration in selected five locations in Sri Lanka

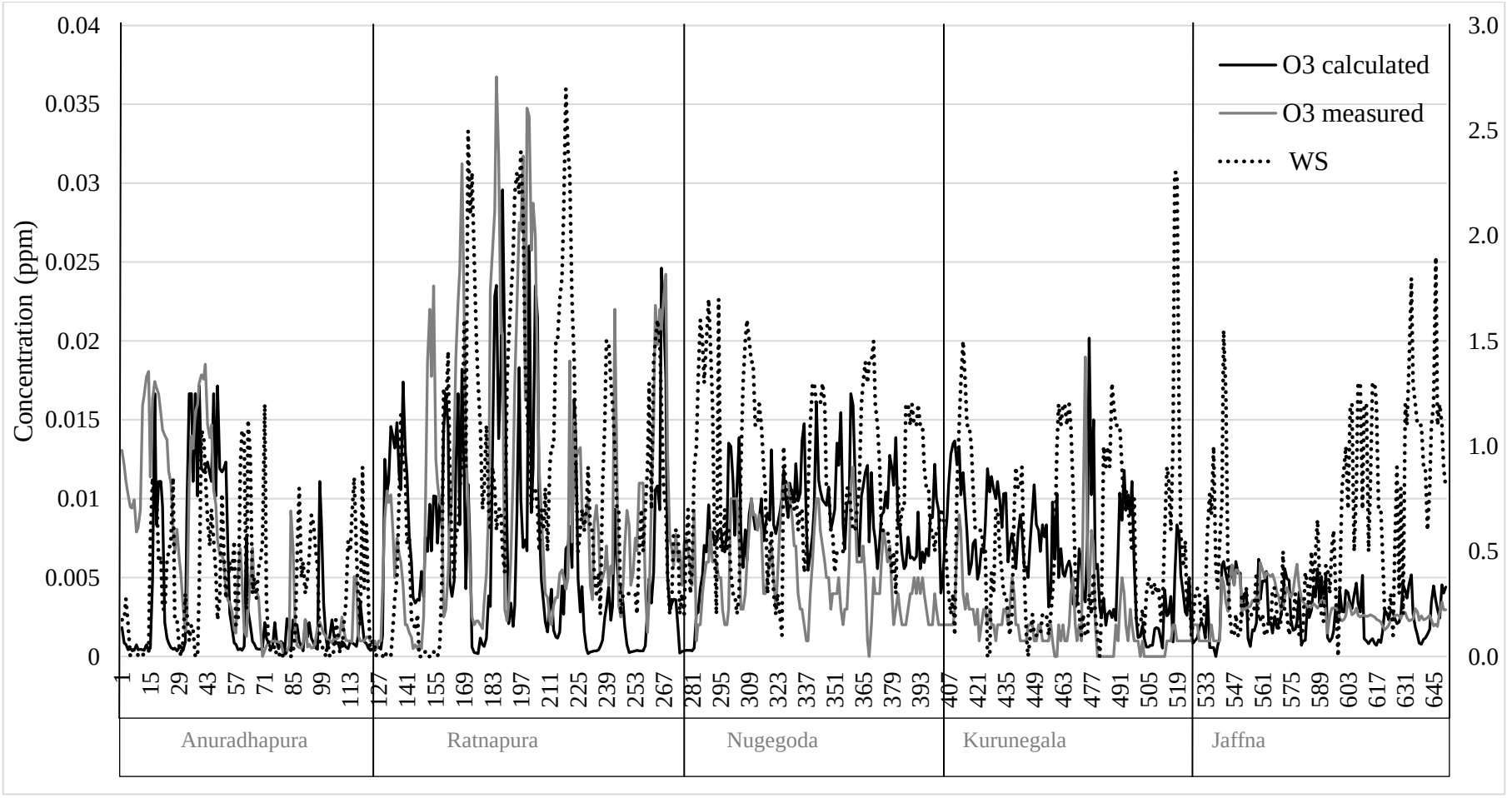


Figure 48: Comparison of measured steady state $O_{3_{ss}}$ concentration, calculated steady state $O_{3_{ss}}$concentration and wind speed in selected five locations in Sri Lanka (*Wind Speed is presented in secondary axis)

5.4.2 Model Calibration

a. Univariate linear regression mode using predicted and observed O_3values

The univariate linear regression mode using predicted and observed O_3values were carried out as presented in Table 16. Accordingly observed O_3 concentration is significantly correlated with the predicted O_3 concentration.

Table 16: Univariate linear regression results using predicted and observed O_3values

Variable	Std. Error	t value	Significance
Intercept	0.0003207	7.256	$P \leq 0.001$
O_3 Predicted	0.0425079	13.392	$P \leq 0.001$

* Dependent variable: O_3Observed Independent variable: O_3Predicted

b. Multivariate regression model using wind speed as an additional independent variable

Further multivariate regression model using wind speed as an additional independent variable also has been carried out as presented in Table 17.

Table 17: Multivariate regression results using wind speed as an additional independent variable

Variable	Std. Error	t value	Significance
Intercept	0.0003905	4.628	$P \leq 0.001$
O_3 Predicted	0.0429194	12.892	$P \leq 0.001$
Wind speed	0.0004158	2.318	$P \leq 0.05$

*Dependent variable: O_3 Observed; Independent variable: O_3 Predicted; Additional independent variable: Wind speed

Accordingly, observed O_3 concentration was significantly correlated with predicted O_3 concentration and wind speed. Correlation was stronger among observed O_3 concentration and predicted O_3 concentration as compared to the correlations between observed O_3 concentration and wind speed.

c. Multivariate regression adding wind speed as a variable which could interact with O_3 level

Results of the multivariate regression adding wind speed as a variable which could interact with O_3 level are presented in Table 18. Observed O_3 concentration was significantly correlated with predicted O_3 concentration; wind speed; and interaction of predicted O_3 and wind speed. As compared to predicted O_3 and the interaction of predicted O_3 and wind speed, wind speed have less significant correlation with observed O_3.

Table 18: Multivariate regression results adding wind speed as a variable which could interact with O_3 level

Variable	**Std. Error**	**T- value**	**Significance**
Intercept	0.0004898	6.920	$P \leq 0.001$
O_3 Predicted	0.0719727	3.485	$P \leq 0.001$
Wind speed	0.0006870	-2.767	$P \leq 0.01$
O_3_Pred:WS	0.0942222	5.181	$P \leq 0.001$

*Dependent variable: $\mathbf{O_3}$Observed; Independent variable: $\mathbf{O_3}$Predicted; Wind speed as a variable which could interact with $\mathbf{O_3}$ level.

CHAPTER 6

ANALYSIS OF COLOMBO AIR-SHED

6.1. BASIC APPROACH OF ANALYSIS OF COLOMBO AIR-SHED

Over-role frame-work of analysis of Colombo air-shed is presented in Figure 49.

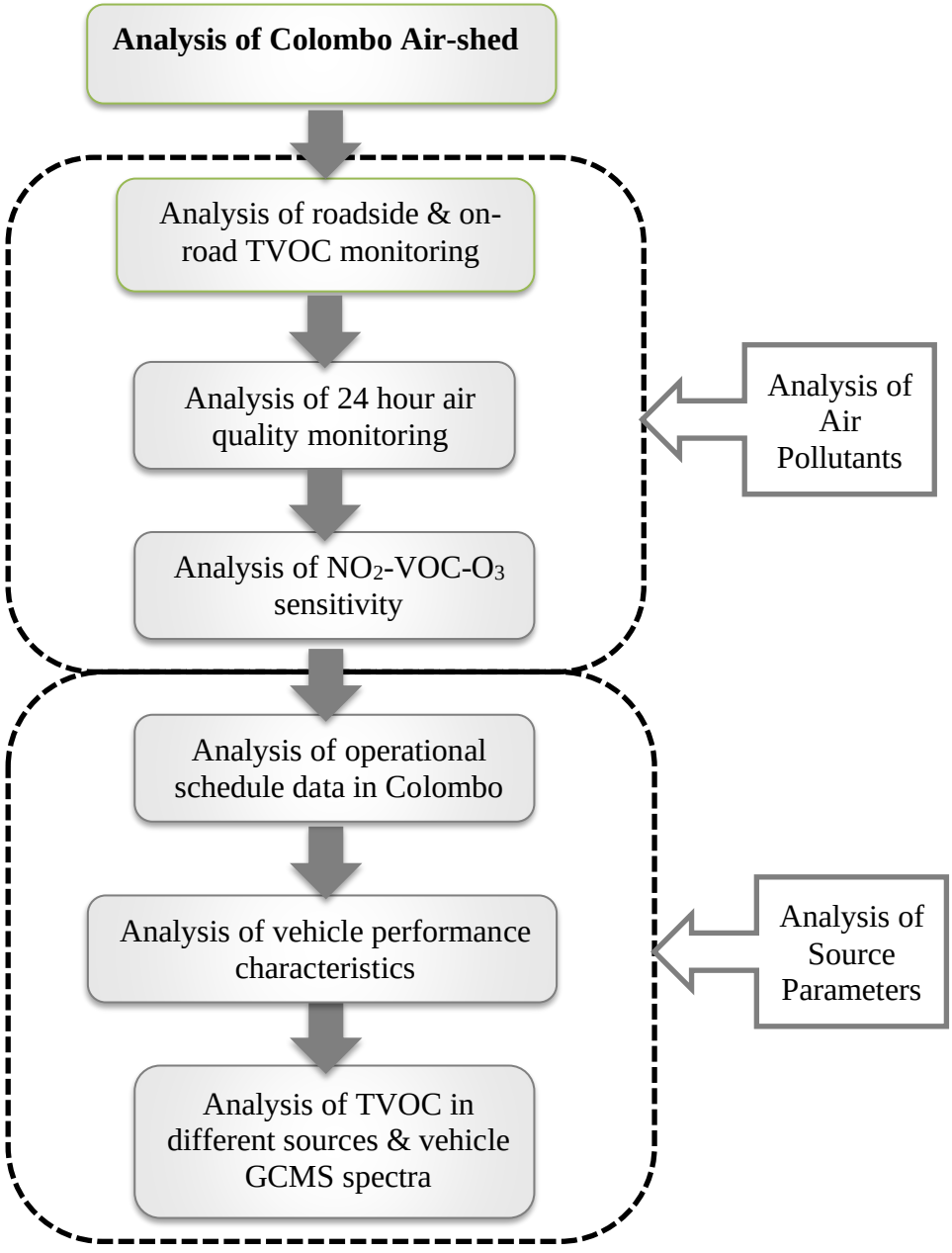


Figure 49: Over-role frame-work of the analysis of Colombo air-shed

Chapter 6 presents the Phase II of Results and Discussion of analysis of Colombo air-shed. Flow of the sections of analysis of Colombo air-shed is presented in Figure 50 as shown below.

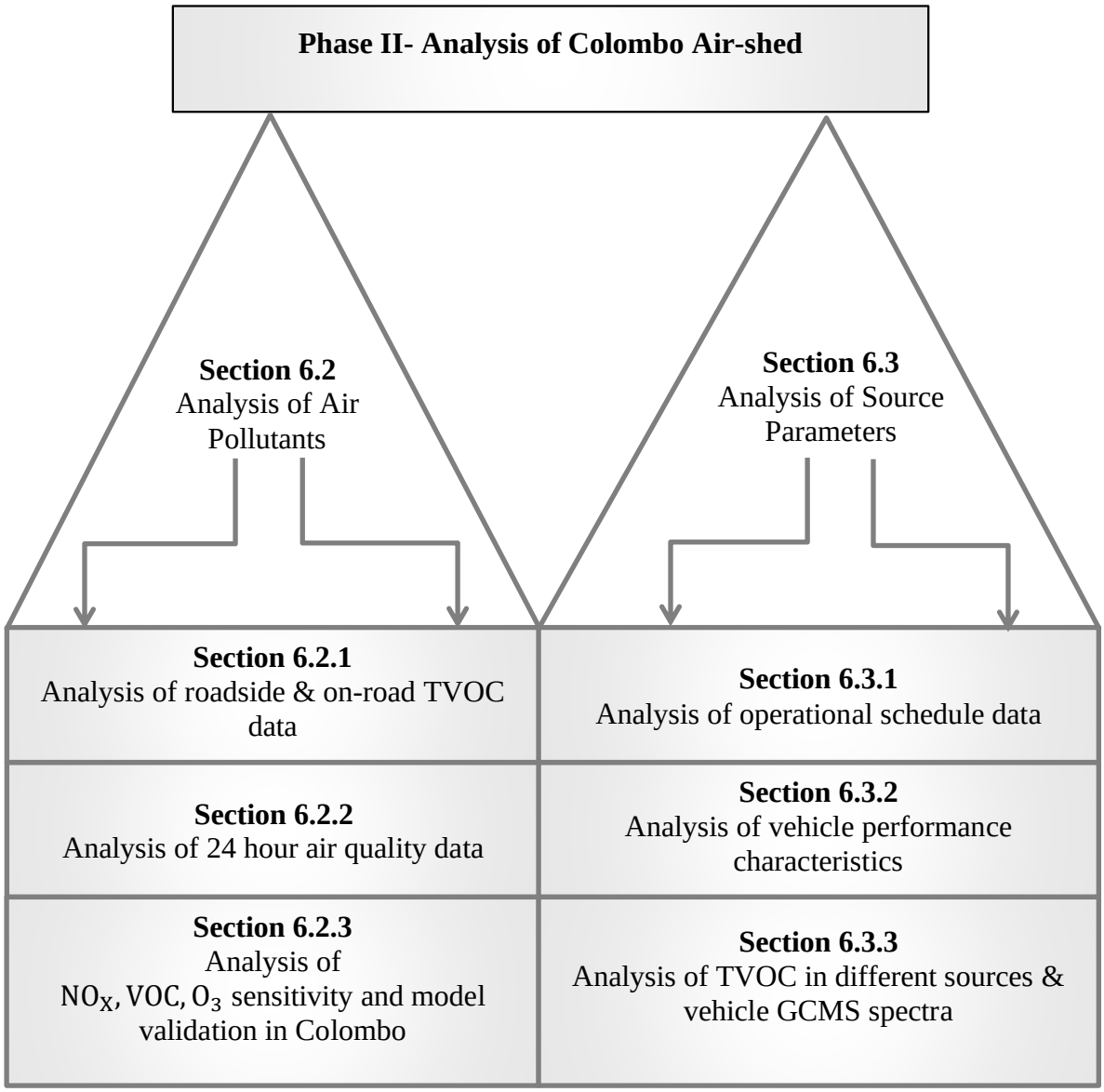


Figure 50: Flow of the sections of analysis of Colombo air-shed

6.2 ANALYSIS OF AIR POLLUTANTS

6.2.1 Analysis of roadside and on-road TVOC monitoring in Colombo

a. Roadside TVOC monitoring

Based on the Table 19, the highest TVOC median concentration (226.5ppb) was observed at the Grandpass junction. Highest TVOC levels at this site could be explained by the most congested Baseline road, Kelanithissa Thermal Power Stations and an industrial zone that situated at this area. Second highest TVOC levels were observed in Fort (205.6ppb). This could be explained by the most popular public transport hub having main bus station and the train station in this area. Maradana (194.5ppb) and Borella (190ppb) junctions also showed high TVOC concentrations. High TVOC levels at these two sites could be explained by the high vehicular traffic congestion during the measurements hour. For the Narahenpita (91.5ppb) and Dehiwala (99ppb) Junctions moderate TVOC levels were observed. This could be explained by the moderate vehicular traffic congestion at these junctions during the measurements hour.

The lowest TVOC levels of Kollupitiya (72.5ppb) junction may be due to the comparatively high sea breeze/ wind which disperse and dilutes the air pollutants. Based on the results, TVOC levels in Colombo was categorized and presented with a colour index as; above 225ppb for very high TVOC level (Red), 225ppb-150ppb for high TVOC level (Orange), 150ppb to 75ppb for medium TVOC level (Yellow), and below 75ppb as low TVOC level (Green).

Table 19: TVOC hourly beside the road measurements in selected locations in Colombo

Site	Mean ±SD (ppb)	Median	Colour index	TVOC range in ppb
Dehiwala	103.62±33.54	99.00		75-150
Kollupitiya	70.41 ± 11.94	72.50		<75
Fort	206.89±14.04	205.6		150-225
Maradana	240.20 ± 177.44	194.50		150-225
Borella	196.15±68.12	190		150-225
Narahenpita	104.76 ± 34.16	91.5		75-150
Grandpass	207.6 ± 57.17	226.5		>225

*Original is in Colour

b. On-road TVOC monitoring

Table 20 explained on road measurements of TVOC levels when the vehicle was moving in between the junctions. It was clearly showed that TVOC levels were high on the road (273.42ppb) than beside the road (132.86ppb). This could be due to the immediate tail pipe emissions (undiluted) from the ongoing vehicles. According to the results when the vehicle was moving from Narahenpita to Grandpass has shown the highest TVOC concentration (536ppb). Maradana to Borella has shown the second highest TVOC concentration (321.5ppb). Borella to Narahenpita has shown the third highest TVOC concentration (216ppb). In these cases results could be explained by the high vehicular traffic congestion during the measurements hour with high numbers of gasoline-fueled motor vehicles present on road. Moderate TVOC concentrations were observed in Fort to Maradana (195ppb), Kollupitiya to Fort (189ppb) and Dehiwala to

Kollupitiya (183ppb). In these cases Moderate TVOC concentrations could be due to the comparatively high sea breeze/ wind which disperse and dilutes the air pollutants.

Table 20: TVOC hourly on- road measurements in between selected locations in Colombo

Site	Mean ±SD (ppb)	Median	Colour index	TVOC range in ppb
Dehiwala to Kollupitiya (Figure 12a)	181.71 ±12.89	183		150-225
Kollupitiya to Fort (Figure 12b)	189.40 ± 38.19	189		150-225
Fort to Maradana (Figure 12c)	202.27 ± 55.29	195		150-225
Maradana to Borella (Figure 12e)	289.69± 75.71	321.5		>225
Borella to Narahenpita (Figure 12f)	215.71± 8.73	216		150-225
Narahenpita to Grandpass (Figure 12d)	560.14±276.68	536		>225

**Original is in Colour*

6.2.2 Analysis of 24 hour air quality monitoring in Colombo

Table 21 summarized the 24-hour average values of air pollutants at six locations in Colombo. Accordingly, high level of air pollutants have shown in different location base on the pollutant sources such as effects of power plant or train emissions or on-road vehicular emission or combine effect of several pollutant sources. Due to the wind effect of the power plant emissions at Narahenpita shows the highest particulate pollution (PM_{10}- 83µgm^{-3}, $PM_{2,5}$- 48.75µgm^{-3}, where in both cases WHO guideline value has exceeded). In Borella and Grandpass also have high PM_{10} (above 50µgm^{-3}) and $PM_{2,5}$ (above 25µgm^{-3}) levels that could be the reason of the power plant effect. Highest oxides of nitrogen (56.796µgm^{-3}) and non-methane hydrocarbon (NMHC-0.994ppm) concentrations were observed at Fort location could be due to the emissions from the trains and on-road vehicles which exceeded the WHO guideline value of 40µgm^{-3}.

Comparison of the detail 24 hour air quality monitoring and wind-rose of six locations (Borella, Grandpass, Narahenpita, Fort, Kollupitiya and Nugegoda) in Colombo are shown in Figure 51. High PM ($PM_{2.5}$ and PM_{10}) levels at Borella, Grandpass and Narahenpita areas could be emitted from adjacent "Oil Power Stations" at Kelanithissa. Further high concentrations of NO at Grandpass and Narahenpita could be also due to the emissions from adjacent "Oil Power Stations" at Kelanithissa. High concentration of air pollutant results matches with the working hours of the oil power stations at Kelanithissa. Findings further confirms that wind directions and wind speed plays an important role in transporting pollutants especially NO pollutant. NO could be emitting from the power station stack and fast dispersions has taken place as NO with less conversion to NO_2. Furthermore there were no effects of the "Oil Power Stations" at

Kelanithissa to Fort, Kollupitiya and Nugegoda locations during working hours of the power station comparing with the air quality monitoring data. Results further demonstrated that Fort and Nugegoda locations have heavily affected by the train emissions apart from the on road vehicles. This also matches with the location vise train scheduled time (Figure 52) obtained from the Sri Lanka Railways [259] for Fort location. Fort is the most popular public transport hub having main bus station and the train station in Colombo. Therefore, many trains stop at the Fort Railway Station resulting high vehicular emissions. Different results were observed in Kollupitiya due to the high sea breeze and the effects from the adjacent Colombo harbor. High NO concentration has observed from early morning until 10 am. Early morning NO concentration may be due to the effects from the harbor and after 6 am it may be due to emissions from the train and the emissions from on-road vehicles. However during day time NO concentration has reduced could be due to the reduction of vehicles because of one-way traffic management plan at Kollupitiya and high sea breeze with wind direction towards land side. Further after 10 am to 8 pm, high PM_{10} levels without increasing $PM_{2.5}$ was observed in Kollupitiya could be due to settling down of "sea salts" and the soil particles of massive constriction of "the port city development project" with the wind direction towards land side. This was further proven by the source appeasement of PM_{10} filter papers in Colombo [48].

Table 21: Comparison of 24-hour average values of air pollutants at six locations in Colombo

Pollutant/ Parameters	Borella	Grandpass	Narahenpita	Fort	Kollupitiya	Nugegoda	Standard/ Guideline [163]
$PM_{2,5}$ (μgm^{-3})	40.708	28.917	48.750	17.785	22.851	19.899	$PM_{2.5}$ SL Standard-50μgm^{-3} $PM_{2.5}$ WHO Guideline-25μgm^{-3}
PM_{10} (μgm^{-3})	69.000	69.042	83.000	37.677	59.762	64.683	PM_{10} SL Standard-100μgm^{-3} PM_{10} WHO Guideline-50μgm^{-3}
THC (ppm)	3.100	2.262	3.781	2.883	2.785	2.282	No standard has been developed yet
CH_4 (ppm)	2.257	1.993	3.571	1.889	2.177	1.652	
NMHC (ppm)	0.844	0.275	0.210	0.994	0.608	0.630	
CO (ppm)	0.888	0.911	1.012	1.389	0.758	0.802	CO I -hour SL Standard-30mgm^{-3} CO 1-hour USEPA Standard-35ppb (35000ppm)/ 40mgm^{-3}
NO (μgm^{-3})	6.920	30.984	19.536	38.746	1.562	40.250	NO_2 SL Standard-100μgm^{-3} (0.0494ppm) NO_2 WHO Guideline-40μgm^{-3} (0.0197ppm)
NO_2 (μgm^{-3})	12.545	8.409	13.969	18.672	4.345	27.500	
NO_x (μgm^{-3})	19.486	40.153	33.585	56.796	5.952	3.568	
O_3 (μgm^{-3})	10.205	15.070	6.559	3.817	20.634	7.042	O_3 1-hour SL Standard--200μgm^{-3}(0.0946ppm), O_3 1-hour USEPA Standard-0.12ppm
Temperature ˚C	30	29.8	30	28	30	28.9	
Relative- Humidity %	62	68.5	59	75	76	75.4	
wind speed m/s	0.4	1.3	0.6	1.3	4.5	0.9	
wind direction degree	164	213.7	142	136.5	271	25	

Figure 51: Comparison of air pollutant monitoring data and wind-rose of the six locations in Colombo **Original is in Colour*

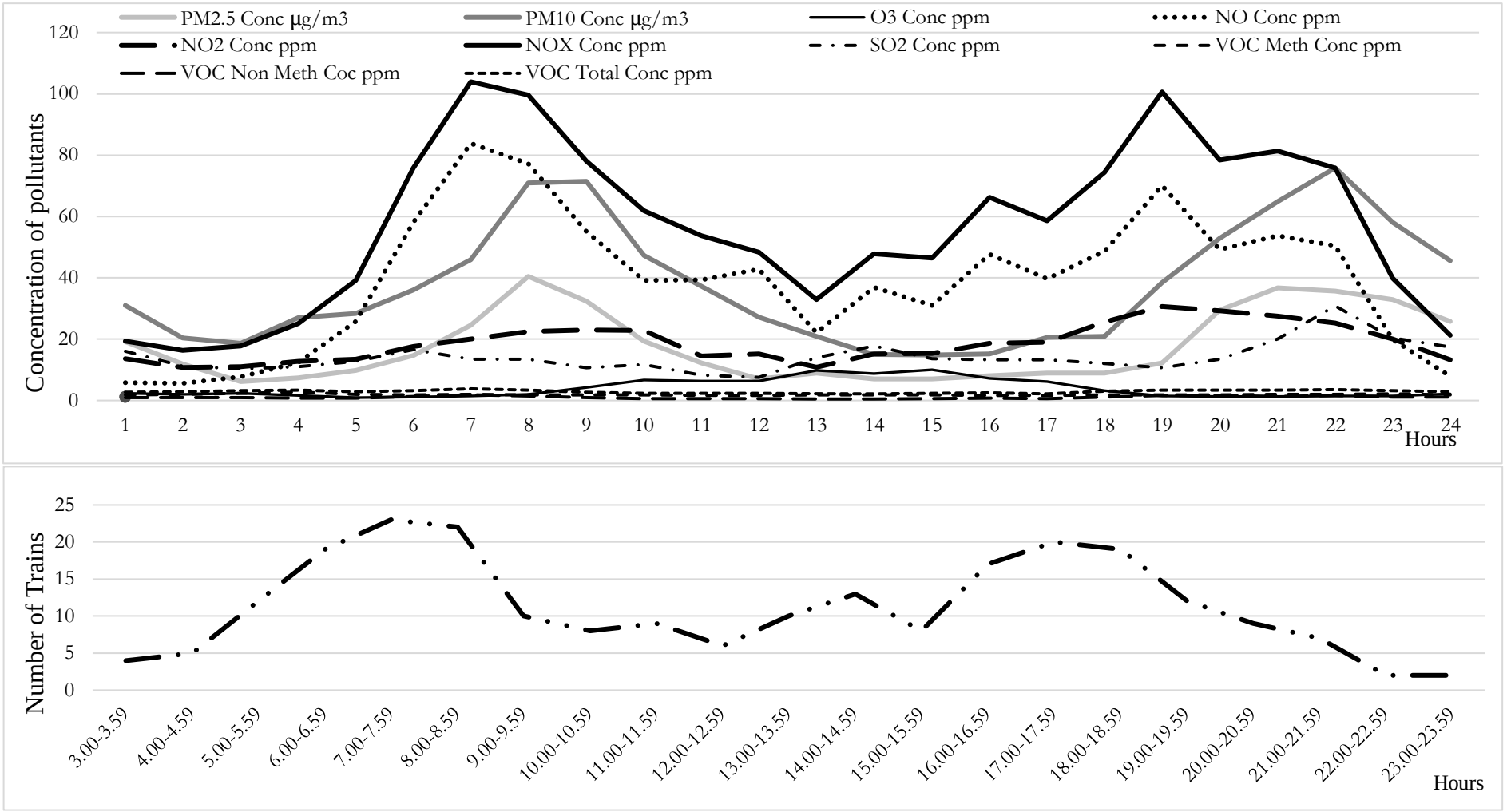


Figure 52: Comparison of air pollution levels with train scheduled data during a day at Fort location

Detail 24 hour air quality monitoring trend patterns of six locations in Borella, Grandpass, Narahenpita, Fort, Kollupitiya and Nugegoda are shown in Figure 53, 54, 55, 55, 56 and 57 respectively.

a. Borella Location

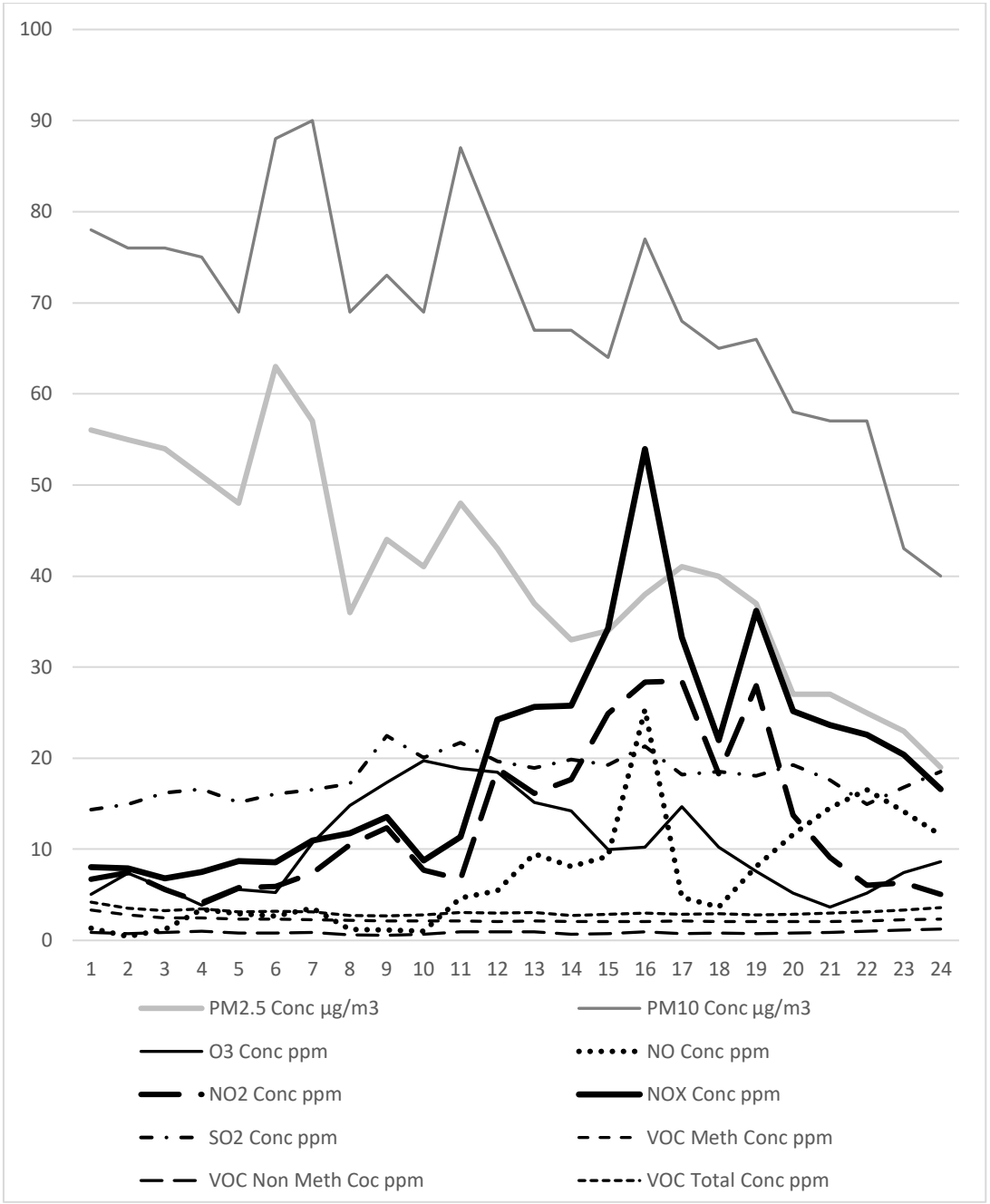


Figure 53: Air pollutants variation with in a day in Borella

b. Grandpass Location

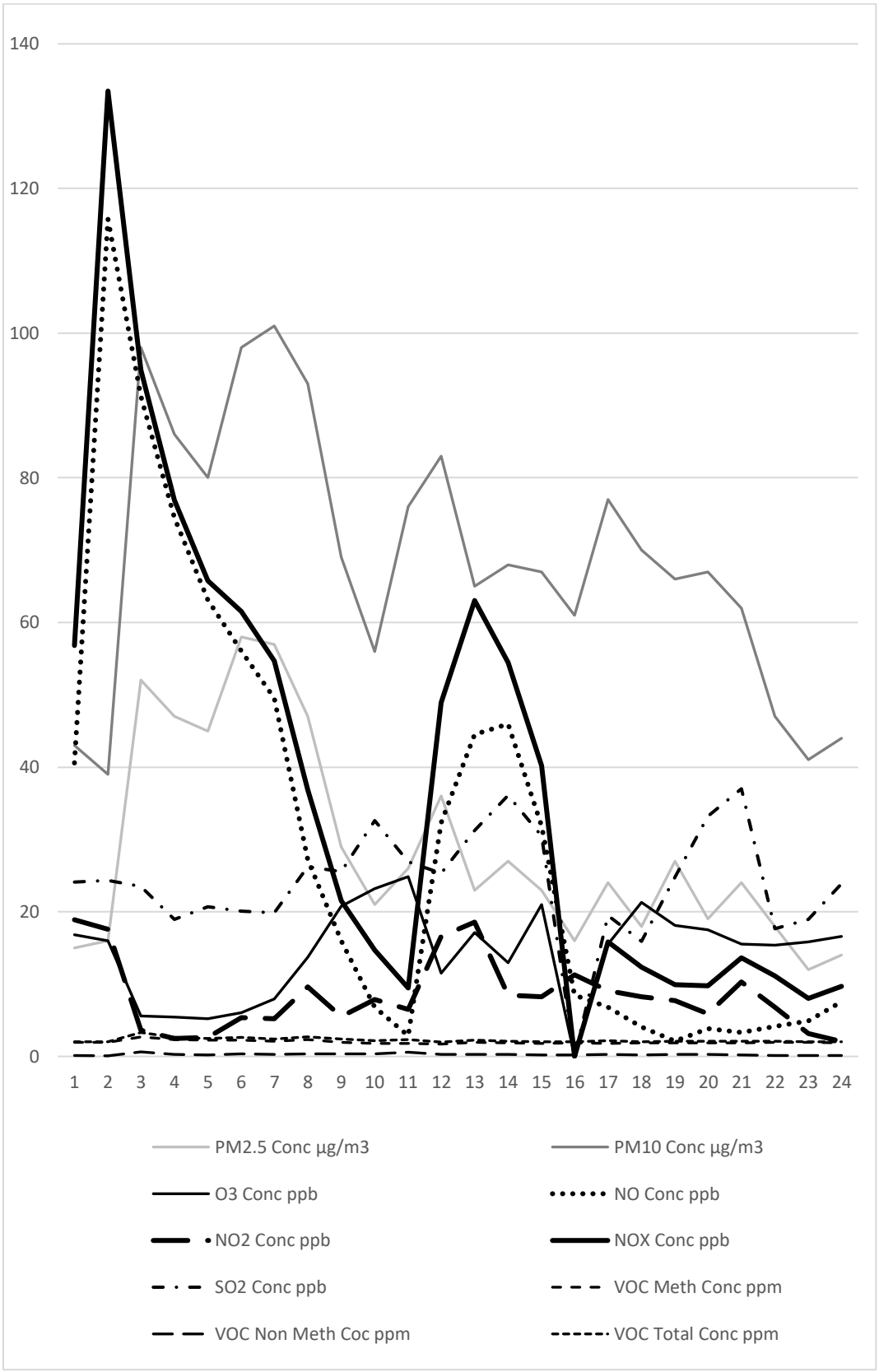


Figure 54: Air pollutants variation with in a day in Grandpass

c. Narahenpita Location

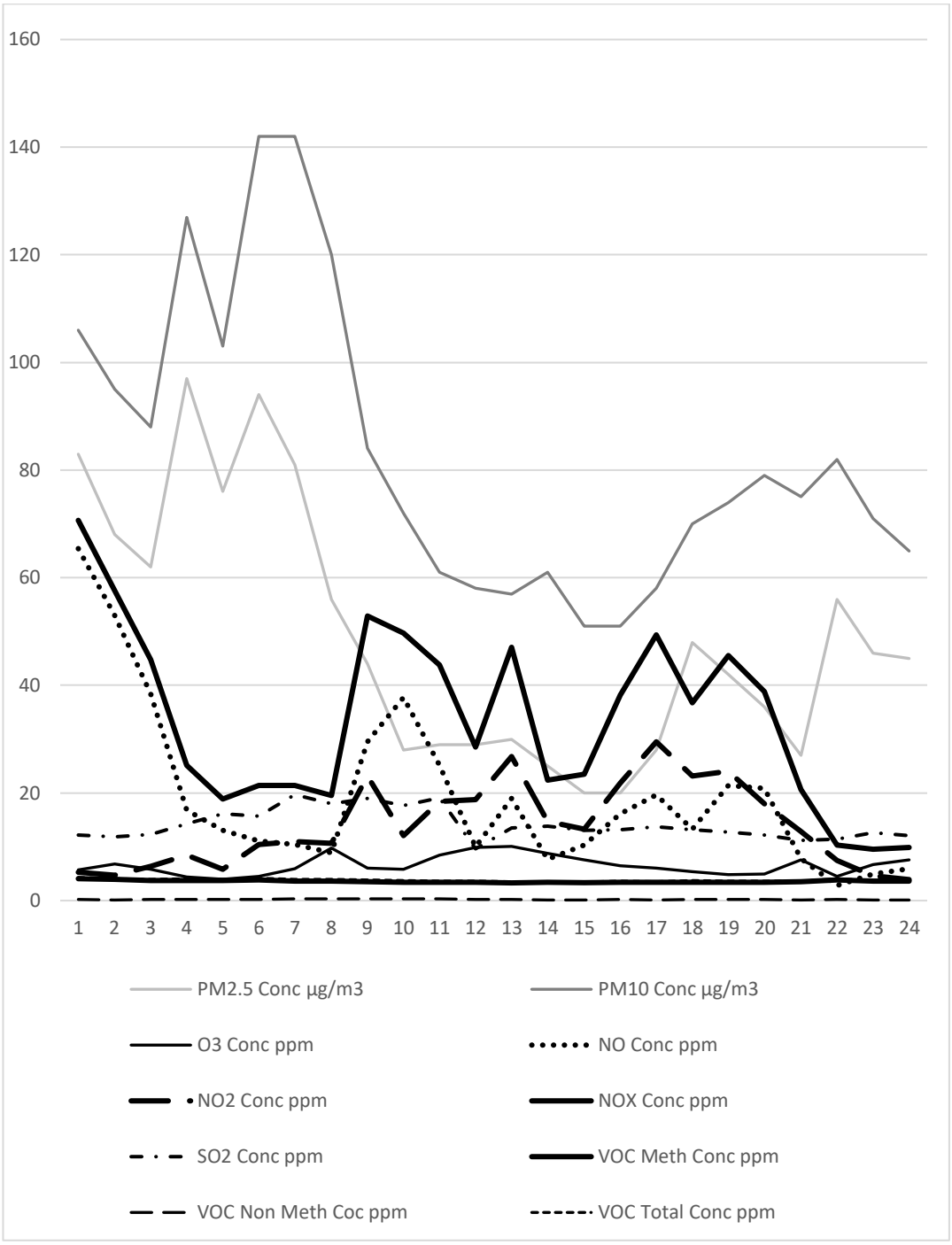


Figure 55: Air pollutant variation with in a day in Narahenpita

d. Fort Location

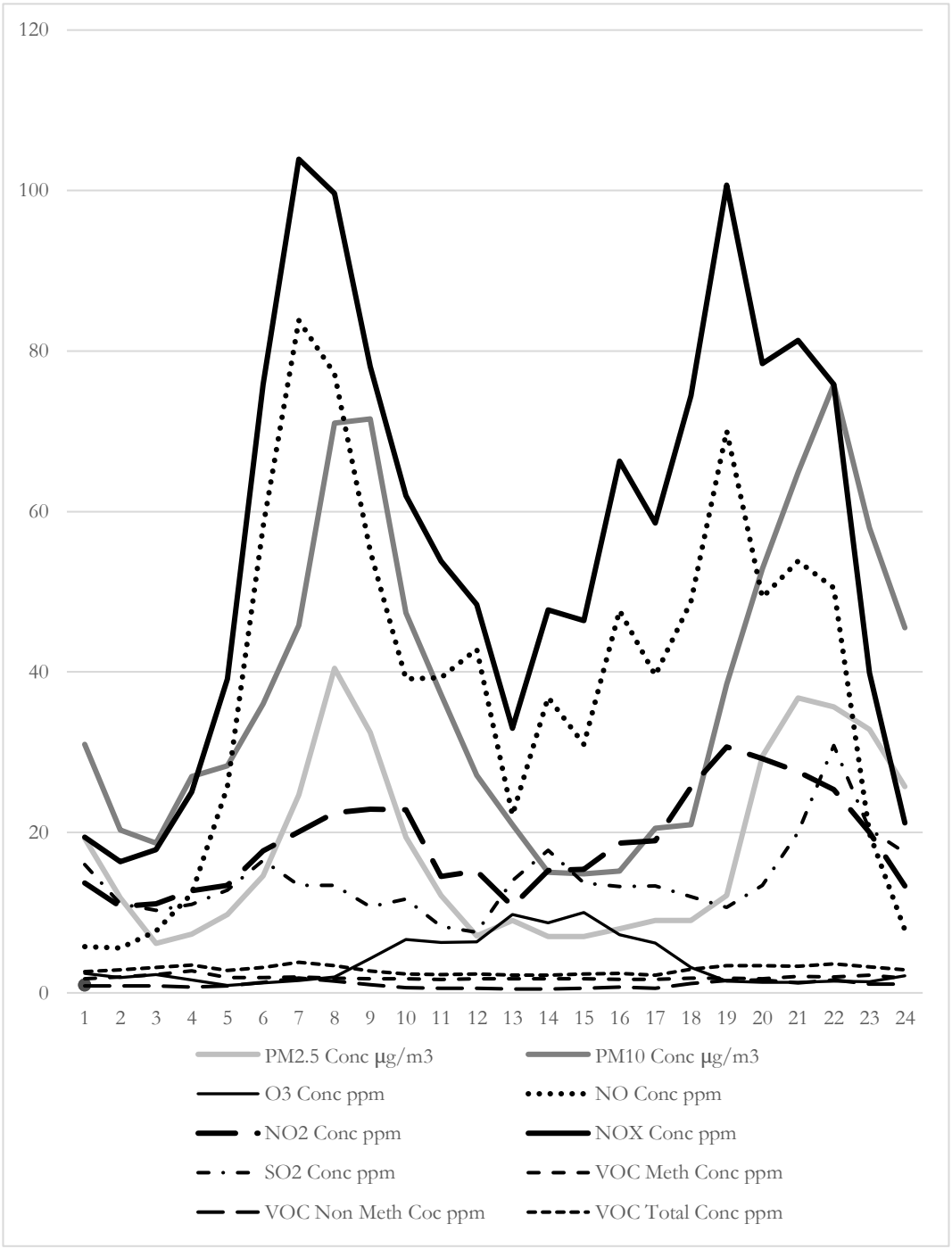


Figure 56: Air pollutant data variation with in a day in Fort

e. Kollupitiya Location

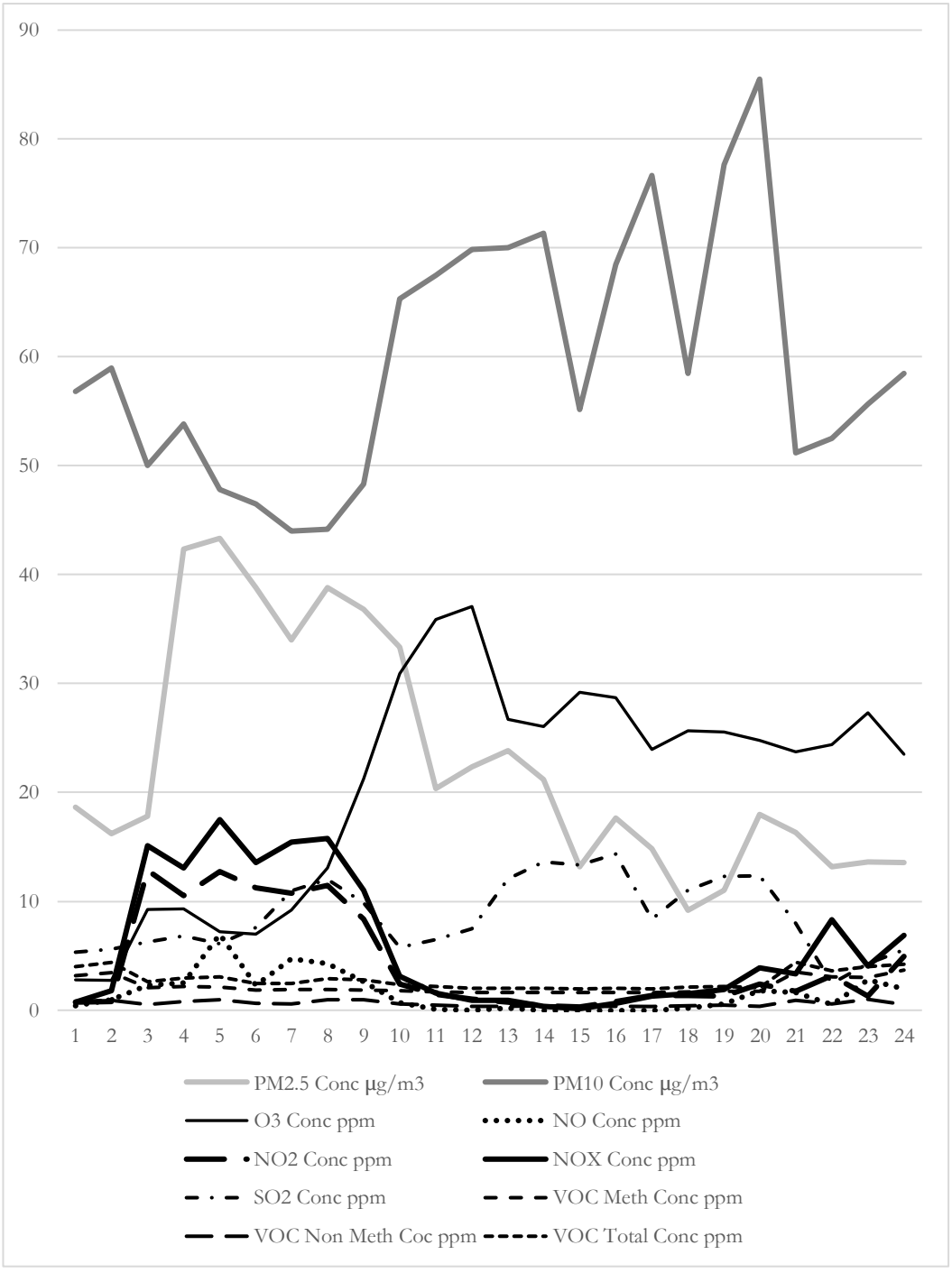


Figure 57: Air pollutant data variation with in a day in Kollupitiya

f. Nugegoda Location

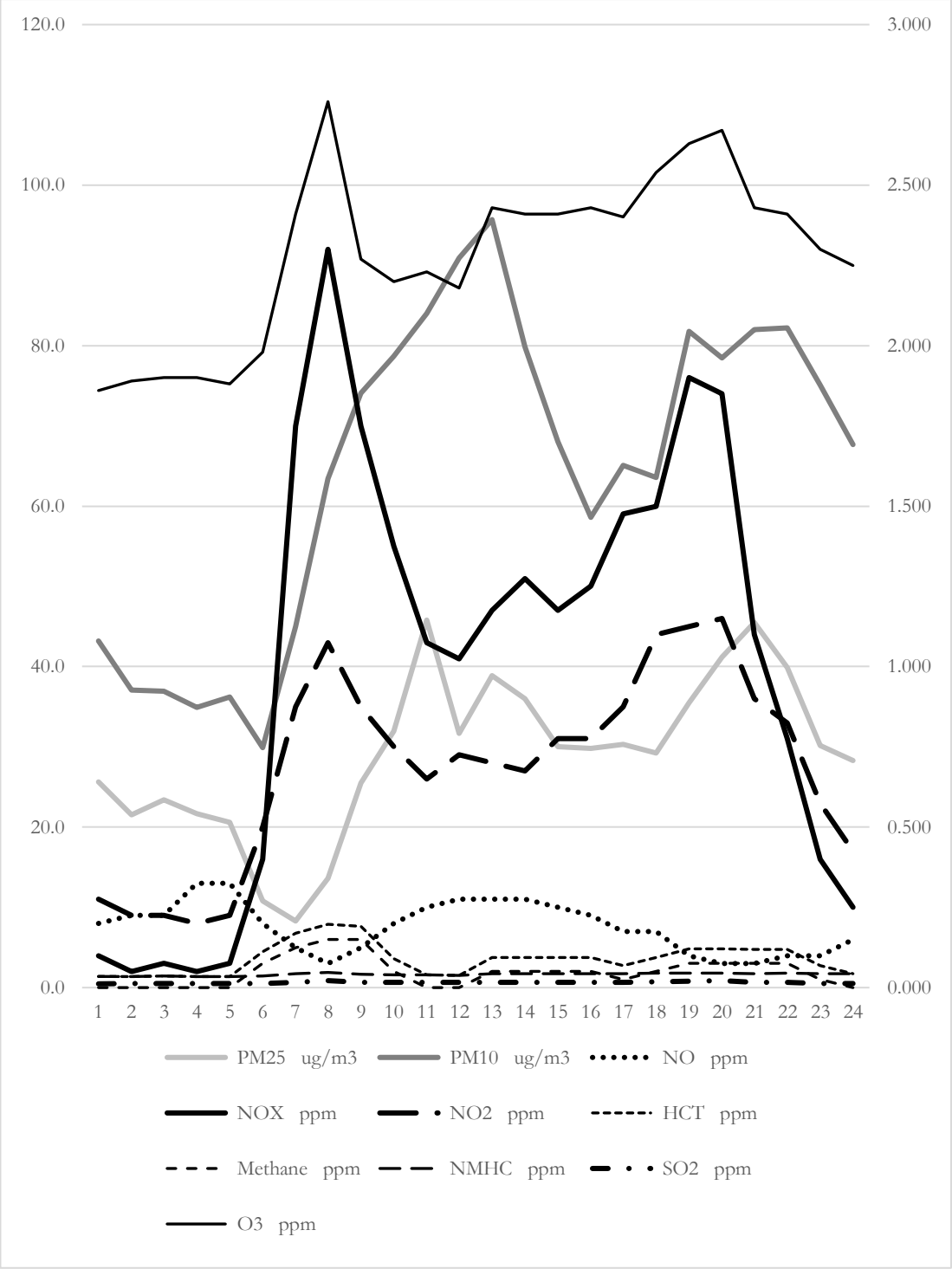


Figure 58: Air pollutant data variation with in a day in Nugegoda

6.2.3 $NO_X - VOC - O_3$ Sensitivity and Model validation using urban air-shed in Colombo

In line with Figure 59, six locations in Colombo verify the NOx-sensitivity or VOC sensitivity where in Colombo all locations shows NOx-sensitivity, nevertheless in few incidents intermediate VOC sensitivity was shown. VOC-sensitivity was observed when very high NO emissions were occurred (such as high NO from power plant emissions and train emissions), otherwise with moderate or low NO concentrations NO_X -sensitivity was observed. Figure 60 shows temperature, pressure, solar radiation, relative humidity, wind speed and wind-rose of the six locations in Colombo within a day. Accordingly, above meteorological parameters are within the close relation and air pollutant variations are not heavily affected. Figure 61 illustrates contributions from NO_X sensitive regime and VOC sensitive regime of the six locations in Colombo within a day. Accordingly it is clearly shows that in Colombo NO_X-sensitivity are dominating over VOC-sensitivity. Further it was observed that when one sensitivity generate other sensitivity degeneration. Furthermore O_3 concentration variation was high in Kollupitiya and this could be due to Kollupitiya is in coastal area having high wind and sea breeze.

Calculations of univariate linear regression mode using predicted and observed ozone values in Colombo confirms that measured O_3 concentration is significantly correlated with the calculated O_3 concentration (Table 22). Furthermore comparison of measured O_3 concentration with calculated O_3concentration in six locations in Colombo within a day in Figure 62 visually represented the correlation. Therefore Urban Air-shed Model applications confirm that measured O_3 concentration is significantly correlated with the calculated O_3 concentration in Colombo air-shed.

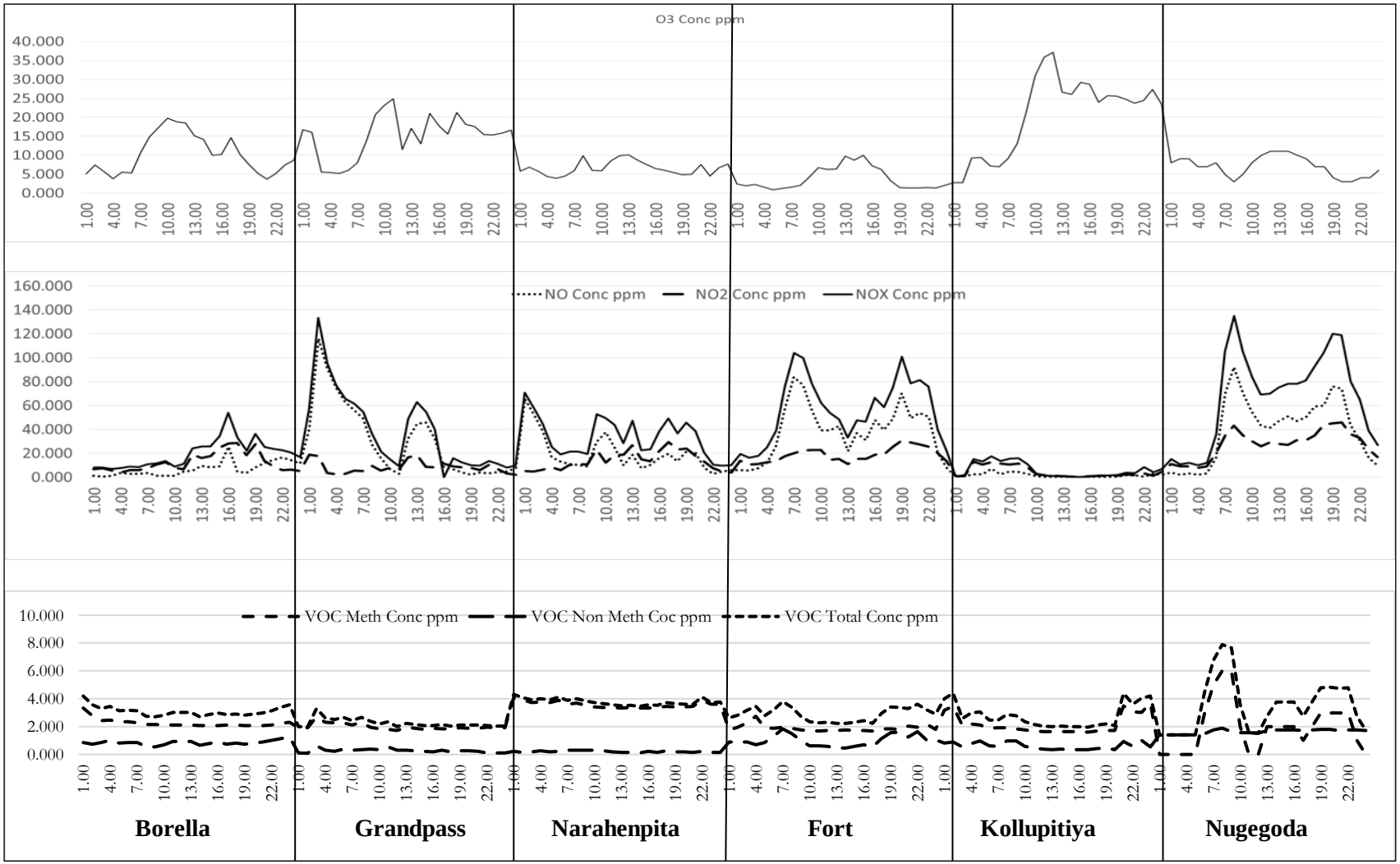
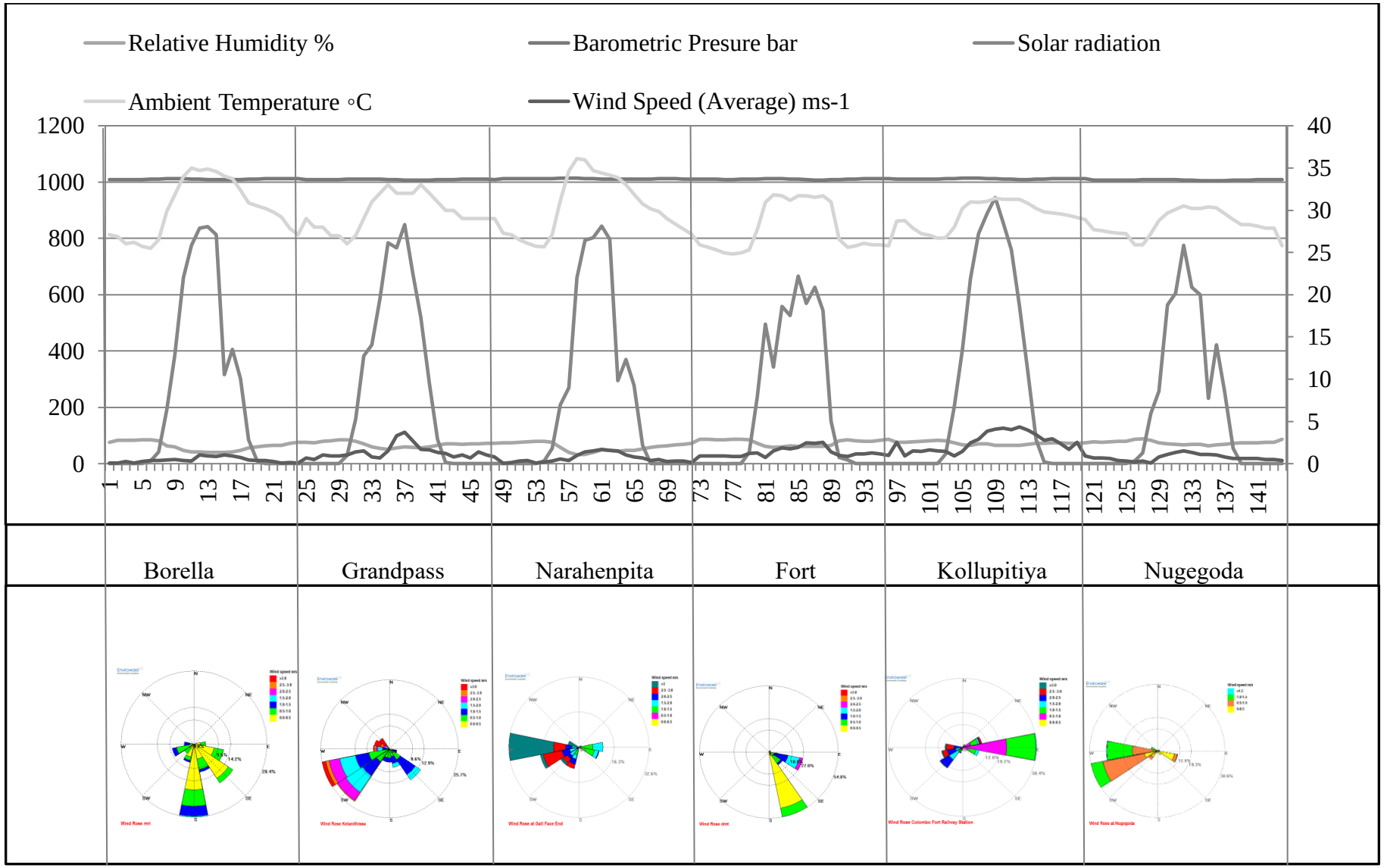
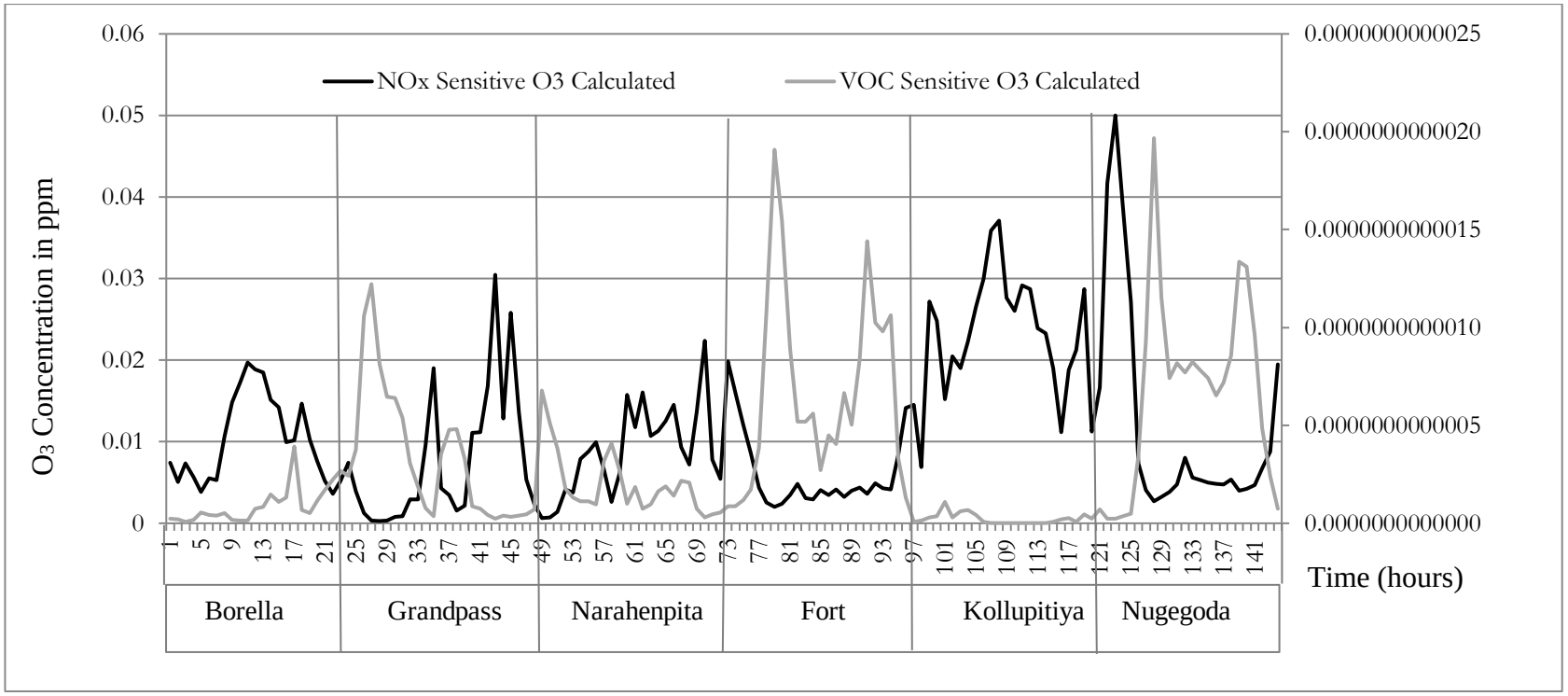


Figure 59: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_X concentration variation of the six locations in Colombo within a day



*Wind speed and the temperature values are represented in the secondary (right hand side) axis.

Figure 60: Temperature, solar radiation, pressure, relative humidity, wind speed and wind-rose of the six locations in Colombo within a day. *Original is in Colour.



*VOC Sensitive O_3 Calculated values are represented in the secondary (right hand side) axis.

Figure 61: Contributions of O_3 from NO_x Sensitive Regime & VOC Sensitive Regime of the six locations in Colombo within a day.

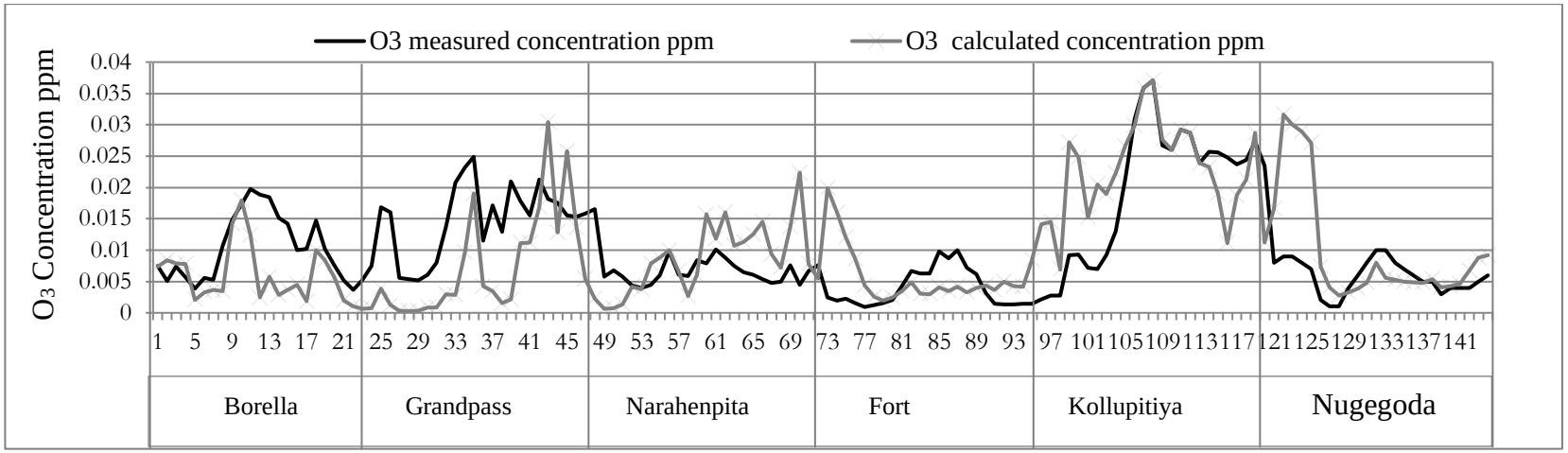


Figure 62: Comparison of measured O_3 concentration with calculated O_3 concentration in the city of Colombo

Table 22: Univariate linear regression mode using predicted and observed ozone values in Colombo

Dependent variable: O_3 Observed Independent variable: O_3 Predicted

Variable	**Correlation**	**t value**	**p value**
Observed O_3 Raw data	0.2039952	2.4831	0.01419

Therefore Measured O_3 concentration is significantly correlated with the calculated O_3 concentration.

Detail $NO_X - VOC - O_3$ sensitivity trend patterns of six locations in Borella, Grandpass, Narahenpita, Fort, Kollupitiya and Nugegoda are shown in Figure 63, 64, 65, 66, 67 and 68 respectively.

According to the Figure 63, within 24 hours concentration of NO_X, VOC and O_3 formation shows NO_X-sensitive regime in Borella. In Figure 64, within 24 hour concentration of NO_X, VOC and O_3 formation shows intermediate of VOC-sensitivity and then NO_X-sensitivity in Grandpass. In the VOC-sensitive regime, O_3 decreases with rising NO_X level and rises with rising VOC levels. Further there was very high concentration of NO, in the early morning confirms the emissions from adjacent "Oil Power Stations" at Kelanitissa. High emissions of NO was observed from 2am to 5am in the early morning in Grandpass, and this emitted NO react with O_3 concentration and depressed through the process of NO titration ($NO + O_3 \rightarrow NO_2 + O_2$) and VOC sensitive regime was observed. However during the day time when the power plant was not in action NO concentration level became moderate and vehicular emission was the major source, NO_X-sensitive regime was observed. In relation to the Figure 65, within 24 hour concentration of NO_X, VOC and O_3 formation shows NO_X-sensitive regime in Narahenpita. At the Narahenpita site showed significantly high concentration of NO, in the early morning confirms the emissions from adjacent "Oil Power Stations" at Kelanitissa. However the NO concentration has not reached the saturation level in this case, therefore NO titration has not taken place. Further vehicular emissions were the next major source of air pollution during the day time when the power plant was not in action. Along with the Figure 66, within 24 hours concentration of NO_X, VOC and O_3 formation shows NO_X-sensitive regime and intermediate VOC-sensitive regime in

Fort. Further highest NO concentration was observed from 6am to 8am in the morning hours, and 7pm to 8pm in the evening hour where O_3 concentration was very low explaining the VOC sensitive regime. When the NO concentration was moderate, in-between 9am to 6pm with the sun lite condition high O_3 concentration was observed confirming NO_X-sensitive in Fort location. According to the Figure 67, within 24 hour concentration of NO_X, VOC and O_3 formation shows NO_X-sensitive regime and intermediate VOC sensitive regime in Kollupitiya. High NO concentration has observed from early morning until 10am and reduced during the daytime. In contrast O_3 concentration was low from early morning until 10am and increases during sun lite condition. In relation to the Figure 68, within 24 hour concentration of NO_X, VOC and O_3 formation shows NO_X-sensitive regime in Nugegoda. Accordingly, when the NO concentration increases O_3 also has increased.

a. Borella Location

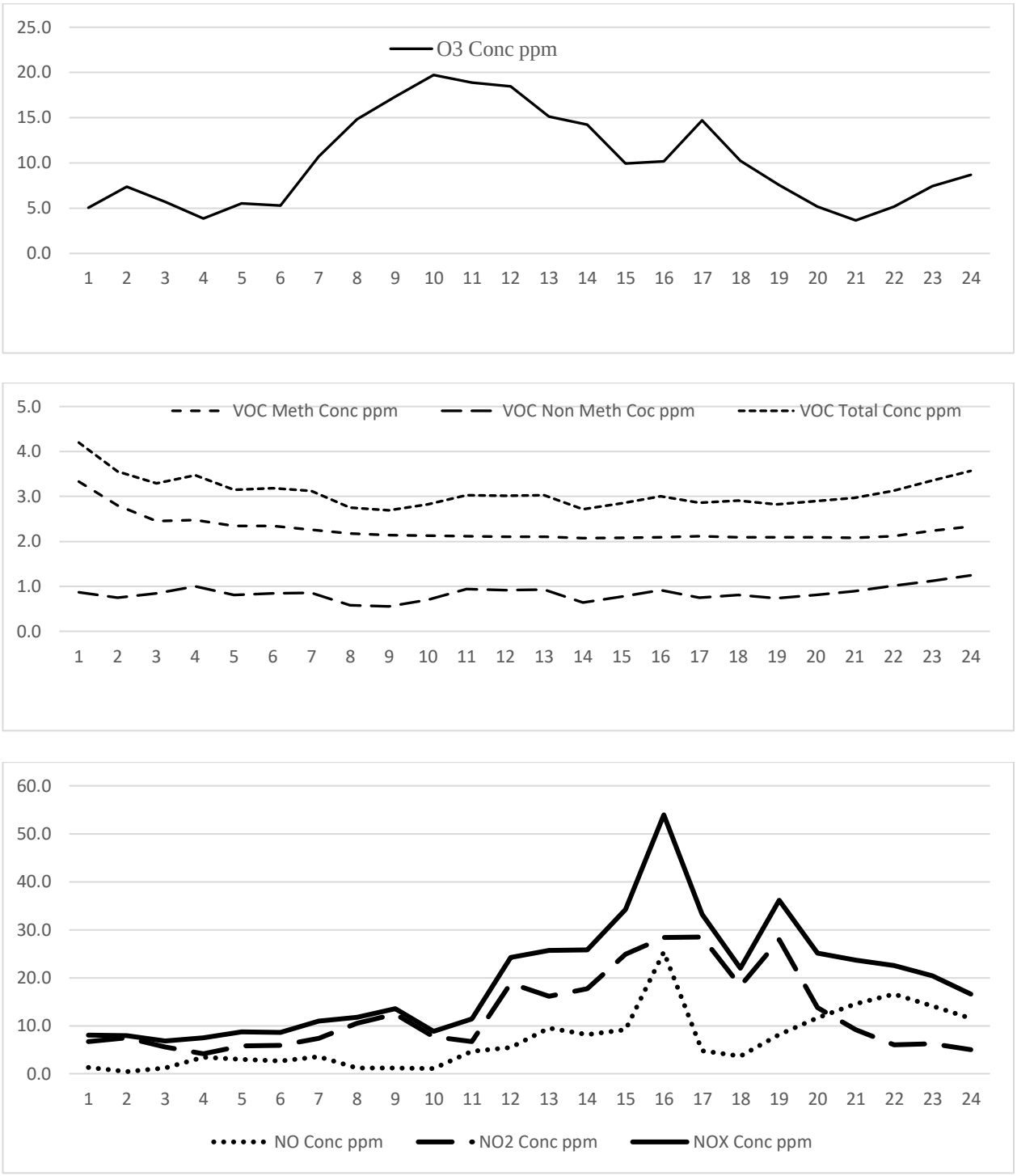
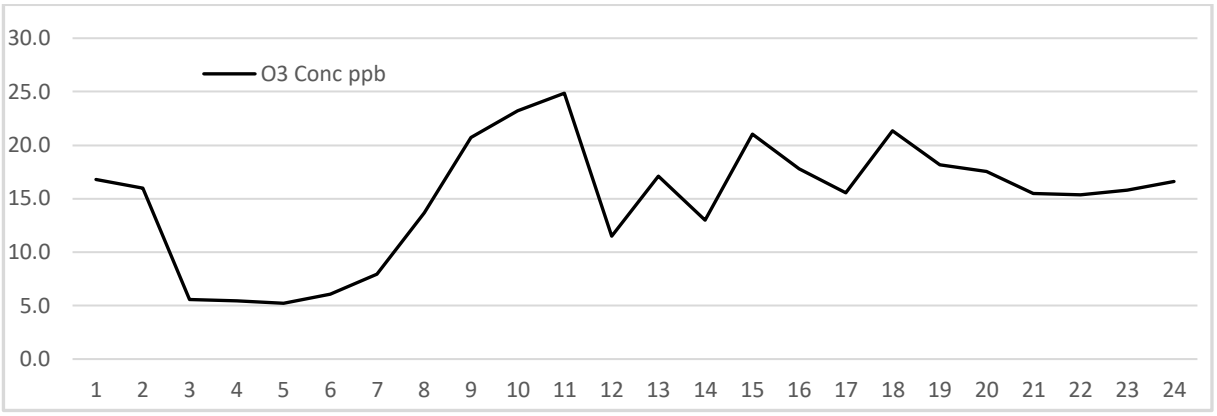
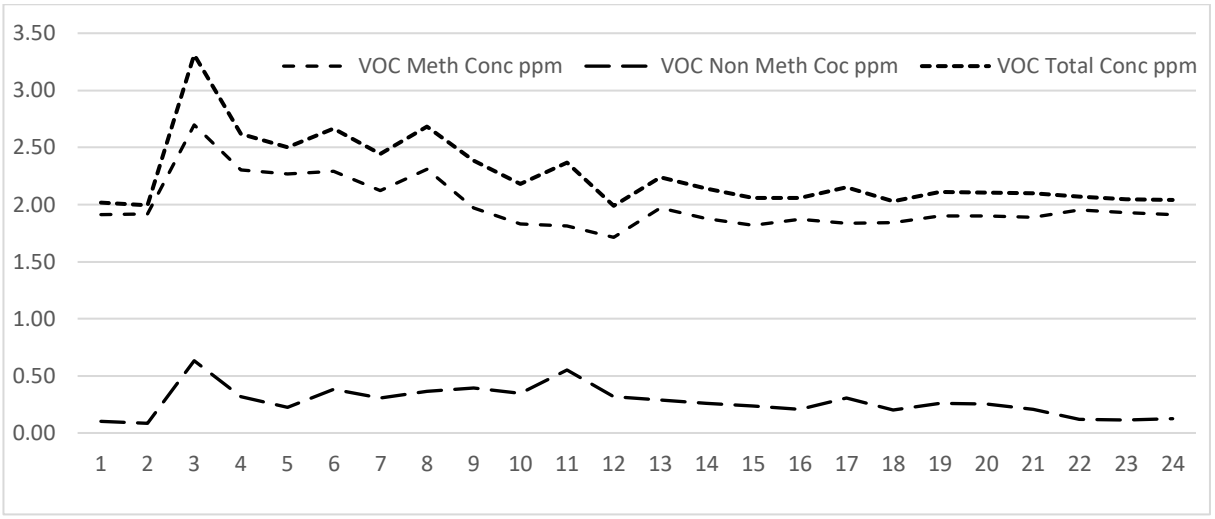


Figure 63: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_X concentration variation within a day in Borella

b. Grandpass Location





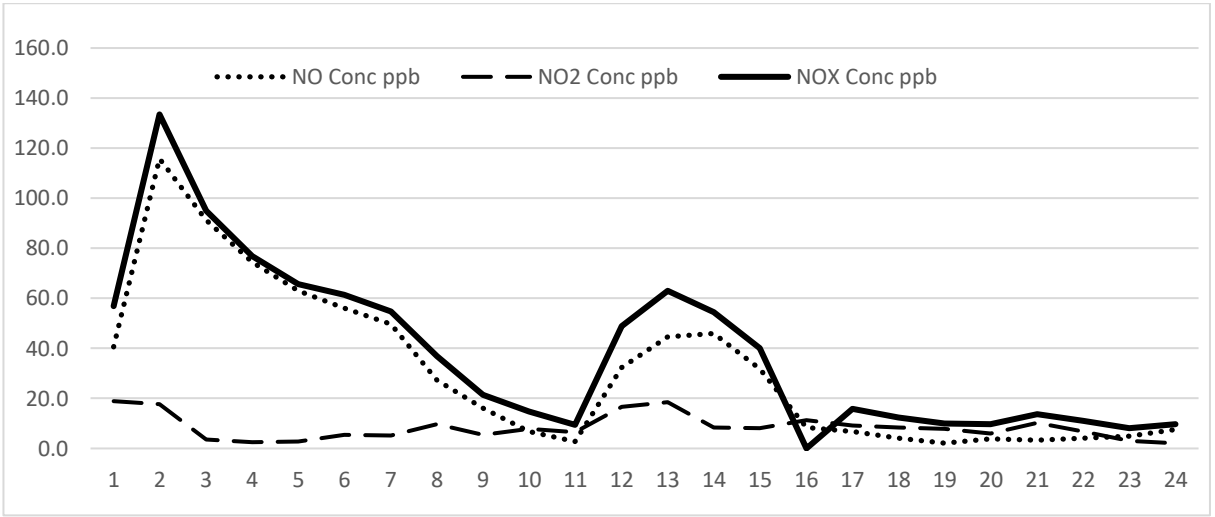


Figure 64: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_X concentration variation within a day in Grandpass

c. Narahenpita Location

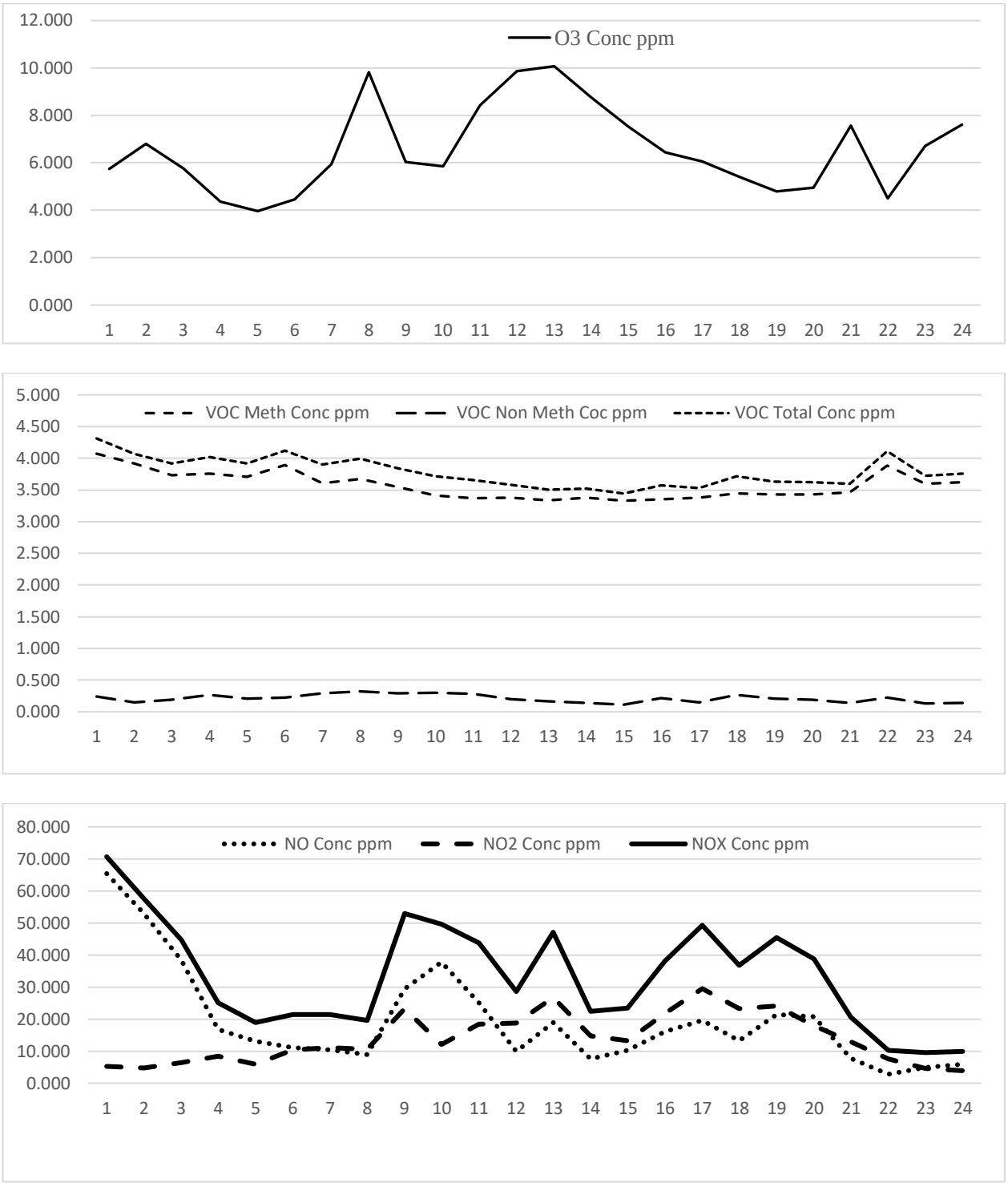
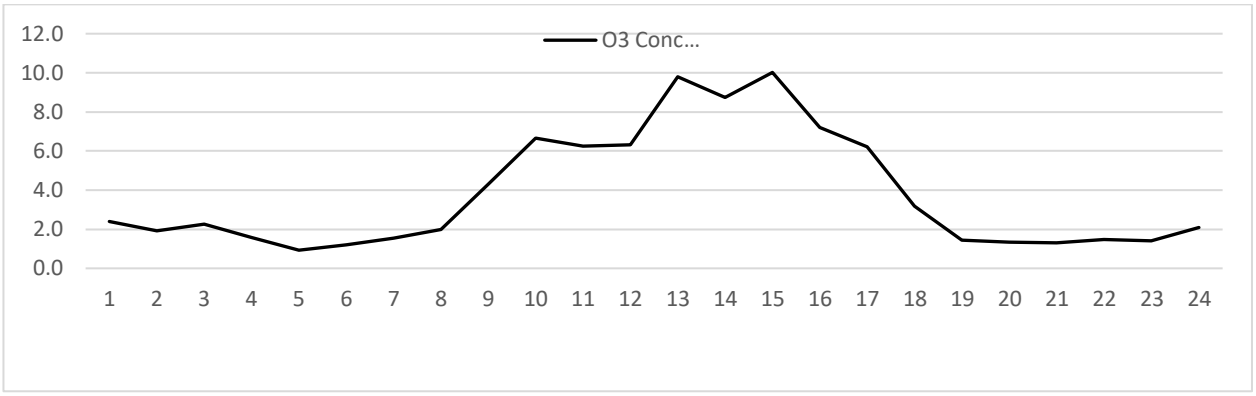
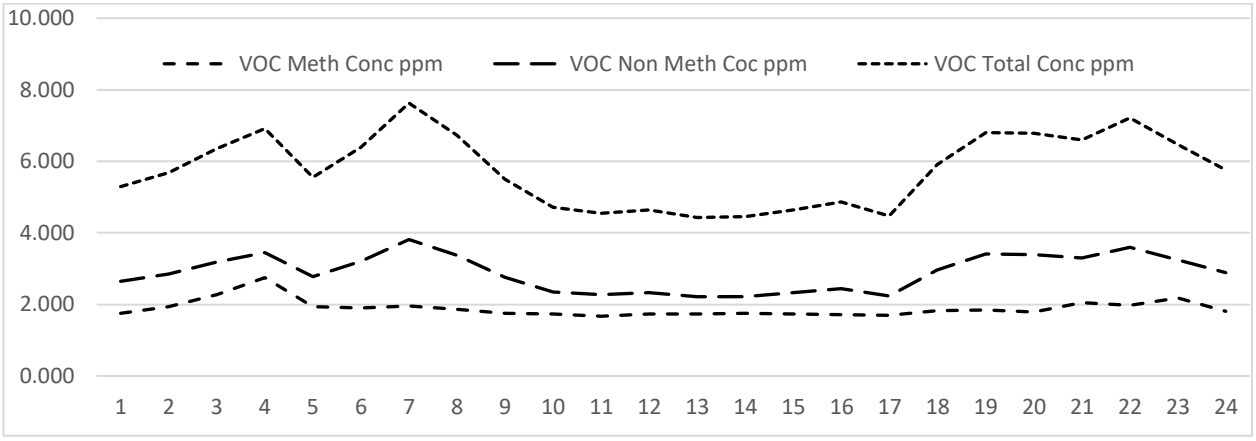


Figure 65: O_3, THC, CH_4, NMHC, NO, NO_2 and NO_2 concentration variation within a day in Narahenpita

d. Fort Location





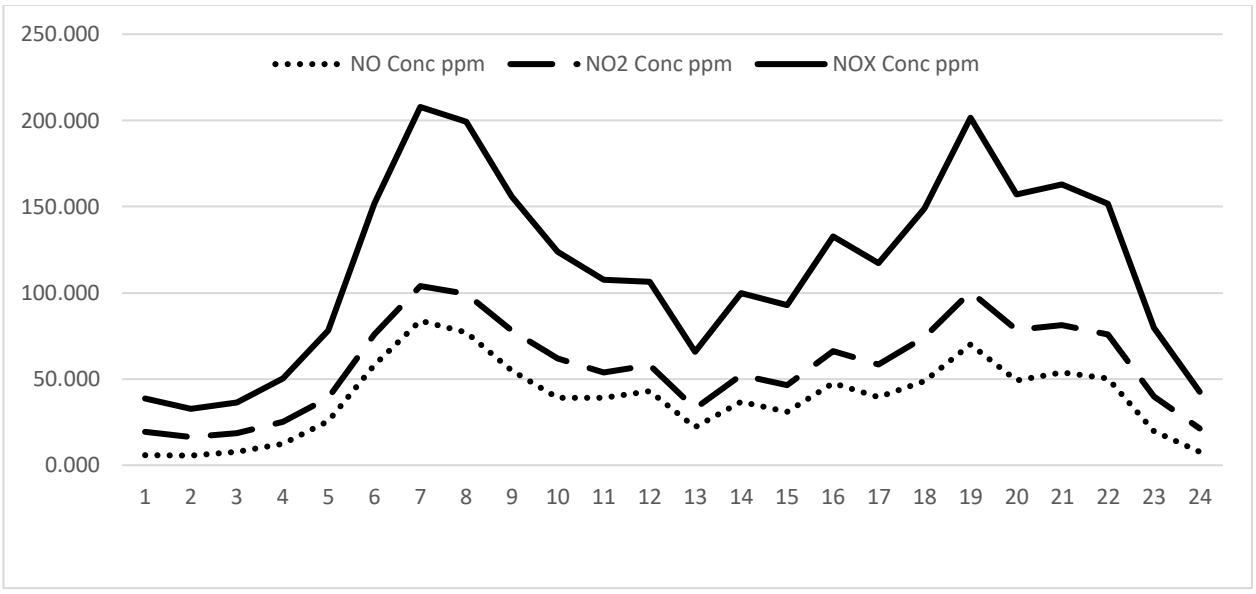


Figure 66: Ozone, THC, CH_4, NMHC, NO, NO_2 and NO_x concentration variation within a day at Fort

e. Kollupitiya Location

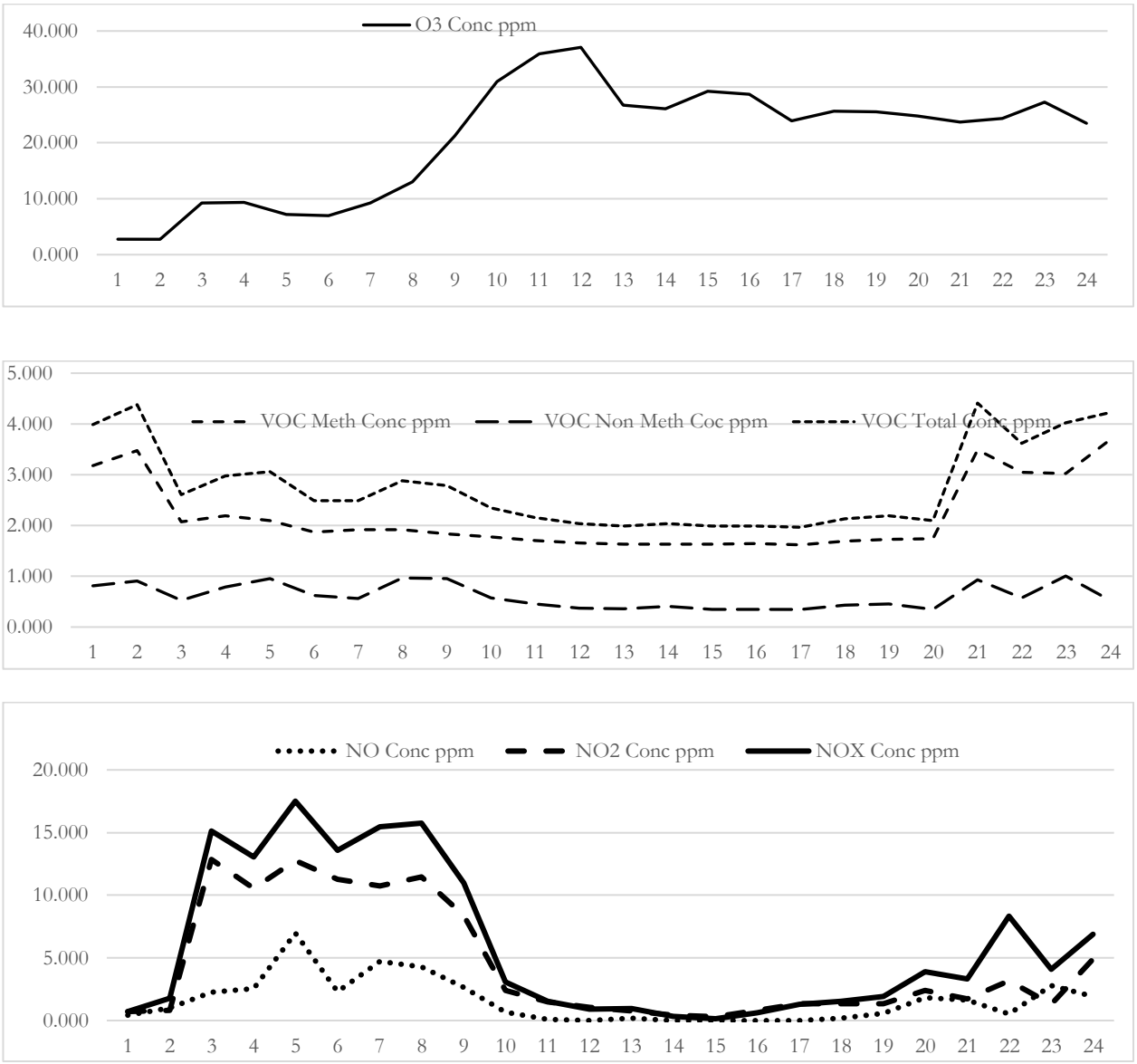


Figure 67: Ozone, THC, CH_4, NMHC, NO, NO_2 and NO_x concentration variation within a day at Kollupitiya

f. Nugegoda Location

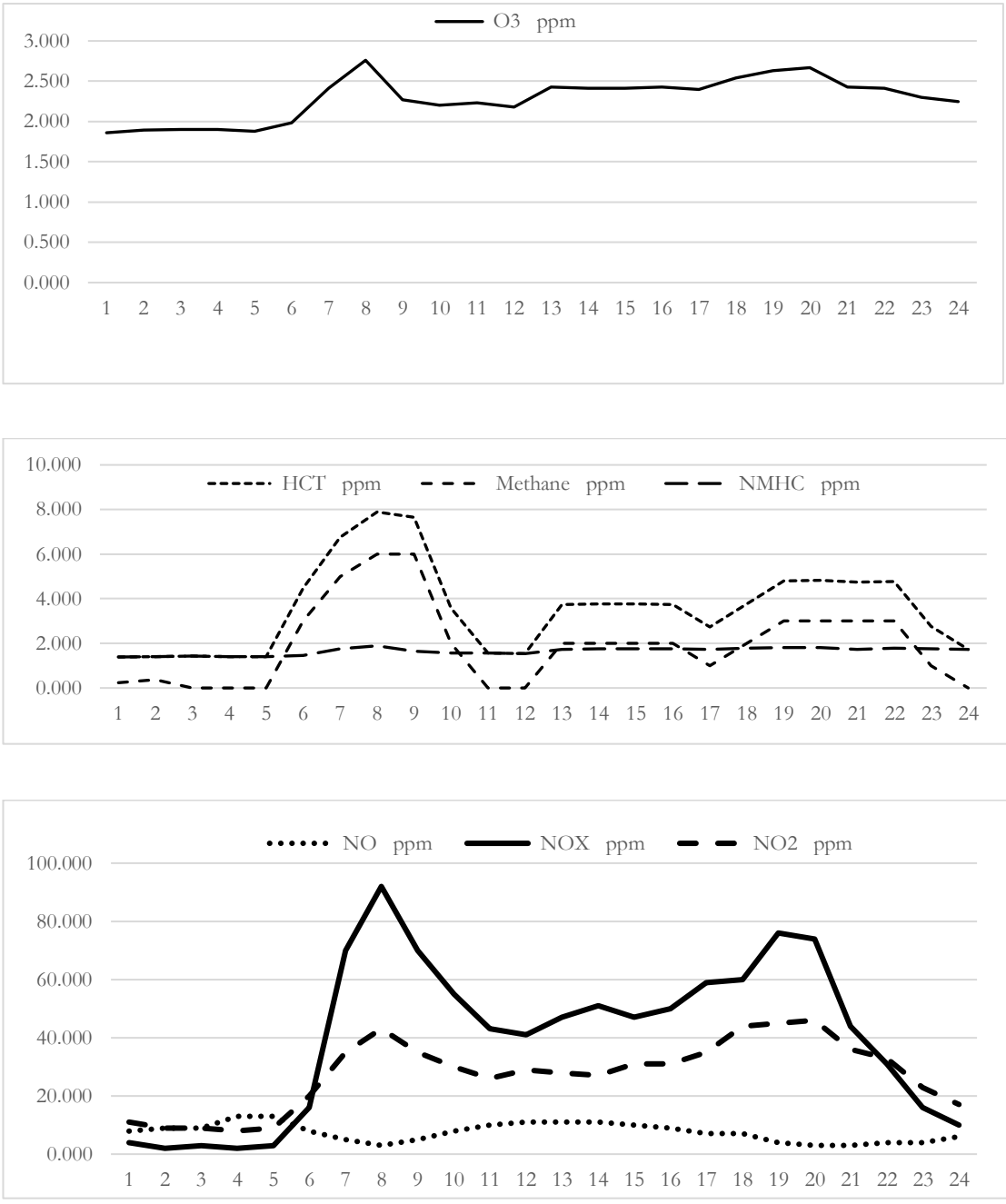


Figure 68: Ozone, THC, CH_4, NMHC, NO, NO_2 and NO_x concentration variation within a day at Nugegoda

6.3 ANALYSIS OF SOURCE PARAMETERS

6.3.1 Analysis of operational schedule data

a. Analysis of vehicle counts data at selected locations in Colombo

Figure 69 showed that vehicle count results of eight locations namely, Kollupitiya, Dehiwala, Maradana, Fort, Borella, Narahenpita, Grandpass and Nugegoda. Further, three main peaks were observed at 7.00am, 2.00pm and 4.00pm which covers the morning, afternoon and evening high traffic hours. The peaks are not prominent in the graph as high traffic dominates in different hours especially in morning and evening office traffic and school traffic in the eight locations in Colombo. Total vehicle count in all eight locations within a day was 474329. Further highest vehicle counts were observed at Maradana (76573 vehicles in 24 hours and 3829 per hour in average). Second highest was in Fort (62796 vehicles in 24 hours per day and 3140 per hour in average). Next high vehicle counts were observed at Dehiwala (60121 vehicles in 24 hours per day and 3006 per hour in average) and Borella, (60082 vehicles in 24 hours per day and 3004 per hour in average). Moderate vehicle counts were observed at Grandpass (55134 vehicles in 24 hours per day and 2757 per hour in average) and Narahenpita (54390 vehicles in 24 hours per day and 2720 per hour in average). Lowest vehicle counts were observed at the Kollupitiya (52278 vehicles in 24 hours per day and 2614 per hour in average) and Nugegoda (52954 vehicles in 24 hours per day and 2648 per hour in average). Three main vehicle count peaks (morning, afternoon and evening) were observed in all sites with different peak times. In some cases, during the day time (evening) prominent peak was observed such as at Kollupitiya (4pm to 6pm), Dehiwala and Nugegoda (6pm to 7pm). In some cases prominent peak was observed during morning hours (7am to 9am) such as Maradana. In some cases prominent peak was observed during afternoon hours such as at Fort 11am to 12 noon. Borella,

Narahenpita and Grandpass have high vehicle count during all three peak hours. When compared with average trend pattern excluding Maradana, Fort and Kollupitiya, other locations have similar patterns. Figure 70 to Figure 77 explained the each case in detail with different type of vehicles and active vehicle fleet of highest to lowest types of vehicles in these eight locations in Colombo.

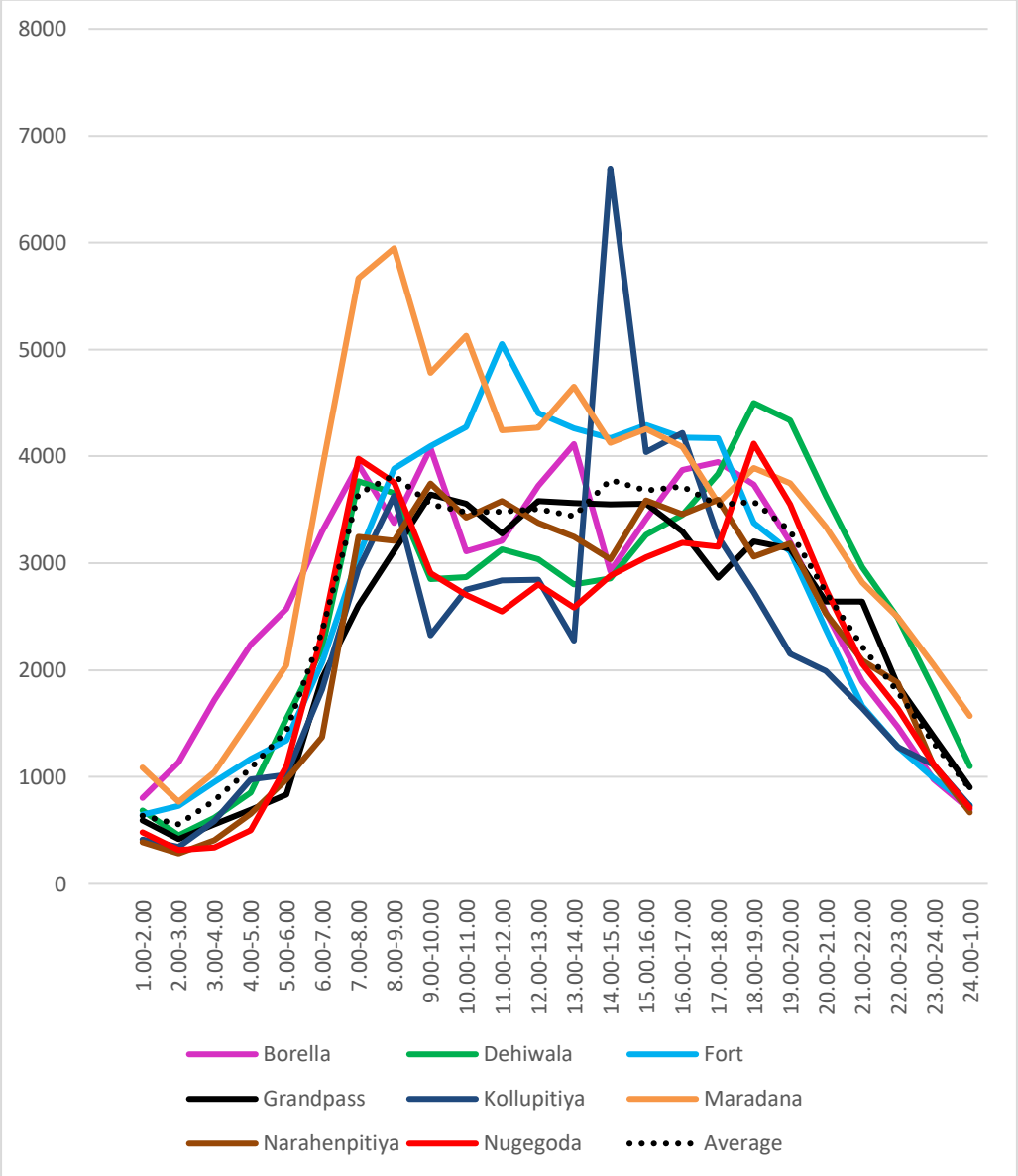


Figure 69: Number of all types of vehicles per hour in three days average in eight locations in Colombo. *Original is in Colour.

i. Maradana Location

Maradana has the highest vehicle fleet (76573 vehicles in 24 hours per day) and it has shown the third highest TVOC levels (194.5ppb) in Colombo. According to Figure 70 and Annexure II, three-wheeler was the highest vehicle type at Maradana. Further three-wheelers were actively moving throughout the day contributing for air pollution. Second highest was cars and then motor bikes. Therefore these three vehicle types dominating active vehicle fleet in Maradana. Peak at 12noon to 2pm represent the active vehicle fleet of school van, cars, three-wheelers, motor bikes and jeeps at this location.

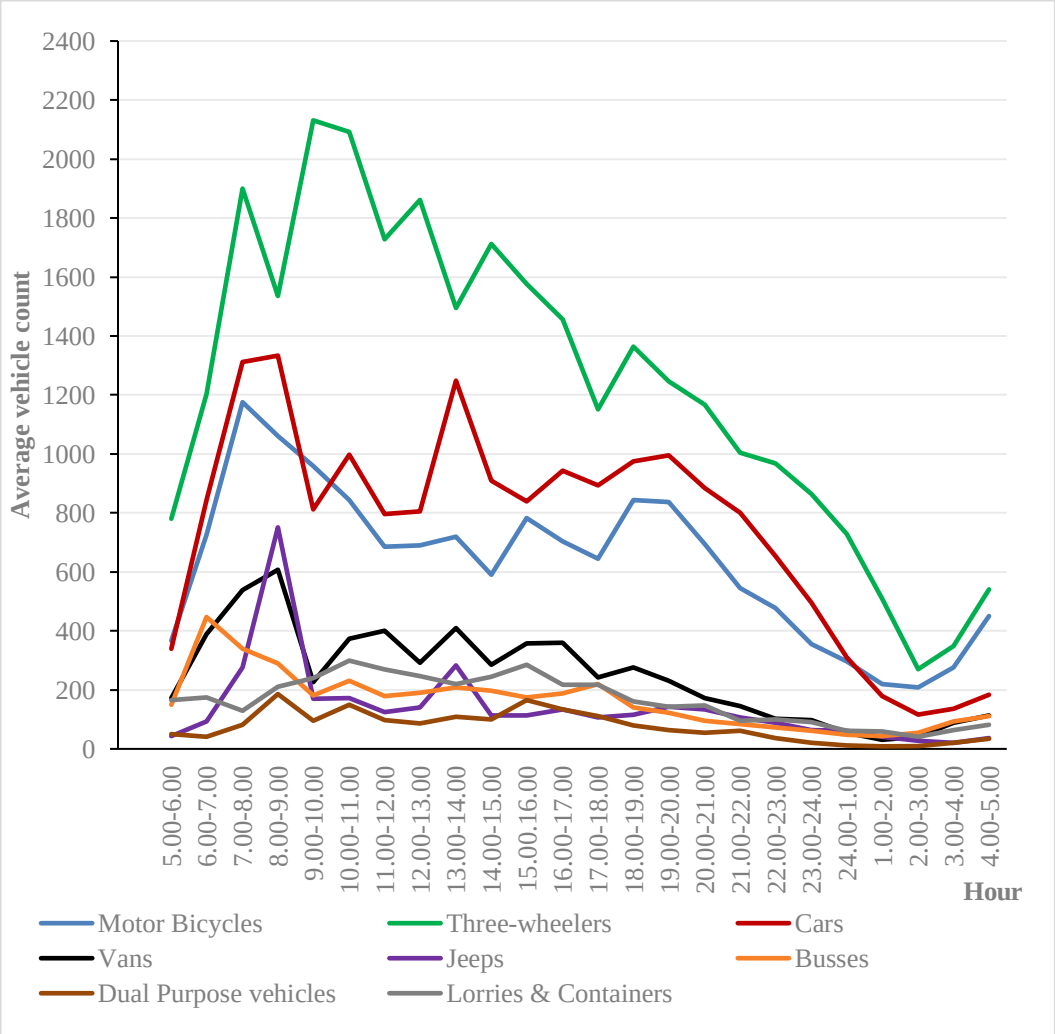


Figure 70: Average vehicle counts in each vehicle types in hours in Maradana

*Original is in Colour

ii Borella Location

According to Figure 71 and Annexure II, similar pattern was shown in Borella when compared to Maradana, where three-wheeler, cars and motor bikes dominating in active vehicle fleet. Further three-wheelers, cars, and motor bikes actively moving throughout the day that contribute to air pollution. Peak at 12noon to 2pm represent the active vehicle fleet of school van, cars, three-wheelers, motor bikes and jeeps in Borella. High bus fleet was observed at 7am to 9am in the morning and again at 4pm to 8pm at night time. Borella has the third highest vehicle fleet (60082 vehicles in 24 hours per day) and it has shown the fourth highest TVOC levels (190ppb) in Colombo.

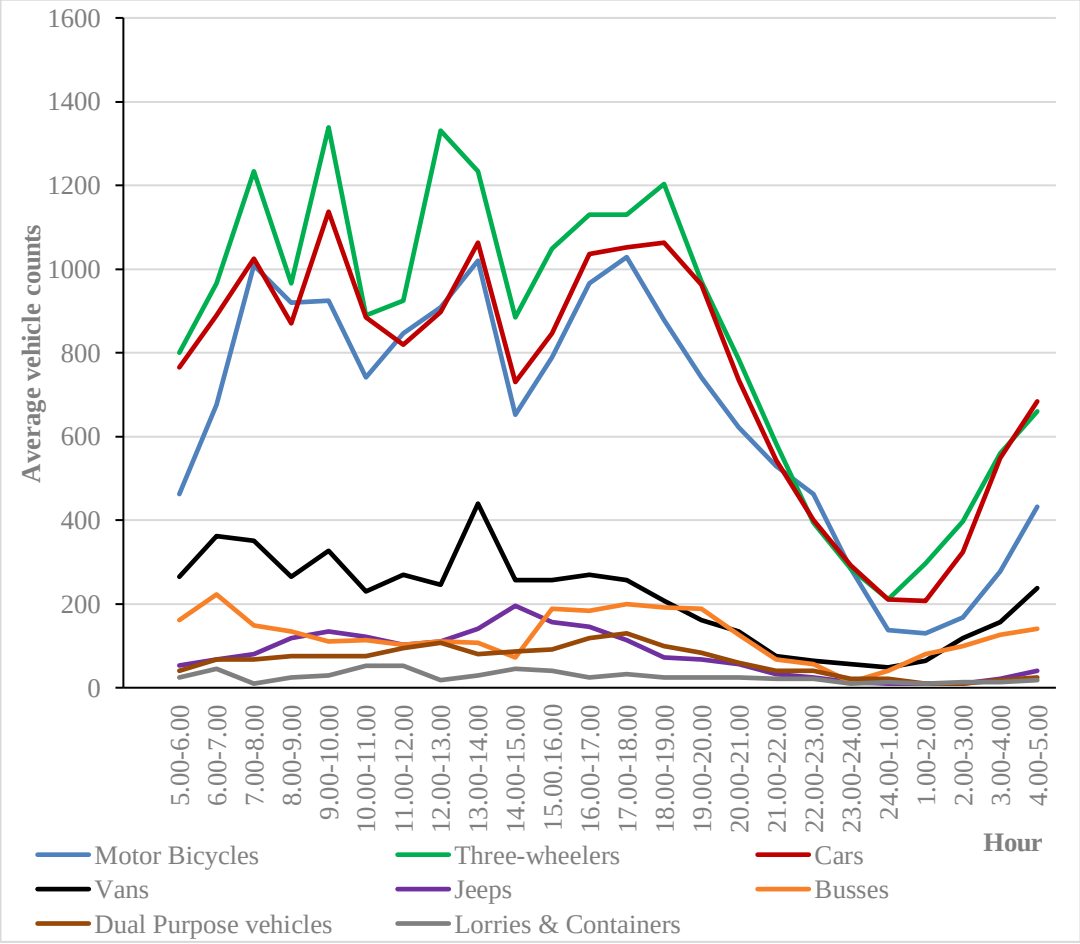


Figure 71: Average vehicle counts of each vehicle type per hour in Borella

*Original is in Colour.

iii Grandpass Location

According to the Figure 72 and Annexure II, three-wheeler was the highest vehicle type at Grandpass. Further three-wheelers were actively moving throughout the day contributing for air pollution. Second highest vehicle types were motor bikes and cars. However motor bikes were peaked at morning hours (7am to 10am) and cars were peaked at late evening or night hours (6pm to 9pm). Fourth highest vehicle type was lorries and containers. It could be explained as Grandpass having an industrial zone high lorries and containers were observed. Even though moderate vehicle counts (55134 vehicles in 24 hours per day) were observed at Grandpass, it has the highest TVOC (226.5ppb) air pollution levels. This could be explained at Grandpass having the highest congested Baseline road, thermal power stations (at Kelanithissa) and a trade zone.

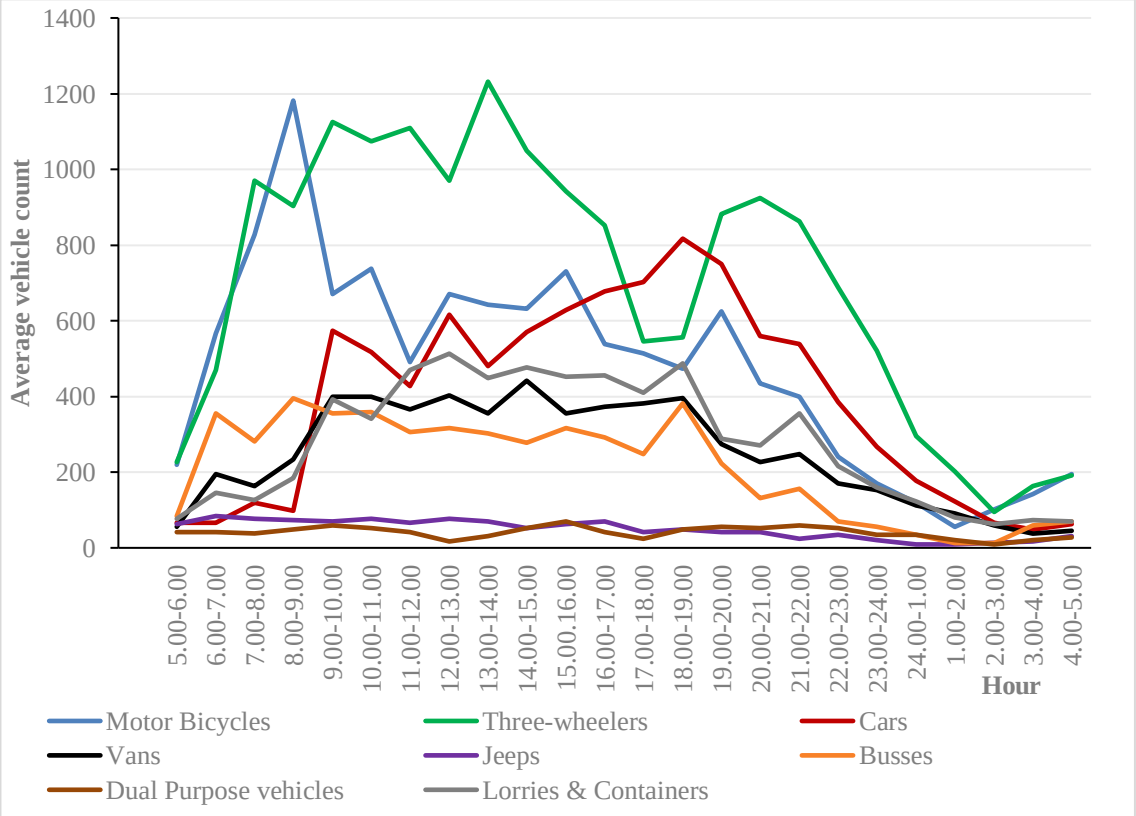


Figure 72: Average vehicle counts of each vehicle type per hour in Grandpass.

*Original is in Colour.

iv Narahenpita Location

According to the Figure 73 and Annexure II, in Narahenpita there were three types of vehicles dominated namely, cars, three-wheelers and motor bikes. Further these three types of vehicles were actively moving throughout the day contributing for air pollution. Most of the privatized hospitals and large three-wheeler parks are situated in this area could be the reasons to have high cars and three-wheelers in the active vehicle fleet at Narahenpita. It has moderate vehicle fleet (54390 vehicles in 24 hours per day) and moderate TVOC levels (91.5ppb) in Colombo.

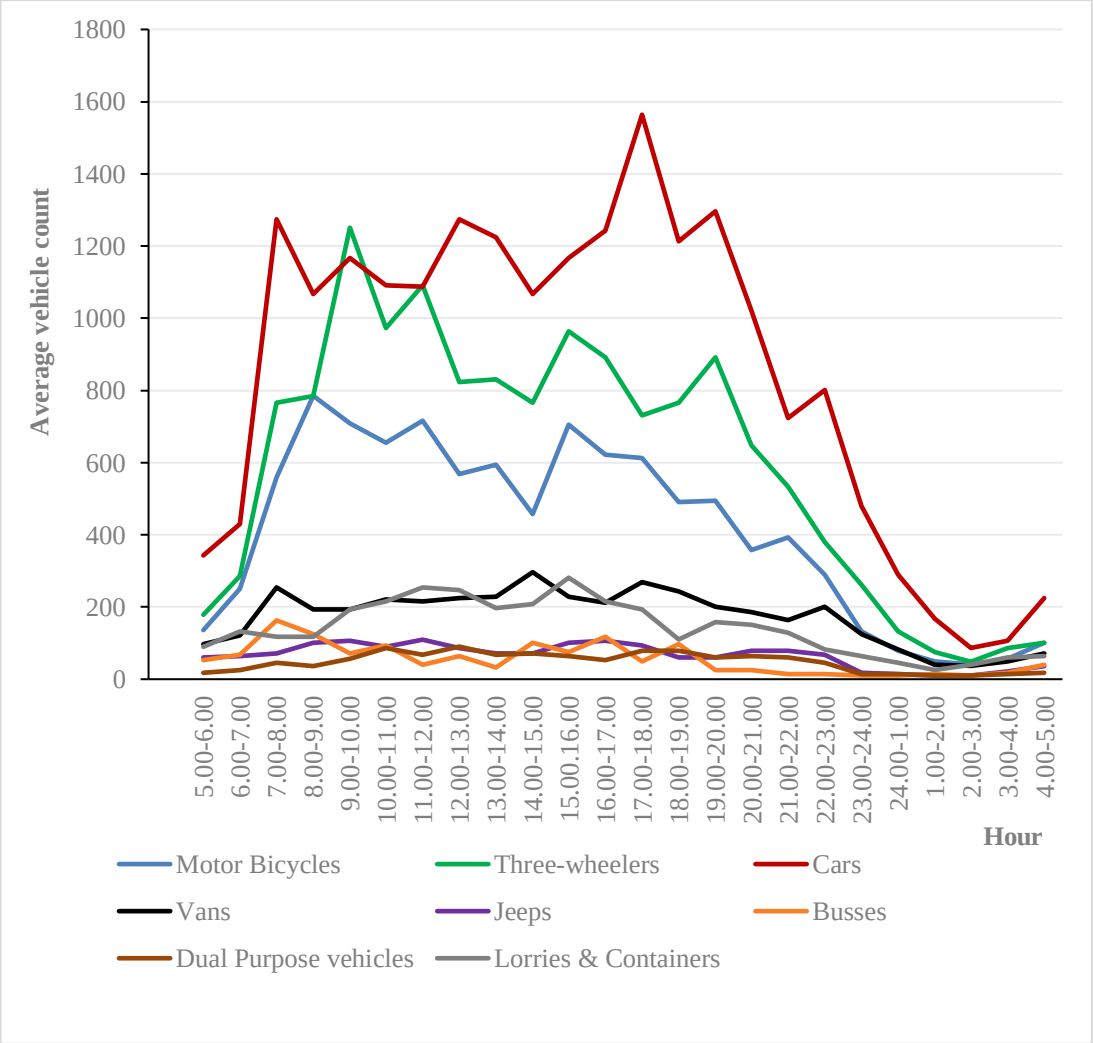


Figure 73: Average vehicle counts of each vehicle types per hour in Narahenpita.

*Original is in Colour.

v Fort Location

Fort has the second highest active vehicle fleet (62796 vehicles in 24 hours per day), and second highest TVOC (205.6ppb) air pollution levels. Fort is the most popular public transport hub having main bus station and the train station. Therefore people are tending to use three-wheelers to reach to this place. This was clearly shown in Figure 74, having very high number of three-wheelers in the active vehicle fleet in Fort throughout the day. Further having the main bus station, buses were also dominating in the active vehicle fleet than cars. Furthermore three-wheelers, motor bikes and buses were actively moving throughout the day that contributes to air pollution in Fort.

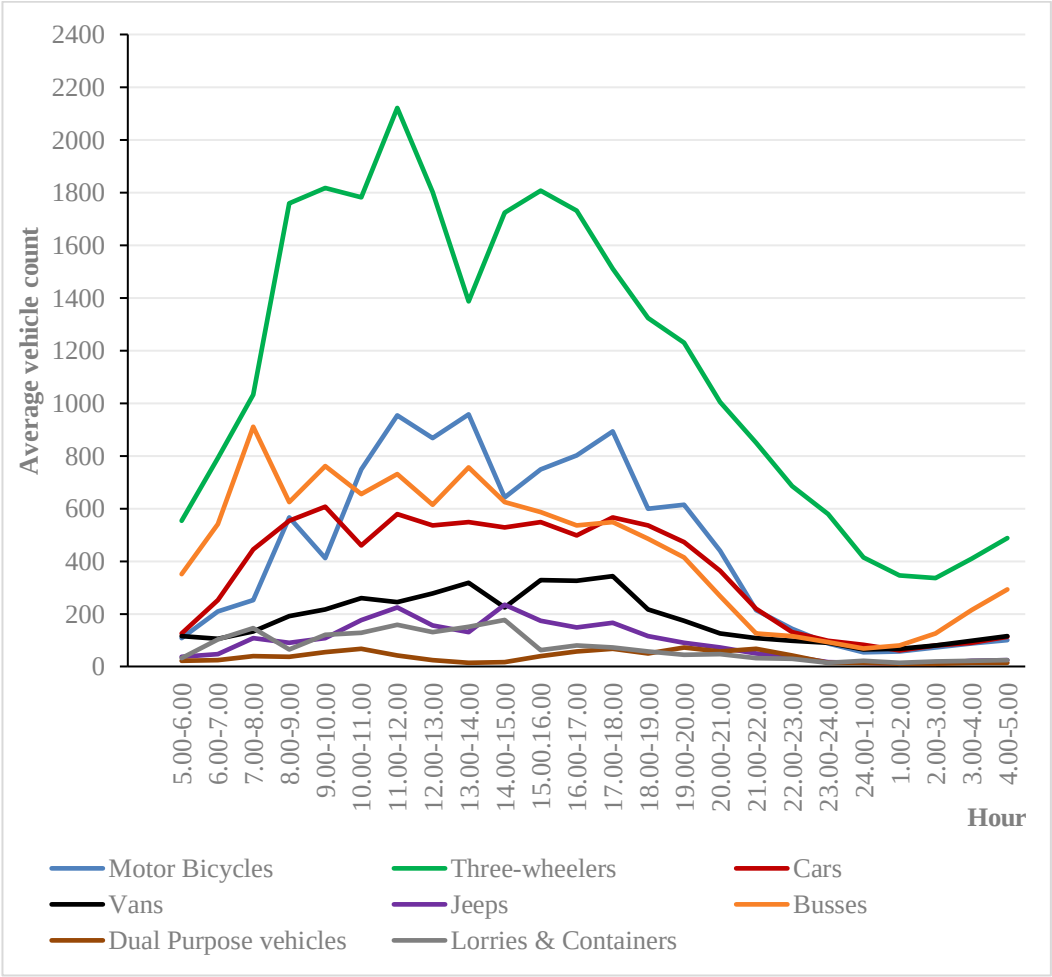


Figure 74: Average vehicle counts of each vehicle type per hour in Fort

*Original is in Colour.

vi Kollupitiya Location

According to Figure 75 and Annexure II, cars, three-wheelers, vans and motor bikes were dominating active vehicle fleet in Kollupitiya. Further three-wheelers and cars were actively moving throughout the day contributing for air pollution. Active vehicle fleet of vans were representing the school van service in-between 2pm to 4pm and office van services in-between 4pm to 7pm. Peak at 2pm represented the active vehicle fleet of school vans, cars, three-wheelers and motor bikes in Kollupitiya. It has the lowest vehicle fleet (52278 vehicles in 24 hours per day) and it has shown lowest TVOC levels (72.5ppb) in Colombo.

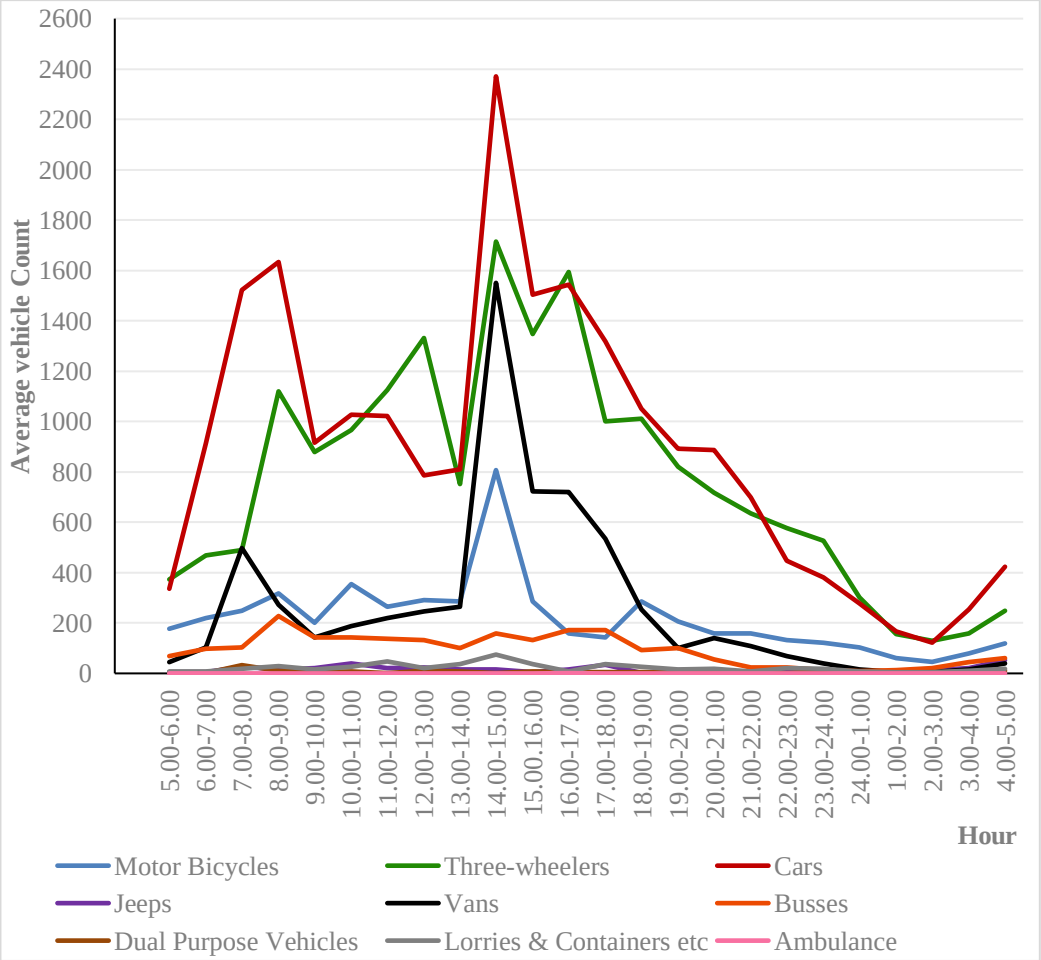


Figure 75: Average vehicle counts of each vehicle types per hour in Kollupitiya

*Original is in Colour.

vii Dehiwala Location

According to the Figure 76 and Annexure II, cars were dominating in the active vehicle fleet having morning prominent peak (7am - 9am) and evening broader peak (5pm - 10pm). Second highest vehicles were three-wheelers. Further three-wheelers were actively moving throughout the day that contributes to air pollution. Motor bikes were showing similar trend as in the case of cars having morning and evening peaks. Dehiwala has the third highest active vehicle fleet (60121 vehicles in 24 hours per day), when compared with moderate TVOC (99ppm) levels. This could be explained as Dehiwala is situated closer to coastal area having high sea breeze which diluted the air pollution levels. Further, it has the second fly over which was constructed to eliminate the traffic congestion at Dehiwala.

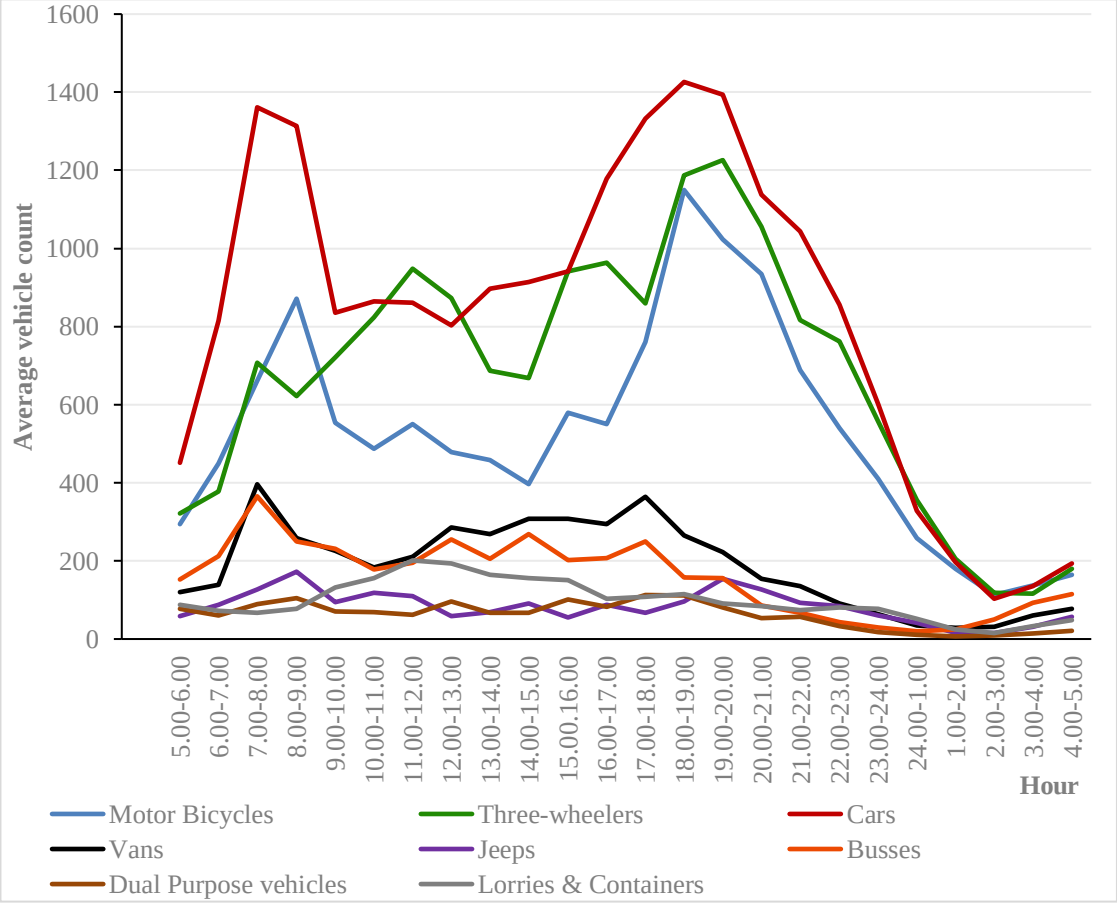


Figure 76: Average vehicle counts of each vehicle types per hour in Dehiwala

*Original is in Colour.

viii Nugegoda Location

According to the Figure 77 and Annexure II, similar active vehicle fleet trend pattern was observed in Nugegoda as in the case of Dehiwala for cars, three-wheelers, motor bikes and vans. Further, cars were dominating in the active vehicle fleet having morning prominent peak (7am - 9am) and evening broader peak (6pm - 10pm). Second highest vehicles were three-wheelers in Nugegoda. Further three-wheelers were actively moving throughout the day. Motor bikes were showing similar trend having morning and evening peaks, as in the case of cars. Nugegoda is a business emporium having large shopping complexes to small shops and flyover was constructed to eliminate the traffic congestion. It has low vehicle fleet (52954 vehicles in 24 hours per day) and it has shown moderate TVOC levels (63.5ppb) in Colombo.

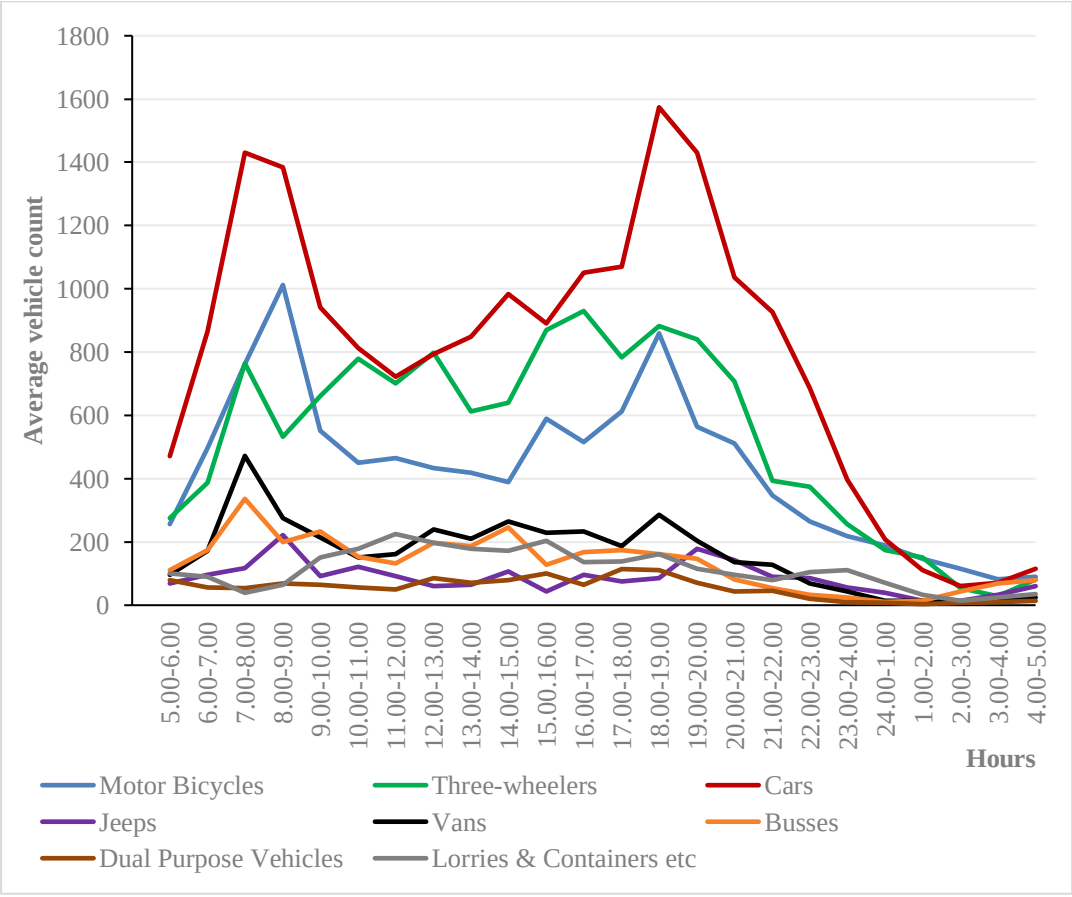


Figure 77: Average vehicle counts of each vehicle type per hour in Nugegoda

*Original is in Colour.

Table 23 summarized the vehicle fleet types (visible observation results of first five vehicle types) in the eight locations in Colombo. Accordingly, it is clear that highest vehicle fleet in many cases were cars, three-wheelers and motor bikes. Furthermore it was noted that highest vehicle fleet was three-wheelers in Borella, Maradana, Grandpass and Fort. Moreover, it was observed that highest vehicle fleet was cars in Kollupitiya, Narahenpita, Dehiwala and Nugegoda. Fort having the public transport hub high bus fleet was observed in third position. Otherwise buses have taken fifth position. According to the findings of the research base on the active vehicle fleet of the on-road vehicles, first five orders of the most polluted vehicle types in descending order would be three-wheelers, cars, motor bikes, vans and buses. However, there are many other parameters also should be considered along with this and a comprehensive analysis has been carried out in Section 5.45.

Table 23: Comparison of first five major vehicle fleet types in eight locations in Colombo

Location	**First five major vehicle fleet types in eight locations**				
Maradana	Three-wheelers	Cars	Motor bikes	Vans	Buses
Borella	Three-wheelers	Cars	Motor bikes	Vans	Buses
Grandpass	Three-wheelers	Cars	Motor bikes	Vans	Buses
Fort	Three-wheelers	Motor bikes	Buses	Cars	Vans
Dehiwala	Cars	Three-wheelers	Motor bikes	Vans	Buses
Kollupitiya	Cars	Three-wheelers	Vans	Motor bikes	Buses
Narahenpita	Cars	Three-wheelers	Motor bikes	Vans	Lorries & containers
Nugegoda	Cars	Three-wheelers	Motor bikes	Vans	Buses

b. Analysis of train scheduled data

Data was obtained from the Fort Railway Station for every minuted, incoming and outgoing trains in all railway tracks (Figure 78, Annexure III) during 24 hour day. Based on the data obtained, number of trains passing the Fort Railway Station within an hour was counted for 24 hour (one day). The analyzed data was graphically presented with the air pollution data within a day (Figure 52).

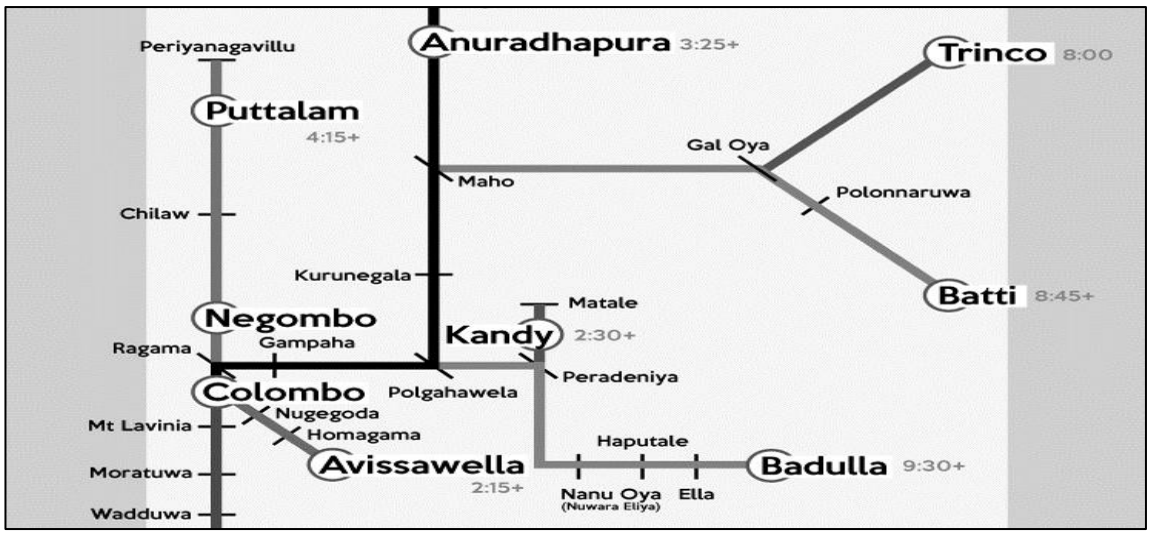


Figure 78: Railway tracks of the incoming and outgoing trains passing Colombo Fort Railway Station

c. Analysis of working hours of the power plant schedule with the air quality monitoring days

Air pollution monitoring days were compared with the working periods of the power plants at Kelanithissa and confirmed source emissions of the power plants as shown in Table 24. Table 25 gives details of the capacity breakdown of thermal power generation and type of fuel usage.

Table 24: The power plant schedule with the air quality monitoring days

24 Hour Air Quality Monitoring days in Colombo	Whether the Power Plants were in Action		
	Kelanithissa Combined Cycle Power plant (165 MW)	Kelanithissa Power Station (360 MW)	AES Kelanithissa Power Station (172MW)
Borella	√	√	√
Grandpass	√	√	√
Fort	√	√	√
Kollupitiya	√	√	√
Narahenpita	√	√	√
Nugegoda	√	√	√

Table 25: Use of fuel type and capacity breakdown of thermal power generation at the power plants in Kelanithissa

Name of the Thermal Power Plant	Type of fuel used	Capacity breakdown [7, 260]	Total capacity
Kelanithissa Combined Cycle Power plant- state owned	Naphtha fuel and diesel fuel	Steam turbine- 55 MW Gas turbine- 110 MW	165 MW
Kelanithissa Power Station - state owned	Furnace oil, diesel, naphtha fuel	Two boiler steam units- 25 MW x 2 Six gas turbines- 20 MW x 6 One gas turbine (110 MW) and one steam turbine (55 MW) in the combined cycle	360 MW
AES (Sojitz) Kelanithissa Power Station - privately-owned	Diesel and naphtha fuel	Gas turbine- 115 MW Steam turbine- 57 MW	172 MW

6.3.2 Analysis of vehicle performance characteristics

Vehicle performance characteristics vary from one vehicle to another due to different factors. The below section discussed some of the important vehicle proformance characteristics such as type of vehicle with their fuel economy; year of manufacture; vehicle current mileage; the number of cylinders; and the number of strokes.

a. Fuel Economy of different type of vehicles

Permitting to the Table 26, the vehicle's fuel economy values have been calculated by the previous researchers [115]. Accordingly, the highest fuel economy values are for petrol motorbikes and three-wheelers. However, when considering average usage vehicle types, diesel lories (52,000 km/year) have taken the first place. The second highest is diesel buses (41,000 km/year)). In contrast, the lowest average usage vehicle types are petrol motorbikes (6,225 km/year), vans, and cars (8,000 km/year). Therefore, the most polluted vehicle type varies due to several factors.

Table 26: Average usage and fuel economy of different type ohf vehicles [115]

Fuel type	**Petrol vehicles**				**Diesel vehicles**			
Type of Vehicle	Motor bikes	Vans	Cars	Three-wheelers	Cars	Vans	Buses	Lorries
Vehicle's Fuel Economy (km/l)	23.5	6.0	7.5	19.0	11.0	8.3	3.2	3.5
Vehicle's average usage km/year	6,225	8,000	8,000	12,000	15,000	21,000	41,000	52,000

Vehicle's fuel economy values were compared with the measure vehicle counts of the different types of vehicles in Colombo as shown in Figure 79. Accordingly, considering the vehicle counts, the first five orders of the most polluted vehicle types in descending order would be three-wheelers, cars, motor bikes, vans and busses. Furthermore considering the fuel economy of the vehicle, first five orders of the most polluted vehicle types in descending order would be motor bikes, three-wheelers, vans, cars, and busses.

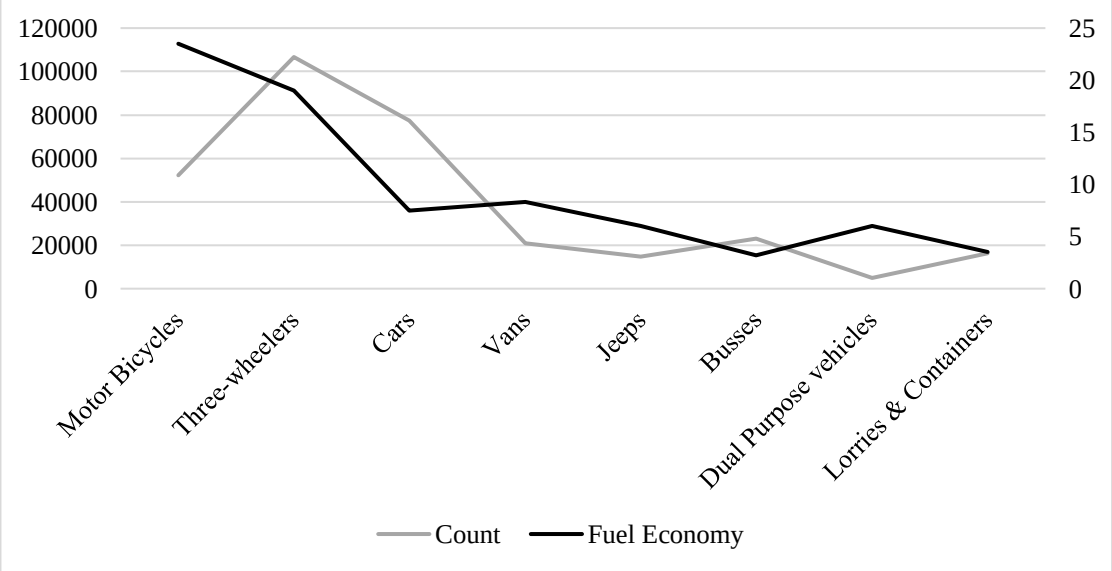


Figure 79: Comparison of the fuel economy with the vehicle counts in Colombo

**Fuel economy values are presented in secondary axis*

The number of passengers carrying by a particular vehicle is also an important parameter to be considered. Fuel economy with passenger km and the vehicle counts of different type of vehicles are compared in Table 27. Accordingly most polluted type of vehicles vary as cars, three-wheelers, motor bikes and busses in descending order.

Table 27: Fuel economy with passenger km of different type of vehicles

Vehicle type	Motor Bicycles	Three-wheelers	Cars	Busses
Vehicle count	52,232	106,675	77,337	23,104
Fuel economy in Liter/passenger km [115]	0.02	0.04	0.05	0.01

a. Analysis of the vehicle exhaust hydrocarbon data

A random sample (43,4497 vehicles) of the vehicle exhaust hydrocarbon data in year 2015 of the VET programme of DMT was analyzed using SPSS version 16. According to Figure 80, 81 and Table 28 and 29 explain that idling hydrocarbon levels were higher than the accelerated hydrocarbon levels. Further Figure 80 data explained that hydrocarbon levels of the older vehicles were very much higher than the newer vehicles. Therefore year of manufacture has a liner relationship with the vehicle exhaust hydrocarbon levels. Figure 81 explains the idling and free accelerated hydrocarbon levels based on the vehicle current mileage. Accordingly when the vehicle current mileage increase then the emission of vehicle exhaust hydrocarbon levels have also increased. Therefore older vehicles contribute to higher air pollution. According to Table 28, when the number of cylinders are above 2 (4 & 6) then the vehicle exhaust hydrocarbon levels have considerably decreased. Accordingly vehicles having single cylinder such as motor bikes; and two cylinder type vehicles such as four-stroke and two-stroke three-wheelers have the highest hydrocarbon levels emitting from the vehicle exhaust line. Four and six cylinder type vehicles have shown the lowest hydrocarbon levels emitting from the vehicle exhaust line. Table 29 explains the idling and free accelerated hydrocarbon levels based on the number of strokes. Data explained

that when the number of strokes increases then the hydrocarbon levels have decreased. Accordingly two-strokes vehicles such as motor bikes and two-strokes three-wheelers have the highest emissions of hydrocarbon levels, whereas in four-stroke vehicles such as four-stroke three-wheelers and other vehicle types have comparatively lower emissions of hydrocarbon levels.

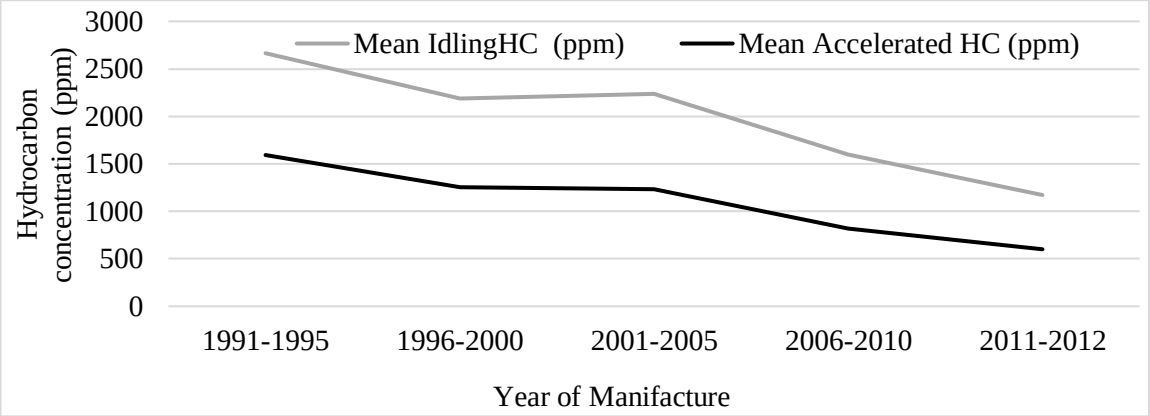


Figure 80: Idling and accelerated HC levels based on the year of manufacture

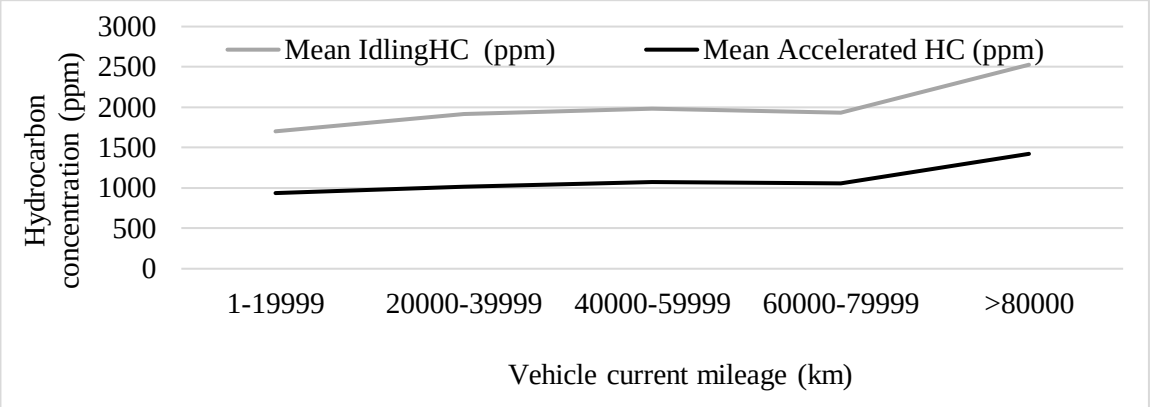


Figure 81: Idling and accelerated HC levels based on the vehicle current mileage

Table 28: Idling and accelerated HC levels based on the number of cylinders

Number of cylinders	Mean Idling HC (ppm)	Mean Accelerated HC (ppm)
1	2,034.52	1,097.08
2	2,200.41	1,151.35
>2 (4 & 6)	267.36	187.31

Table 29: Idling and accelerated HC levels based on the number of strokes

Number of strokes	Mean Idling HC (ppm)	Mean Accelerated HC ppm)
2	4,122.64	2,506.96
4	1,535.23	798.76

Table 30 summarized the cross tabulation of province and strokes category of the vehicle. The highest two-stroke vehicles (19,317) and four-stroke vehicles (137,821) were noticed from the Western province. The second highest two-stroke vehicles were noticed in the Southern province (6,436). Other provinces have less number of two-stroke vehicles. Therefore, there is a high possibility that when considering the stroke type, Western province vehicles contribute high hydrocarbon emissions than other provinces.

Apart from the above-described parameters, there are other important parameters that are available in literature such as driver's behavior, driving patterns, speeds of a vehicle, whether the vehicle is under proper maintenance, road conditions (whether the road is carpeted or concrete or soil, main road or secondary road), and evaporation losses from the vehicles. Further, tree cover, building height, also involves in the pollution dispersion [21]. Therefore, it is important to develop a comprehensive strategy that shelters, effective maintenance of vehicles, efficient vehicle technologies, quality of fuels, traffic & demand management, awareness, and education of the vehicle owners.

Table 30: Cross tabulation of province and the vehicle stroke category

Stroke	Variable	Province									
		1.Western	2.Central	3.Southern	4.Northern	5.Eastern	6.North Western	7.North Central	8.Uva	9.Sabaragamuwa	Total
2 Stroke	Number of vehicles	19317	5429	6436	28	1636	5994	2162	1370	4142	46514
	Provincial distribution (%)	41.5	11.7	13.8	0.1	3.5	12.9	4.6	2.9	8.9	100.0
	Stroke type within Province (%)	12.3	13.0	11.3	7.4	5.6	8.5	7.0	10.4	12.2	10.7
4 Stroke	Number of vehicles	137821	36295	50742	348	27731	64646	28890	11782	29728	387983
	Provincial distribution (%)	35.5	9.4	13.1	0.1	7.1	16.7	7.4	3.0	7.7	100.0
	Stroke type within Province (%)	87.7	87.0	88.7	92.6	94.4	91.5	93.0	89.6	87.8	89.3
Total	Number of vehicles	157138	41724	57178	376	29367	70640	31052	13152	33870	434497
	Provincial distribution (%)	36.2	9.6	13.2	0.1	6.8	16.3	7.1	3.0	7.8	100.0
	Stroke type within Province (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Figure 82 presents the historical data on the active vehicle fleet by Revenue License from 2002 to 2018 in Sri Lanka. According to the statistics, the entire number of registered vehicles at the DMT from the year 2002 to 2018 has increased nearly by 5 folds [21, 115]. Highest contributions are made by the two-wheelers (971,954) and

three-wheelers (2,729,762). Furthermore, cars (582,575) and dual-purpose vehicles (363,553) have placed the third and fourth positions with the increasing vehicle number. Buses which are the main public transportation mode on road have not attractively increased in number.

According to Table 31, there are 7.21 million vehicles in Sri Lanka in the year 2018 registration data out of which 4.04 million are motorcycles, 1.14 million three-wheelers and 747,126 cars. The number of motorbikes is dominating in the registered vehicles or the active fleet by revenue license. However, in the city based vehicle count results showed that three-wheelers are dominating in the active vehicle fleet on-road. This could be explained as the three-wheeler moves around the city throughout the day as a taxi service and motorbikes are frequently personal usage vehicles which are mainly used to travel to the work place in the morning and return to residential locations. Table 30 further explained that the registered vehicles are not fully represented in the active vehicle fleet by the revenue license.

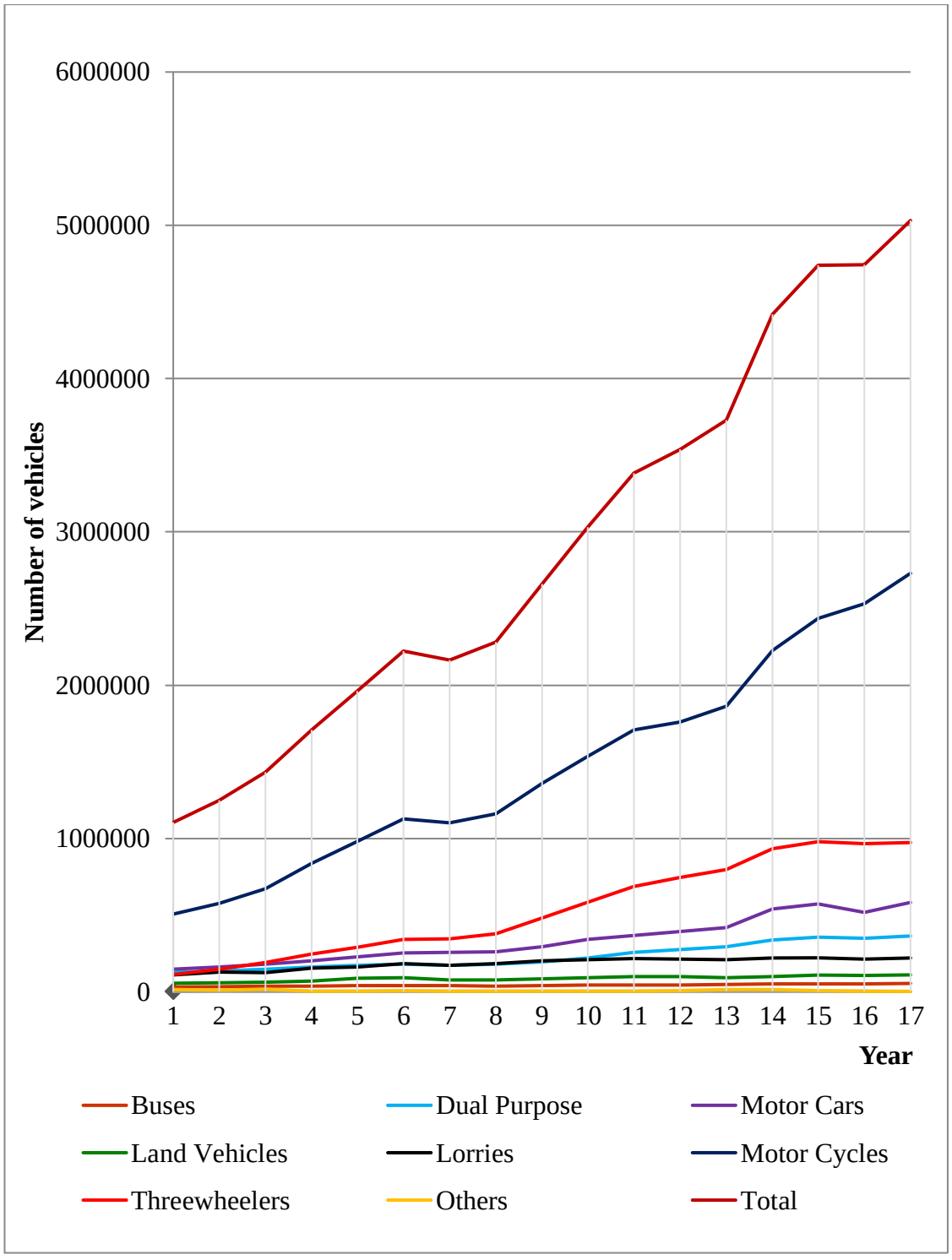


Figure 82: Active vehicle fleet by Revenue License from 2002 – 2018

**Original is in Colour*

Table 31: Variation between the active vehicle fleet by Revenue License with total registration

Vehicle Category	Active Fleet by Revenue License				Total Registration	Survival rate	Active Fleet%
	2015	2016	2017	2018	2018	2018	2018
Buses	51636	52203	52,494	54,189	111,616	48.5	0.0108
Dual Purpose Vehicles	336,542	357,125	349,907	363,553	411,294	88.4	0.0723
Cars	540,806	573,920	519,231	582,575	747,126	78.0	0.1158
Land Vehicles	100,433	108,849	105,193	108,176	412,839	26.2	0.0215
Goods Transport Vehicles	219,619	221,260	214,493	219,052	349,225	62.7	0.0435
Motor Cycles	2,227,120	2,437,105	2,531,606	2,729,762	4,041,703	67.5	0.5426
Three-wheelers	932,016	978,977	966,448	971,954	1,139,218	85.3	0.1932
Others	13,119	7,875	3,493	1,895			0.0004
Total	4,421,291	4,737,314	4,742,865	5,031,156	7,213,021	69.8	1.0000

6.3.3 Analysis of TVOC monitoring data & GCMS spectra

a. Analysis of TVOC monitoring in different sources in Sri Lanka

International research studies have found that exposures to typical mixtures of VOCs in the range of 1 to 10 ppm or above results serious health effects. Based on the results in Table 32, TVOC levels in different Sri Lankan environments were categorized and presented with a colour index as; above 75ppm for very high TVOC level (Red), 75ppm

-10ppm for high TVOC level (Orange), 1ppm to 10ppm for medium TVOC level (Yellow), and below 1ppm as low TVOC level (Green). According to the TVOC results in table 32, obtained from the Photo Ionization Detector (PID), highest TVOC was observed at ambient environments in petroleum station when filling petrol to a vehicle (603.10ppm). Therefore, worker in the petroleum stations are exposed to high concentrations of VOC's. Direct vehicle exhaust TVOC value was extremely high (1972.9ppm), however when the vehicles were moving on road TVOC value was comparatively low (273.42ppm) due to high dilution with ambient air. When compared TVOC levels of on road measurements with the road side 1ft away from high traffic road, due to dilution with ambient air TVOC value (132.87ppm) became low. Considering the factors from vehicle exhaust to roadside ambient air, second highest TVOC levels were observed from vehicle emissions. Third highest TVOC levels were observed at vehicle spray paint area (78.30ppm); and then at kerosene using cook stove area (73.40ppm). It should be noted that 5ft away from the petroleum station also showed a TVOC value of 65.40ppm which has exceeded the international standard value. Moderate TVOC levels (15.40ppm) were observed at outdoor garbage burning area. This value may vary according to the composition of polythene and other garbage. Considerable TVOC levels were observed at the Kerosene lamp burning area (7.20ppm) and Mosquito coil burning area (6.60ppm).

Table 32: Ambient TVOC monitoring results of selected sites measured from Photo Ionization Detectors (PID)

No	Measurement area	Distance	Average VOC (ppm)	Colour index	TVOC range in ppm
1	Wood using cook stove area	1 ft away	1.89		1-10
		10 ft away	-		< 1
2	LPG using cook stove area	1 ft away	1.00		1-10
		10 ft away	-		< 1
3	Petroleum station	when filling petrol to a vehicle	603.10		>75
		5 ft away	65.40		>75
		20 ft away	6.00		1-10
4	Vehicle spray paint area	1 ft away	78.30		
		10 ft away	4.40		1-10
5	Tobacco smoking area	1 ft away	2.00		1-10
		10 ft away	-		< 1
6	Incent sticks burning	1 ft away	2.22		1-10
		10 ft away	-		< 1
7	Outdoor garbage burning area polythene / other garbage	1 ft away	15.40		10-75
		5 ft away	3.22		1-10
8	Vehicle service area	1 ft away	3.43		1-10
9	Mosquito coil burning area	1 ft away	6.60		1-10

10	Kerosene using cook stove area	1 ft away	73.40		>75
		5 ft away	5.44		1-10
11	Kerosene lamp burning area	when burning - 5 ft away	2.00		1-10
		when close the lamp - 1 ft away	7.20		1-10
		when close the lamp - 5 ft away	2.67		1-10
12	Vehicle exhausts	from the exhaust line	1972.9		>75
13	Road side (heavy traffic)	1ft away from road side	132.86		>75
14	On road measurements (heavy traffic)	outside the shatter of the vehicle	273.42		>75

b. Constituents in the vehicle exhausts- GCMS spectra

Table 33 summarized the constituents identified from GCMS analysis of selected samples of vehicle exhaust namely dual-purpose van, lorry, four-stroke three-wheeler, four-stroke motor bike and cars. Accordingly, in the samples, air toxic compounds such as benzoquinoline derivatives, naphthalene derivatives and benzene derivatives were observed from the GCMS spectra and it could be due to the incomplete combustion of petroleum products mainly arises from vehicle emissions. Further it was observed that vehicles that have older manufacturing years emitted high VOC compounds than the newer vehicles. Hybrid petrol vehicle with older manufacturing years also emitted certain VOC compounds; however it is comparatively low with other vehicle types. Emissions from vehicle exhaust of a four stroke three-wheeler with newer (2016) manufacturing year still showed higher VOC compounds.

Table 33: GCMS analysis of vehicle emission samples from different types of vehicles in Sri Lanka

No	Emissions of vehicle exhaust from different types of vehicles	Identified VOC Components from GCMS spectra
1.	Emissions from vehicle exhaust of a dual purpose van Cylinder capacity: 2500cc; Make: Mazda; Fuel type: diesel; Manufacturing year:1998) Retention time:8-20 min	Benzaldehyde, 2,3-dimethyl-naphthalene, 1,6,7-trimethyl-naphthalene, 4-ethyl-benzaldehyde, 2,4-dimethyl-benzoquinoline, 1,2-bis(trimethylsilyl)benzene,
2.	Emissions from vehicle exhaust of a lorry. Cylinder capacity: 3000cc; Make: JAC; Fuel type: diesel; Manufacturing year:2008 Retention time:8-20 min	Benzaldehyde, 2,6-dimethyl-naphthalene, 1,6,7-trimethyl-naphthalene, 2,4-dimethyl-benzoquinoline, 9H-fluorene-2-carboxylic acid, 1(3H)-isobenzofuranone, 1,2-bis(trimethylsilyl)benzene, benzene acetic acid
3.	Emissions from vehicle exhaust of a four-stroke three-wheeler. Cylinder capacity: 200cc; Make: Bajaj; Fuel type: Petrol; Manufacturing year: 2016. Retention time:8-20 min	Benzaldehyde, 1,6,7-trimethyl-naphthalene, 2,4-bis[(trimethylsilyl)oxy]-benzene, 2,4-dimethyl-benzoquinoline, 1,2-bis(trimethylsilyl)benzene, benzene acetic acid, 9H-fluorene-2-carboxylic acid

4.	Emissions from vehicle exhaust of a four-stroke motor bike. Cylinder capacity: 100cc; Fuel type: Petrol; Manufacturing year: 2012 Retention time:8-20 min	7-methyl-dibenzocarbazole, 2,5-bis[(trimethylsilyl)oxy]-benzaldehyde, 1,2-bis(trimethylsilyl)benzene, 2,4-bis[(trimethylsilyl)oxy]-benzoic acid, 2,4-dimethyl-benzoquinoline, 2,5-bis(1,1-methylethyl)-1,4-benzenediol
5.	Emissions from vehicle exhaust of an Aqua car. Cylinder capacity: 1500cc; Make: Toyota; Fuel type: petrol; Manufacturing year: 2013 Retention time:8-20 min	2-[(tert-butyldimethylsilyl)oxy]-1isopropyl-4-methyl- benzene, 1,2-bis(trimethylsilyl)benzene, 1,2-benzisothiazol-3-amine, 5-(2-nitro-1-propenyl-1,3-benzodioxole
6.	Emissions from vehicle exhaust of a Prius car (Figure 16). Cylinder capacity: 1500cc; Make: Toyota; Fuel type: petrol; Manufacturing year: 2012. Retention time:8-20 min	1,2-bis(trimethylsilyl)benzene, 1,6,7-trimethyl-naphthalene, trans-4-(2-(5-nitro-2-furyl)vinyl-2-quinolinamine

CHAPTER 7

CONCLUSIONS AND FUTURE DIRECTIONS

7.1. CONCLUSIONS

It could be concluded, that two concepts exist for $NO_X - VOC - O_3$ sensitivity as NO_X-sensitivity and VOC-sensitivity. NO_X-sensitive regime has comparatively low NO_X concentrations and high VOC concentrations and O_3 concentration rises with rising NO_X concentration. Nevertheless, O_3 concentration changes slightly in reply to rising VOC concentration. In the VOC-sensitive regime, the course of O_3 formation rises with rising VOC. Further, the course of O_3 formation rises or occasionally even reduces with increasing NO_X. This sensitivity varies from area to area depending on the concentrations of pollution sources of NO_X and VOC in a particular area.

When the NO is in extremely high concentrations, certain concentrations of O_3 removes from the atmosphere. This is due to the excessive NO concentrations reacts with the produced O_3 concentration and this is known as NO_X titration. The study further concludes solar radiation, air temperature, and speed of the wind (meteorological parameters) also have a relationship with O_3 production and it is an increasing trend. The developed urban air-shed model could calculate the steady state ozone concentration (O_{3SS}). Model recoganized NO_X-sensitive regime from VOC-sensitive regime. It can calculate quantitative contributions from each regime type. Validation results of the univariate linear regression model using predicted and observed ozone values confirmed that (O_{3ss}) concentration was significantly correlated with the predicted ozone concentration. Analysis of urban air shed in Colombo also confirms the

predicted and observed (O_{3ss}) concentration was significantly correlated. It could be concluded that the developed urban air-shed model can contribute in developing suitable interventions to regulate O_3 in a specific city.

The study concludes that certain cities have high air pollution due to emissions from on-road vehicles or train emissions or power plant emission or industrial emission or a combination of several or all in Colombo. Furthermore, findings confirm that year of manufacture, current mileage, cylinder type, and number of strokes of vehicles have a linear relationship on HC concentration of vehicle exhaust that contributes to air pollution. It could be concluded that in the city of Colombo, the active vehicle fleet was dominated by three-wheelers, cars, and motorbikes that contribute to a higher percentage of vehicular air pollution. Further three-wheelers used the road throughout the day. It could be further concluded that cars, three-wheelers, and motorbikes are the foremost polluted vehicles when considering the vehicle type, vehicle number, active vehicle fleet, fuel economy, and the passenger-km. The analysis of registered vehicles at the DMT in Sri Lanka confirms that the vehicle fleet is characterized by a large portion of three-wheelers and motorbikes both of which have presented a substantial growth in the past years which lead to high air pollution as well as vehicle safety. The study concluded that apart from the domestic on-road vehicles train was a key source of vehicle emission that contributes to air pollution in Sri Lanka. It could be further concluded that GCMS spectra of vehicle exhausts contain some of the known carcinogenic compounds.

This research provides a detailed understanding of photochemical degradation in urban air sheds of Sri Lanka and provides critical information's for the scientific community and decision-makers to formulate air pollution mitigation policies. Looking at the macro

picture of the problem of air pollution in relation to O_3 in Sri Lanka holistic approach is a must to obtain comprehensive solutions.

7.1.1 Limitations

Seasonal variation was unable to study in this research due to unavailability of long terms of air pollution data and high cost for the mobile air quality monitoring station measurements in researchers level. Since the atmosphere is so complex, and cannot be readily studied in the laboratory environment, chemical and mathematical modeling has being used to overcome this limitation.

7.1.2 Contribution to the knowledge

On site measurements together with the model results provides a detail understanding of photochemical degradation in Sri Lanka. Developed model could calculate steady state ozone concentration (O_{3ss}) in both regimes. Further, the developed Urban Air-shed Model provides a platform for other countries to develop similar models to control O_3 in a particular city. Methodology of model development procedure could be applied for future researchers to develop models for other air pollutants. Furthermore applicability of the model during COVID 19 pandemic situation have proven the validity of the developed model. The existing theoretical models in the world largely failed to explain the worldwide observation of indifference of O_3 concentrations during lockdown period [261]. The model developed in the present study illustrates the phenomena behind the above observation.

7.2. FUTURE DIRECTIONS

Applications of the developed “Urban Air-shed Model” to derive critical information in policy decisions when developing appropriate interventions to control O_3 in Sri Lanka. It is proposed to continue air quality monitoring at major urban locations countrywide. This could improve the sensitivity and the accuracy of the developed “Urban Air Shed Model" with regards to seasonal variations such as monsoons. Further, new researches could develop relationships among other air pollutants leading to developing a combined air quality prediction model for Sri Lanka. It is important to identify all possible VOC species and their rection rates in different temparatures through advanced research. This will further improve the developed “Urban Air-shed Model” by improving the k1 and k2 rate constant values in this model development. Study further endorsed developing a district vise complete emission inventory for Sri Lanka. It is important to identify all point sources and mobile sources in that particular district and develop emission inventory. Then based on these inventory data new regulations can be introduced for the country. This emission inventory could be linked with the developed model and based on the findings decisions could be established by the policymakers.

A detail research could be carried out on train emissions in Sri Lanka and new regulations can be introduced to improve the fuel quality of trains, along with emission standards and cleaner technology train engines. Further, a detail investigation can be carried out on representative samples of vehicle exhaust GCMS spectra for Sri Lankan vehicles and the findings could be incorporated in necessary regulations on the vehicle emission testing programme to amend vehicle exhaust emission standards accordingly. Finally, a detailed national level study on VOCs towards formulating ambient air quality standards for VOCs in Sri Lanka.

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ANNEXURES

ANNEXURE I

Methodology followed and temperature programme used for the GCMS analysis

……..**INSTRUMENT CONTROL PARAMETERS : UOC_GCMS**……

Control Information

Sample Inlet : GC

Injection Source : Manual

Mass Spectrometer : Enabled

Oven

Equilibration Time : 3 min

Max Temperature : 300 degrees C

Slow Fan : Disabled

Oven Programme : On

: 80 C for 2 min, then 10 C/min to 220 C for 2 min then 4 C/min to290 C for 4.5 min

Run Time : 40 min

Back SS Inlet He

Mode : Splitless

Heater : On 280 C

Pressure : On 8.1469 psi

Total Flow : On 18.9 ml/min

Septum Purge Flow : On

Gas Saver : Off

Purge Flow to Split vent : 15 ml/min at 0.75 min

Thermal Aux 2 (MSD Transfer Line)

Heater : On

Temperature Programme : On 280 C

Run Time : 40 min

Column # 1

Agilent 19091S-433 : 2486.94522

HP-5MS : 5% Phenyl Methyl Silox

325 C : 30 m x 250 µm x 0.25µm

In : Back SS Inlet He

Out : Vacuum

Initial Temperature : 80 C

Pressure : 8.1469 psi

Flow : 0.9 ml/min

Average velocity : 35.069 cm/sec

Holdup Time : 1.4258 min

Flow Programme : Off, 0.9 ml/min for 0 min

Run Time : 40 min

Signals

Signal # 1: Test Plot : Save off 50Hz

Signal # 2: Test Plot : Save off 50Hz

Signal # 3: Test Plot : Save off 50Hz

Signal # 4: Test Plot : Save off 50Hz

MS Acquisition Parameters

General Information

Tune File : atune.u

Acquistion Mode : Scan

MS Information

Solvent Delay : 0.00 min

EMV Mode : Relative

Relative voltage : 0

Resulting EM Voltage : 1165

[Scan Parameters]

Low Mass : 50.0

High Mass : 550.0

Threshold : 150

Sample # : 2

Plot 2 low mass : 50.0

Plot 2 high mass : 550.0

[MS Zone]

MS Source : 230 C maximum 250 C

MS Quad : 150 C maximum 200 C

……END OF MS ACQUISITION PARAMETERS…….

TUNE PARAMETERS FOR SN: US13342B07

TRACE ION DETECTION IS OFF

EMISSION : 34.610

ENERGY : 69.922

REPELLER : 31.463

IONFOCUS : 90.157

ENTRANCE_LE : 25. 500

EMVOLTS : 1164.706

Actual EMV : 1200

GAIN FACTOR : 0.33

AMUGAIN : 1361.000

AMUOFFSET : 123.625

FILAMENT : 1.000

DCPOLARITY : 0.000

ENTLENSOFFS : 17.820

MASSGAIN : -1012.000

MASSOFFSET : -35.000

……..END OF TUNE PARAMETERS……...

……..END OF INSTRUMENT CONTROL PARAMETERS……

ANNEXURE II

Comparison of Average vehicle count data at eight different locations in Colombo

Hour	Borella	Dehiwala	Fort	Grandpass	Kollupitiya	Maradana	Narahenpita	Nugegoda
1.00-2.00	806	684	647	593.8167	411.1048	1087.056	390.8987	484.2923
2.00-3.00	1139	453	730	418.6417	345.0296	767.4974	284.0199	316.1404
3.00-4.00	1720	620	951	558.0667	588.8984	1046.285	409.9842	337.6066
4.00-5.00	2240	854	1171	690.3417	974.5984	1546.283	658.0957	498.6031
5.00-6.00	2573	1547	1342	833.3417	1019.22	2047.54	974.915	1099.204
6.00-7.00	3297	2205	2072	1923.717	1817.286	3881.873	1375.711	2337.541
7.00-8.00	3925	3766	3066	2602.967	2941.589	5668.517	3249.907	3976.127
8.00-9.00	3375	3657	3885	3117.767	3631.338	5948.252	3211.736	3757.888
9.00-10.00	4076	2852	4096	3643.292	2327.369	4784.657	3746.13	2906.395
10.00-11.00	3111	2871	4273	3557.492	2753.155	5129.199	3425.493	2702.466
11.00-12.00	3212	3131	5051	3278.642	2836.386	4246.742	3581.994	2548.625
12.00-13.00	3727	3037	4407	3582.517	2844.26	4269.715	3375.871	2802.642
13.00-14.00	4115	2803	4261	3561.067	2275.326	4654.036	3246.09	2587.98
14.00-15.00	2925	2859	4171	3550.342	6694.424	4127.114	3039.966	2881.351
15.00.16.00	3417	3265	4291	3557.492	4042.763	4257.848	3585.811	3053.081
16.00-17.00	3874	3455	4175	3300.092	4219.601	4091.854	3459.847	3192.611
17.00-18.00	3944	3836	4168	2863.942	3244.829	3561.905	3593.446	3153.256
18.00-19.00	3739	4500	3380	3207.142	2728.059	3889.938	3059.052	4119.235
19.00-20.00	3200	4339	3109	3135.642	2152.781	3747.134	3188.833	3550.381
20.00-21.00	2542	3631	2379	2638.717	1991.623	3338.195	2532.292	2756.132
21.00-22.00	1895	2965	1667	2642.292	1642.552	2822.538	2093.325	2062.058
22.00-23.00	1465	2486	1280	1855.792	1277.693	2490.86	1879.568	1636.312
23.00-24.00	977	1818	990	1376.742	1110.393	2046.982	1104.696	1117.545
24.00-1.00	694	1099	734	904.8417	727.6706	1568.407	665.7299	713.2651

ANNEXURE III

Data from the Fort Railway Station for every minuted incoming and outgoing trains in all railway tracks during 24 hour day

To Awissawella	To Ragama	Nugegoda to Colombo	Ragama to Colombo	Total data points	Time	Category	Number of trains
10.35	3.00	6.12	3.03	1	3.00	3.00-3.59	4
13.55	3.25	6.33	3.35	2	3.03	4.00-4.59	5
16.10	4.00	6.59	4.47	3	3.25	5.00-5.59	12
16.35	4.40	7.16	5.10	4	3.35	6.00-6.59	19
17.05	5.00	7.35	5.32	5	4.00	7.00-7.59	23
17.20	5.10	7.49	5.55	6	4.32	8.00-8.59	22
17.40	5.41	8.22	5.58	7	4.34	9.00-9.59	10
18.30	6.00	13.08	6.02	8	4.40	10.00-10.59	8
19.15	6.05	14.53	6.28	9	4.47	11.00-11.59	9
20.00	6.17	16.30	6.34	10	5.00	12.00-12.59	6
	6.23	21.19	6.56	11	5.02	13.00-13.59	10
	6.45		7.09	12	5.10	14.00-14.59	13
	7.02		7.25	13	5.10	15.00-15.59	8
	7.14		7.33	14	5.10	16.00-16.59	17
	7.35		7.39	15	5.32	17.00-17.59	20
	7.40		7.55	16	5.41	18.00-18.59	19
	8.00		7.57	17	5.41	19.00-19.59	12
	8.06		8.05	18	5.42	20.00-20.59	9
	8.30		8.07	19	5.55	21.00-21.59	7
	8.35		8.16	20	5.56	22.00-22.59	2
	8.50		8.25	21	5.58	23.00-23.59	2

	8.50		8.32	22	6.00		
	8.55		9.16	23	6.02		
	9.30		9.46	24	6.05		
	9.35		9.54	25	6.12		
	9.45		10.13	26	6.14		
	10.10		10.19	27	6.17		
	10.35		10.26	28	6.22		
	10.35		10.50	29	6.23		
	11.15		11.09	30	6.28		
	11.55		11.18	31	6.30		
	12.05		11.23	32	6.33		
	12.40		11.28	33	6.34		
	12.50		11.52	34	6.35		
	13.10		12.52	35	6.37		
	13.15		13.41	36	6.45		
	13.45		13.53	37	6.45		
	13.55		14.09	38	6.56		
	14.20		14.40	39	6.56		
	14.35		14.48	40	6.59		
	14.45		14.58	41	7.01		
	15.20		15.05	42	7.02		
	15.45		15.25	43	7.04		
	16.10		15.50	44	7.06		
	16.25		16.09	46	7.09		
	16.30		16.55	47	7.14		
	16.50		17.31	48	7.16		

	16.55		17.35	49	7.16		
	17.00		17.57	50	7.19		
	17.20		18.00	51	7.25		
	17.30		18.02	52	7.32		
	17.40		18.07	53	7.33		
	17.55		18.16	54	7.35		
	18.05		18.25	55	7.35		
	18.15		18.34	56	7.39		
	18.35		18.35	57	7.40		
	18.45		18.58	58	7.40		
	19.05		18.59	59	7.42		
	19.15		19.24	60	7.45		
	19.15		19.42	61	7.49		
	19.20		19.55	62	7.55		
	19.50		20.06	63	7.57		
	20.00		20.36	64	7.59		
	20.20		20.45	65	8.00		
	20.45		20.50	66	8.01		
	21.30		21.03	67	8.05		
	21.45		21.21	68	8.05		
	23.00		21.37	69	8.06		
			22.04	70	8.06		
			22.48	71	8.07		
				72	8.16		
				73	8.17		
				74	8.22		

				75	8.25		
				76	8.30		
				77	8.32		
				78	8.35		
				79	8.35		
				80	8.39		
				81	8.40		
				82	8.49		
				83	8.50		
				84	8.50		
				85	8.55		
				86	8.58		
				87	9.00		
				88	9.10		
				89	9.16		
				90	9.27		
				91	9.30		
				92	9.35		
				93	9.45		
				94	9.46		
				94	9.50		
				96	9.54		
				97	10.10		
				98	10.13		
				99	10.19		
				100	10.26		

				101	10.35		
				102	10.35		
				103	10.35		
				104	10.50		
				105	11.09		
				106	11.14		
				107	11.15		
				108	11.18		
				109	11.23		
				110	11.24		
				111	11.28		
				112	11.52		
				113	11.55		
				114	12.05		
				115	12.09		
				116	12.35		
				117	12.40		
				118	12.50		
				119	12.52		
				120	13.08		
				121	13.10		
				122	13.15		
				123	13.20		
				124	13.34		
				125	13.41		
				126	13.45		

				127	13.53		
				128	13.55		
				129	13.55		
				130	14.05		
				131	14.09		
				132	14.18		
				133	14.19		
				134	14.20		
				135	14.35		
				136	14.35		
				137	14.40		
				138	14.45		
				139	14.48		
				140	14.53		
				141	14.58		
				142	14.59		
				143	15.05		
				144	15.12		
				145	15.20		
				146	15.25		
				147	15.25		
				148	15.45		
				149	15.50		
				150	15.54		
				151	16.02		
				152	16.09		

				153	16.10		
				154	16.10		
				155	16.19		
				156	16.25		
				157	16.25		
				158	16.29		
				159	16.30		
				160	16.30		
				161	16.35		
				162	16.42		
				163	16.45		
				164	16.49		
				165	16.50		
				166	16.55		
				167	16.55		
				168	17.00		
				169	17.05		
				170	17.06		
				171	17.14		
				172	17.20		
				173	17.20		
				174	17.20		
				175	17.30		
				176	17.31		
				177	17.34		
				178	17.35		

				179	17.40		
				180	17.40		
				181	17.42		
				182	17.44		
				183	17.52		
				184	17.55		
				185	17.55		
				186	17.55		
				187	17.57		
				188	18.00		
				189	18.00		
				190	18.02		
				191	18.05		
				192	18.07		
				193	18.13		
				194	18.14		
				195	18.15		
				196	18.16		
				197	18.25		
				198	18.30		
				199	18.30		
				200	18.34		
				201	18.35		
				202	18.35		
				203	18.45		
				204	18.50		

				205	18.58		
				206	18.59		
				207	19.05		
				208	19.10		
				209	19.15		
				210	19.15		
				211	19.15		
				212	19.20		
				213	19.24		
				214	19.27		
				215	19.42		
				216	19.49		
				217	19.50		
				218	19.55		
				219	20.00		
				220	20.00		
				221	20.06		
				222	20.20		
				223	20.36		
				224	20.39		
				225	20.45		
				226	20.45		
				227	20.50		
				228	21.03		
				229	21.19		
				230	21.21		

				231	21.30		
				232	21.34		
				233	21.37		
				234	21.45		
				235	22.04		
				236	22.48		
				237	23.00		
				238	23.26		

ANNEXURE IV

Urban air-shed model parameters in Excel sheet

j	**NO_2**	**JNO_2**	**k**	**NO**	**kNO**	**jNO_2/kNO**	**k_1**	**10^{-12}**	**$k_1 x\ 10^{-12}$**	**HO_2**	**$k_1 x\ 10^{-12} x HO_2$**	**k_2**	**1000000000000**	**$k_2 x 10^{-12}$**	**RO_2**	**$k_2 x\ 10^{-12} x RO_2$**	**L+Q**	**(L+Q)xNO**	**$O_{3\ SS}$**	**O_3 Measured in micro gram per cubic meter**	**O_3 Measured (ppm)**

ANNEXURE V

Every minuted data of ambient TVOC monitoring results of selected sites measured from Photo Ionization Detectors (PID)

No	Measurement area	Distance	VOC (ppm)									
1	Wood using cook stove area	1 ft away	2	2	2	-	1	2	2	2	2	2
		10 ft away	-	-	-	-	-	-	-	-	-	-
2	LPG using cook stove area	1 ft away	1	1	-	-	-	-	1	1	1	-
		10 ft away	-	-	-	-	-	-	-	-	-	-
3	Petrol shed	when filling petrol to a vehicle	586	585	580	572	620	664	635	605	594	590
		5 ft away	67	68	62	55	64	76	71	72	58	61
		20 ft away	6	6	6	4	7	8	6	6	5	6
4	Vehicle spray paint area	1 ft away	70	76	81	92	88	72	84	80	72	68
		10 ft away	4	4	4	6	4	2	4	6	6	4
5	Tobacco smoking area	1 ft away	2	2	2	-	-	2	-	2	2	-
		10 ft away	-	-	-	-	-	-	-	-	-	-
6	Incent sticks burning	1 ft away	2	2	2	4	2	2	2	-	2	2
		10 ft away	-	-	-	-	-	-	-	-	-	-
7	Outdoor garbage burning area polythene / other garbage	1 ft away	15	18	12	14	19	20	14	14	12	16
		5 ft away	2	4	4	2	-	4	5	4	2	2
8	Vehicle service area	1 ft away	4	4	-	-	2	2	4	4	-	4
9	Mosquito coil burning area	1 ft away	8	12	6	6	4	6	6	8	6	4

10	Kerosene using cook stove area	1 ft away	78	84	82	76	68	62	74	74	56	80
		5 ft away	6	6	6	4	-	4	6	6	7	4
11	Kerosene lamp burning area	when burning - 1 ft away	-	-	-	-	-	2	2	-	2	-
		when burning - 5 ft away	-	-	-	-	-	-	2	-	-	-
		when close the lamp - 1 ft away	8	9	8	5	9	9	8	4	5	7
		when close the lamp - 5 ft away	4	-	2	2	-	-	4	2	-	2
12	Vehicle exhausts	1ft away	1923.1	1998.9	1966.1	1992.3	1956.4	1987.7	1945.9	1971.4	1952.3	1972.9
13	Road side (heavy traffic)		133.11	131.15	136.76	135.91	132.36	134.14	131.55	134.67	132.07	132.86
14	On road measurements (heavy traffic)		261.12	266.55	269.31	268.07	270.92	278.77	275.33	271.12	276.57	273.42