# Development of Low Cost Passive sampling diffusion tubes for Spatial monitoring of $NO_2$, $SO_2$ and $O_3$ In Kathmandu valley

**Ph.D. Thesis**

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**Nepal**

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**By**

**Rejina Maskey Byanju**

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Institute of Science and Technology

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Kirtipur, Kathmandu

Nepal

The dissertation entitled "**Development of Low Cost Passive sampling diffusion tubes For Spatial monitoring of $NO_2$, $SO_2$ and $O_3$ in Kathmandu valley",** Submitted by Rejina Maskey Byanju has been accepted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry.

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# Recommendation

This is to certify that Mrs Rejina Maskey Byanju has completed dissertation entitled "Development of Low Cost Passive sampling diffusion tubes for spatial monitoring of $NO_2$, $SO_2$ and $O_3$ in Kathmandu valley "for the award of Doctor of Philosophy degree in Chemistry under our supervision. To our knowledge this work has not been submitted for any other degree.

Professor Mohan Bikram Gewali (PhD)
Supervisor

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Co Supervisor

Date: / 06 / 2012

# Certificate of Approval

On the recommendation of Prof, Dr. Mohan Bikram Gewali and Prof, Dr. Krishna Manandhar, this dissertation work of Mrs. Rejina Maskey Byanju, is forwarded for the examination and is submitted to the IOST, Tribhuvan University for the award of Doctor of Philosophy in Chemistry.

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Rejina Maskey Byanju

# Abstract

The work embodied in this research was to find out the solution for the difficulties often encountered by the resource limited countries in using high cost automatic instruments for air pollution monitoring and assessment. Monitoring and assessment is an important aspect in the protection of the public from the air -pollution –induced- health- hazard by improving exposure assessment and formulating mitigations. The overall goal of this study was to develop low cost passive samplers logistically feasible and technically suitable to use for ambient $NO_2$, $SO_2$ and $O_3$ monitoring in Kathmandu. Locally available polyethylene tubes were developed as diffusion tubes for ambient passive sampling. These tools were then applied to assess the spatial variability in $NO_2$, $SO_2$ and $O_3$ across the Kathmandu valley.

The passive measurements include development of these tubes into diffusive tubes using triethanolamine (TEA) for $NO_2$, $SO_2$ and nitrite- coated filter (GF/A filter paper) for $O_3$ as absorbent bases. After extraction with water, modified Griese-Saltzmann method and West-Gaeke method were used for analysis of nitrite and sulphate adduct formed due to reaction of $NO_2$ and $SO_2$ respectively. Azide modified sodium salicylate method was used for analysis of nitrate formed by the oxidation of nitrite by ozone from the air using uv visible spectrophotometer. The results were compared with ferm- badge type passive samplers from IVL-Sweden and other active methods.

The detection limits of the passive sampling methods were found to be suitable for use in tested environment. The instrumental detection limits obtained from calibration curve were 0.09 μg/ml and 0.05μg/ml for $NO_2^-$ and $SO_4^{2-}$, respectively. The detection limits of $NO_2$ were in the range of 1.75 to 2.73 $\mu g/m^3$; and that for $SO_2$ were 1.12 to 5.85$\mu g/m^3$ for different tested exposure periods.

Precision of the method as expressed as coefficient of variation was good enough for the monitoring of $NO_2$ $SO_2$ and $O_3$ in ambient air of Kathmandu. The method showed strong correlation with high volume sampler and no significant difference with ferm badge –IVL samplers at $p$=0.05.

Precision of the passive sampling method for measurement expressed as coefficient of variation (CV) was 13.3% with an overall range of 2.3-20.8% for $NO_2$ and it was 14.5% with an overall range of 3.4-20.2%. The results of all the exposure analysis provided a reliable ambient $O_3$ sampling with good precision. Precision of $O_3$ measurements were found to be in the range of 0.1 to 14%. The prepared diffusion tubes were suitable for 24 hour sampling in the tested environments. The tested method overestimates of 22.77% and 7.9% in compare to that of automated ozone analyzer and Ferm-IVL sampler respectively. The result was acceptable according to US National Institute of Safety and Health (Seethapathy et al., 2007) The limit of detection for developed passive sampling method was 0.011 µg/ $m^3$, which was suitable to measure $O_3$ in the study area .

The passive monitoring and the assessment of the quality of air prevailing in the urban Kathmandu revealed that all the three pollutants monitored $NO_2$, $SO_2$ and $O_3$ concentrations in winter dry season were higher than in rainy season. $NO_2$ and $SO_2$ were below National Ambient Air Quality Standard (NAAQS) for both the monitoring period however, $NO_2$ at several points exceeded the NAAQS. Higher concentrations of $NO_2$ were observed at the high traffic density areas. Transportation was the major source of $NO_2$ in the city. $SO_2$ pollution in the city other hand was related with the industrial emission especially due to the brick kilns and hotels. The $O_3$ concentrations varied between 25 and 100 µg /$m^3$ with an average of 47 µg /$m^3$. The maximum was observed from rural site Matsygaun while minimum observed from Baudha. The pre-monsoon months specially March –May was the most vulnerable period for high concentration ozone exposure in Kathmandu valley.

Key words: Diffusive, Passive sampler, Nitrogen dioxide, Sulphur dioxide, Ozone.

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# Acronyms and Abbreviations

| | |
|---|---|
| AQM | Air Quality Management |
| ADB | Asian Development Bank |
| CBS | Central Buru of Statistics |
| CV | Coefficient of variation |
| CO | Carbon monoxide |
| dd | Double distilled water |
| d/w | Distilled water |
| DL | Detection limit |
| DANIDA | Danish International Development Agency |
| DoTM | Department of Traffic Management |
| ENPHO | Environment and Public Health Organization |
| EPA | Environmental Protection Agency |
| HCs | Hydrocarbons |
| IC | Ion chromatography |
| ICIMOD | International Center for Integrated Mountain Development |
| ITDG | Integrated Technology Development Group |
| JICA | Japanese International Corporation |
| KVVEP | Kathmandu Valley Vehicular Project |
| Milli Q | Ultra pure water created by milli pore corporation |
| MoE | Ministry of Environment |
| MoEST | Ministry of Environment Science and Technology (now called as MoE) |
| MoPE | Ministry of Population and Environment (now called as MoE) |

| | |
|---|---|
| NAST | National Academy of Science and Technology |
| NAQG | National Air Quality Guideline |
| NAAQS | National Ambient Air Quality Standards |
| NESS | Nepal Environmental and Scientific Services |
| NRs | Nepalese Rupees |
| NHRC | National Health Research Council |
| NOx | Oxides of Nitrogen |
| $NO_2$ | Nitrogen dioxide |
| $O_3$ | Ozone |
| PAN | Peroxyacetyl nitrate |
| PBN | Peroxybenzonyl nitrate |
| PDT | Passive diffusion tubes |
| $PM_{10}$ | Particulate matter of 10 micron aerodynamic diameter |
| $PM_{2.5}$ | Particulate matter of 2.5 micron aerodynamic diameter |
| RONAST | Royal Nepal Academy of Science and Technology (now NAST) |
| SOE | State of Environment |
| SOx | Oxides of Sulphur |
| $SO_2$ | Sulphur dioxide |
| $SO_4$ | Sulphate |
| TEA | Triethanolamine |
| TSP | Total Suspended Particles |
| TWA | Time weighted average |
| UVF | Ultraviolet fluorescence |
| URBAIR | Urban Air Quality Management Strategy in Asia |

| | |
|---|---|
| UNEP | United Nations Environmental Protection |
| VDCs | Village Development Committees |
| WECS | Water and Energy Commission Secretariat |
| WHO | World Health Organization |

**Weights and Measures**

| | |
|---|---|
| π | pie |
| r | radius |
| % | percentage |
| s | second |
| t | time |
| $^0$C | degree centigrade |
| μg | micro gram |
| μl | micro liter |
| μS | micro Siemens |
| Km | kilo meter |
| kmph | kilo meter per hour |
| m | meter |
| $m^3$ | cubic meter |
| M | molar |
| Min | minute |
| ml | milliliter |
| mm | milli meter |

| | |
|---|---|
| mM | milli molar |
| msl | mean sea level |
| *p* | level of confidence |
| pe | polyethylene |
| ppm | parts per million |
| ppbv | part per billion volume |
| psi | pascle |
| sd | standard deviation |
| %rsd | percentage standard deviation |

# Chapter 1: Introduction

## 1.1: Urban air pollution and information on selected pollutants

Air pollution is a serious public health problem in most of the major metropolitan areas of the developing world (Ozden *et al.,* 2008). In fact, this is becoming a serious problem in most of the rapidly urbanizing cities of South and East Asia, especially in mega cities such as Bombay, Calcutta, Delhi, Dhaka, Karachi in South Asia, and Bangkok, Beijing, Shanghai, Jakarta, and Manila in East Asia (Faiz, 2000). The problem is rapidly spreading in other urban centers of the region including Kathmandu (Schwela *et al.*, 2006). In these cities, pollution levels of pollutants such as $PM_{10}$, CO, NOx, $SO_2$, $O_3$ often exceeds international and national norms (CAI-Asia, 2006). The air pollution is likely to continue to pose an increasing threat as the cities undergo rapid industrialization and economic development (Baldasano *et al*., 2003). In other words, the developments without adequate assessment of environmental impacts and management planning could have many adverse effects (Schwela *et al*., 2006).

The rapid and continuing increase in motorized and polluting forms of transport combined with inadequate transport infrastructure, lax proper environmental legislation and enforcement, weak institutions, and lack of skilled manpower, have resulted in poorly planned urban growth with sever air pollution problems (Ozden *et al*., 2008; Schwela *et al*., 2006; Cole, 2003). Urban air pollution affects the health, well being and life chances of hundreds of millions of men, women and children. It is responsible for an estimated 537,000 premature deaths annually (WHO, 2002). The associated human health and welfare costs run into hundreds of millions of dollars and far exceed the prevention costs in terms of the control measures (Faiz, 2000). In recent decades, the type and amount of air pollutants have been increasing due to increase in emission sources. There are about 400 gaseous pollutants in automobile exhaust alone (Godish, 1997). It is not feasible to measure all pollutants of the environment (Godish, 1997). Air pollution monitoring programs have to be chosen carefully according to the kinds of emission sources and pollutants. All the selected pollutants for current study, nitrogen dioxide ($NO_2$) and sulfur dioxide ($SO_2$) and ozone ($O_3$) are of major environmental concern. They are criteria pollutants and are very often included in air quality monitoring programs (EPA, 2010).

Nitrogen dioxide and sulfur dioxide are relatively toxic and their increased concentrations in the atmosphere are due to anthropogenic sources (Santis *et al*., 1997). They also act as precursor molecules for many atmospheric reactions including environmental acidification (Cox, 2003). Nitrogen oxides act as precursors to nitric acid in rainwater while $SO_2$ is a precursor to sulfuric acid. Such acidification processes can cause eutrophication, killing aquatic organisms, damage to the habitats and eroding of buildings (Cox, 2003, EEA, 2005).

Anthropogenic $SO_2$ is emitted by energy production plants, industrial combustion and industrial processes, particularly from roasted sulfide ores and combustion of sulfur containing fuels (Pandurangappa and Balasubramanian, 1996). It is the second most important pollutant of the atmosphere, next only to oxides of carbon in magnitude and severity of effects on a biological system.  It is capable of causing a wide variety of harmful effects both on plants and animals. The oxidizing power of dissolved sulfur dioxide affects electron transport system adversely in plant. It competes with carbon dioxide, retards photosynthesis and carbon assimilation. Plants exposed to this gas for long durations suffer from necrosis inter-venial chlorosis and damaged chloroplasts (Spence *et al.*, 1990, Zhu *et al*., 2001).

Sulfur dioxide is capable of causing thickening of mucous layer of trachea, hypertrophy goblet cells and mucous glands, bronchial constriction which results in a mark degree of resistance to flow of gases features resembling the pathology of chronic bronchitis. Hence, People with asthma, cardiovascular diseases, or chronic lung disease, both children and the elderly, are most sensitive to $SO_2$ pollution in the air. Presence of $SO_2$ at 500 ppm level in the air causes death in humans, however no harmful effects has been noted in case of laboratory animals at 5 ppm level (Manahan, 1999).

Anthropogenic $NO_2$ is produced mainly from combustion processes in vehicles and industry. Nitrogen dioxide together with nitric oxide, are formed simultaneously in combustion processes and other high temperature operations such as metallurgical furnaces, blast furnaces, plasma furnaces and kilns (DNR, 2010). Nitrogen oxides can also be released from nitric acid plants and other types of industrial processes involving in generation and/or use of nitric acid, microbial action on nitrogenous organic matter and on chemical fertilizers applied in agricultural fields. It has been estimated that about 70-80% of the total input of nitrogen oxide comes from natural sources and from the breakdown of solar flares and volcanic emissions (Manahan, 1999).

Nitrous oxide is reacted upon very slowly in the atmosphere, slower than the rate of the input and hence it has been accumulating in the atmosphere at a rate of about 0.3% per year (Ramanathan *et al*, 1985). Nitrous oxide is not very harmful to plants and animals but it gives rise to nitric oxide and nitrogen dioxide which are much more injurious. These gasses are responsible for the formation of peroxyacetyl nitrate (PAN) and peroxybenzonyl nitrate (PBN) and can cause acute irritation of eyes, including respiratory problems (Persinger *et al*., 2002; Pandey *et al*., 2008). Nitric oxide is responsible for depletion of the stratospheric ozone layer catalytically while nitrogen dioxide is an important constituent of the photochemical smog or oxidizing type of air pollution. It is also partially responsible for causing acid rains (Chestnet and Mills, 2005) that can lead to nutrient overload and deterioration of water quality (Bytnerowicz *et al*., 2007). Nitrogen oxides are responsible for environmental problems in a broad scale such as global warming, as they can travel very far from their origin in compliance with prevailing winds (Peace *et al*., 2004).

Recent epidemiological findings have, in fact, confirmed that urban NOx are directly or indirectly associated with adverse effects on the cardiovascular system and on the respiratory system of the local inhabitants (Maitre *et al*.., 2006). Furthermore, nitrogen dioxide is capable of causing pulmonary oedema at 5 ppm and pulmonary emphysema at concentration between 10 to 40 ppm level. The amount of nitrogen dioxide in ambient air rarely exceeds 0.1- 0.2 ppm and as such it does not cause much damage. But, the prolonged exposure to this concentration has been found to be associated with a number of diseases in human beings. Moreover, children are found to be more susceptible to the $NO_2$ exposures that lead to the asthma (Delfino *et al*., 2003; 2006). Leaf injury and retardation of growth have also been observed in some sensitive plants. Nitrogen dioxide can damage cotton materials, causes fading of dyes and paints and upon reacting with water forms nitric acid which has a strong corrosive action (Tucker, 2005).

Ozone is a secondary pollutant that forms photochemically (i.e. a reaction caused by solar radiation) in the lower atmosphere (troposphere) in the presence of nitrogen dioxides, volatile organic compounds (VOCs) and carbon monoxide (CO) (Koutrakis *et al.*, 1993; Sanz *et al.*, 2006; Caballero *et al.*, 2007). The emission rates of these precursor compounds are regulated in order to minimize the formation rate of ozone and the other photochemical reaction products (EPA, 2003). In ambient air, ozone is attributable also due to the intrusion of stratospheric ozone, especially in the spring when the stratospheric–tropospheric air exchange is greatest (Lippmann, 1989).

Ozone ($O_3$) is a colorless, odorless gas and is extremely reactive and toxic. Among various air pollutants, it plays an important role due to the characteristics of its occurrence and possible health effects (Lippmann, 1989). As an ambient air pollutant, ozone has become a subject of great interest because of its effects on both humans and plants (Monn and Hagartner, 1990). Exposure to ozone is associated with various respiratory symptoms including dyspnea, upper airway irritation, coughing and chest tightness (Chen *et al*, 2007). Since ozone initiate lung inflammation (Uysal and Schapira, 2003; Valavanidis *et al.*, 2009), such effects can be observed within first few hours after the start of the exposure, and may persist for many hours or days after the exposure ceases (Lee and Tsai, 2008). Besides the effects mentioned above, headache, asthma and tiredness have also been reported (Chan and Wu, 2005). Chronic exposure to ozone, on the other hand, will reduce lung function (Rastogi *et al.*, 1991; Tager *et al.*, 2005). An alteration of semen quality due to the exposure of ozone was also observed (Sokol *et al.*, 2006). The formation of ambient levels of ozone is highest during the summer months from May through September (Northern hemisphere). This is often termed ozone season (Caballero *et al.*, 2007). The intensity of sunlight necessary for the photochemically initiated reactions is highest during this time period.

Ozone can also form even in apparently clean rural environments. In these areas, the pollutants are apparently low levels of organic compounds emitted from trees and vegetation and low levels of nitrogen oxides emitted from natural biological activity. The photochemical reactions are similar to those in polluted urban areas; however, the concentrations of rural ozone are limited by the very low concentrations of nitrogen dioxides that are usually available. Rural ozone is considered natural. However, ambient concentrations in rural and forested areas can reach concentrations high enough to produce phytotoxic effects in native vegetation (Sanz *et al*., 2000; Innes *et al*., 2001; Ferretti *et al*., 2007) because ozone formation is favoured due to the intense solar radiation, high temperature and re-circulation of the polluted air masses (Millan *et al*., 1997, 2000; Sanz and Millan, 1998).

At high concentrations, ozone is very toxic. At moderate concentrations, ozone is associated with a variety of adverse health effects. Due to these characteristics, ozone is regulated as one of the criteria pollutants (EPA, 2003).

As an ambient air pollutant, its further effects involve oxidation of a number of macromolecules within a biological system and produces free radicals which have been implicated in a number of ozone induced pulmonary damages (Lee and Tsai, 2008). It has been suspected that these free radicals can damage DNA molecules and cause carcinogenesis. Ozone can crack and deteriorate rubber, damage textiles and other materials due to its strong oxidizing action. It is a deep lung irritant and when inhaled in large concentrations may cause pulmonary oedema leading to death of individuals (Asthama and Asthama, 2003).

## 1.2: Monitoring air quality

Air quality monitoring is perhaps the most important component in an air quality management system (Langgons, 2004). The data collected from monitors provide critical information needed to develop and implement air quality regulations and policies. It aims to achieve many broad objectives such as:

- Judge compliance with air quality objectives
- Determine trends in pollutant concentrations
- Identify source contributions to air pollution
- Development and evaluation of control strategies
- Development of air quality data for public information needs
- Exposure and health effects evaluation and research
- Atmospheric process characterization and verification of dispersion models
- Developing and evaluating air quality modeling tools

Air monitoring programs are often limited by the available resources; this is particularly true in developing countries like Nepal (Namiesnik *et al*., 2004). Among others, such as selecting parameters, number and location of monitoring points and frequency of sampling, the methods for monitoring plays vital role. In recent time, air monitoring methodologies can be divided into four main generic types, covering a wide range of costs and performance levels: active manual samplers, passive monitors, continuous analyzers and remote sensing devices. Each of these methodology types has advantages and disadvantages (Box 1). Brief description on each of these air monitoring methods are discussed below based upon documents Air quality monitoring training resource pack (Langgons, 2004).

Box 1: Air quality monitoring methods

### Active samplers

Advantages:

- Improved spatial monitoring
- Good for periodic studies, troubleshooting or complaint investigation
- Can be use to identify sites for permanent stations
- Simple to use
- Low initial cost but analysis costs can be high

Disadvantages:

- Can be labor intensive
- Not good for assessing short term variations and longer term trends

### Continuous analyzers

Advantages:

- Continuous data collection
- Easier to ensure adequate control
- Excellent for assessing short term, diurnal, seasonal and long term trends

Disadvantages:

- High initial cost
- Not portable
- Technically more complex than manual sampling

### Passive samplers

Advantages:

- Improved spatial monitoring
- Good for periodic studies, troubleshooting or complaint investigation
- Can be use to identify any sites for permanent stations
- Simple to use, required no power supply
- Low cost

Disadvantages:

- Can be labor intensive
- Not good for assessing short term variations and longer term trends

### Remote sensors

Advantages:

- Good for assessing impacts from emission sources
- Real time data

Disadvantages:

- Technically very complex
- Sample is integrated over the path length (several hundred metres)
- Affected by atmospheric conditions.

*(EPA, 2010; Langgons, 2004).*

### 1.2.1: Active samplers

Active samplers draw ambient air through a collecting medium for some specified time, typically 24 hours, with the volume of air being metered. The collecting medium is subsequently analyzed and the concentration of pollutant in the sampled air is determined. The active sampling methodologies offer reliable performance, with an extensive historical database because most of these methods have been in operation for many years. Active sampling methods require labor-intensive sample collection and analysis, and require laboratory analysis after the ambient air sample is collected. Figure 1.1 shows a high volume sampler as example of an active sampler monitoring ambient air.

Figure 1.1: High volume sampler (active sampler).

Manual sampling is event-specific, that is, the sampler usually operates over a fixed period of time accumulating and integrating sample. Integrating measurement methods, although fundamentally limited in their time resolution, are useful for the assessment of long-term exposure, as well as being invaluable for a variety of area-screening, mapping and network design functions. Manual sampling is still widely used world-wide because manual methods offer a wider variety of pollutant monitoring and can be relatively straightforward.

### Active gas sampling

In the past, active sampling of gaseous pollutants was typically carried out. This can be done by using wet absorption techniques, where sample air is introduced into a liquid reagent through impingers (figure 1.2). The pollutant is absorbed in the reagent and the reagent is then analyzed using various methods (usually some sort of chromatography) to determine the concentration of pollutant in the batch sample.

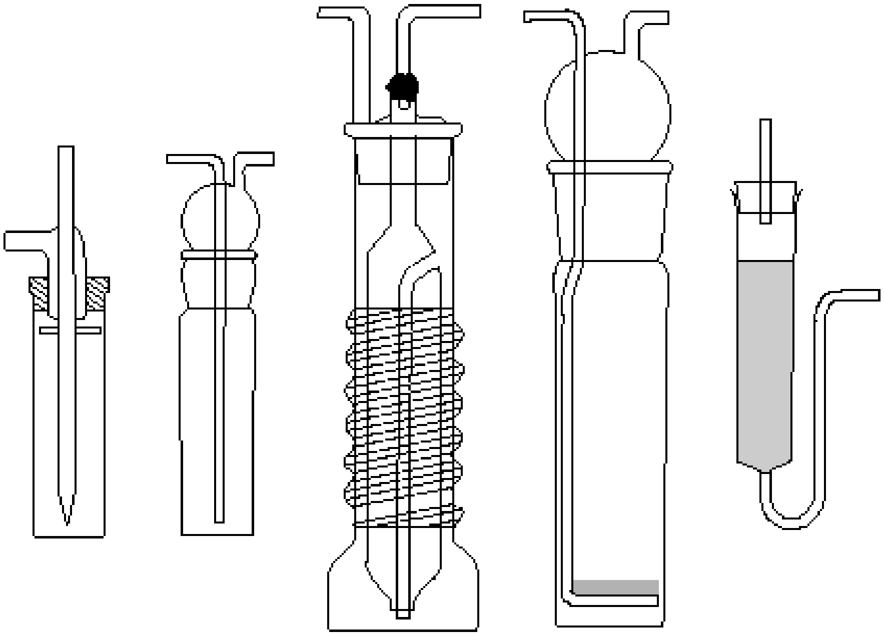


Figure 1.2: Gas absorption bottles or impringers (Environment Agency UK).

Another method of batch sampling is where sample air is drawn through a porous bed of solid adsorbent over a period of time. The pollutant is then extracted from the adsorbent and analyzed.

Collection efficiencies from this type of sampling apparatus can often exceed 90%.

### 1.2.2: Passive samplers

Passive samplers include items such as diffusion tubes and badges. They tend to be simple and low cost, and can be deployed in large numbers with no reliance on access to electrical connections. This type of sampler is useful for screening studies, for mapping, and for baseline studies. While the samplers are often used for monitoring $O_3$, NOx and $SO_2$, the technology is unproven for some pollutants. Passive samplers are labor-intensive for their deployment and analysis. Passive samplers generally provide only monthly or weekly averages.

Passive samplers are an excellent tool for saturation sampling. This involves the collection of many samples in a small, well-defined area over a short duration, to provide an in-depth characterization. Saturation sampling is typically conducted to gather data necessary to properly site long-term monitoring devices. Detail on this method discussed in coming sections.

### 1.2.3: Continuous analyzers

Continuous analyzers provide high resolution measurements (typically hourly averages or better) at a single point for most of the Criteria Pollutants ($SO_2$, $NO_2$, CO, and Suspended Particulate Matter) as well as for other important species such as volatile organic compounds. The sample is analyzed on-line and in real time, usually by electro-optic methods: UV or IR absorption, fluorescence, or chemiluminescence are common detection principles.

To ensure that data from continuous emission monitoring systems are accurate and reliable, a high standard of maintenance, operational and quality assurance and quality control procedures is invariably required. The advantages of continuous analyzer systems are that they offer a proven technology, high performance, hourly data, and/or on-line information. Disadvantages of continuous emission monitoring systems include the complexity and cost of the instrumentation, the requirement for a high level of skill in the operation of the instrumentation, and high recurrent costs.

### Continuous NOx analyzer

NOx is typically monitored using a chemiluminescent gas analyzer (Figure 1.3). Sample air is drawn through a molycon converter that converts $NO_2$ to NO. The sample air is then mixed with a defined concentration of ozone that is provided by an internal ozone generator. The chemiluminescent reaction between the NO and the Ozone is measured to obtain the NO concentration. The process is repeated without the sample air passing through the molycon converter. The difference in the measured concentrations can be calculated to determine the $NO_2$ concentration.

When using this method, care needs to be taken to ensure that the converter is working efficiently and the ozone generator is appropriately calibrated.

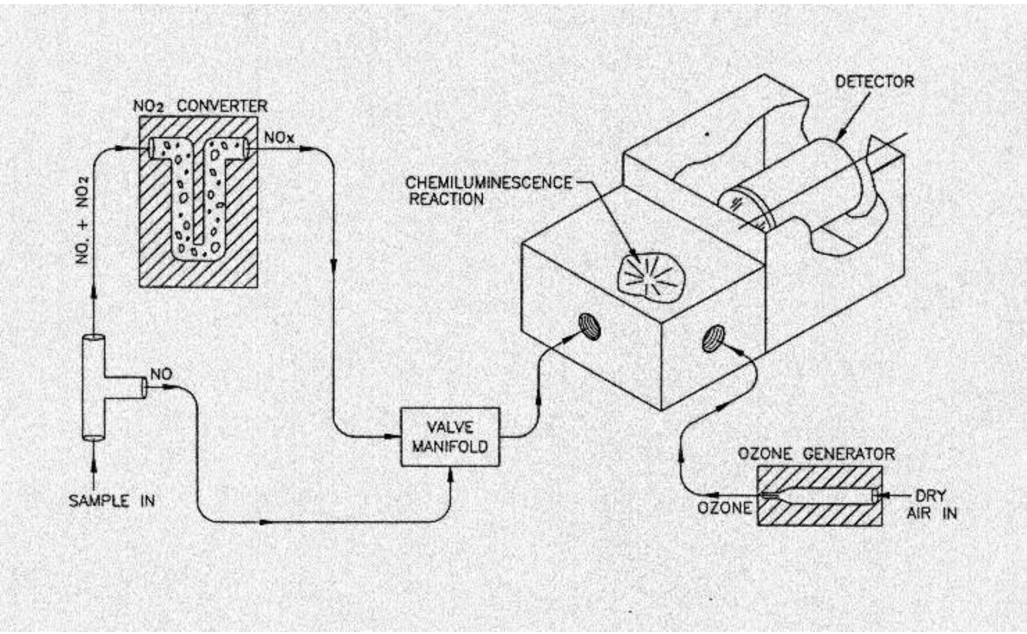


Figure1.3: Chemiluminescent gas analyzer for analyzing NOx

**Continuous $O_3$ analyzer**:

Ozone is typically measured using the UV absorption method. Sample air is drawn into an absorption cell. A mercury vapor lamp is used to emit UV light at 254 nm wavelength. In the measurement cell this UV light is absorbed by the sample. After absorption the intensity of UV light is measured.

Sample air is then drawn into the absorption cell again. However, this time this is being done after passing through an ozone scrubber. The ozone scrubber contains manganese dioxide which removes only ozone from the sample air. This scrubbed sample absorbs UV light in the measurement cell and the intensity of UV light is measured again.

Finally, the difference between the two intensity of UV light (absorption by non-scrubbed sample and absorption by scrubbed sample) is used to determine the ozone concentration. Figure 1.4 presents a typical Ozone analyser.

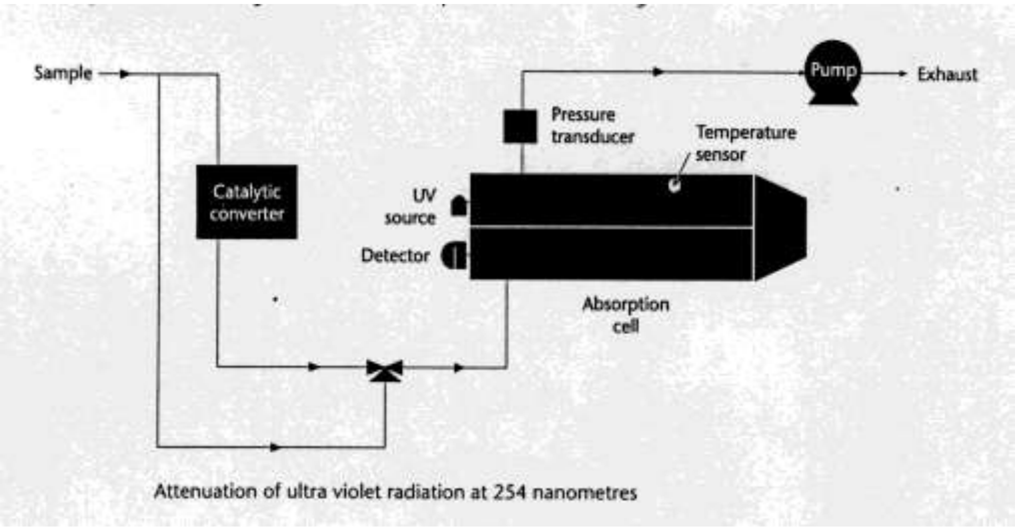


Figure 1.4: Ozone measurement using UV absorption method

**Continuous $SO_2$ analyzer**

$SO_2$ is typically measured using the UV fluorescence method. Sample air passes through a hydrocarbon scrubber which removes hydrocarbon from the sample. The sample then enters into the fluorescence cell. A zinc lamp is used as a UV source. This UV lamp supplies UV light of 214 nm wavelength which passes through an optical filter and enters in to the fluorescence cell. In the fluorescence cell $SO_2$ molecule absorb the UV light and become excited.

When the excited $SO_2$ molecule returns to the ground state it emits radiation. This radiation produces a small electric current which is detected by a Photo Multiplier Tube [PMT]. The intensity of this current is directly proportional to the concentration of $SO_2$. Figure 1.5 presents a typical $SO_2$ analyser.

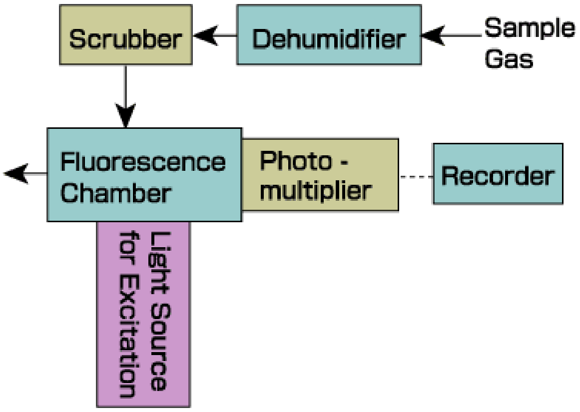


Figure 1.5: $SO_2$ measurement using UV Fluorescence method.

### 1.2.4 Remote sensors

Remote sensors have recently been developed. They use long-path spectroscopic techniques to make real-time concentration measurements of a range of pollutants. The data are obtained by integrating along a path between a light source and a detector. Long-path monitoring systems can have an important role in a number of monitoring situations, particularly in proximity to sources.

Remote sensing systems provide path or range-resolved data with multi-parameter measurements and are useful near emission sources. The remote sensing systems, however, are very complex and expensive, and are difficult to support, operate, calibrate, and validate.

Data from remote sensing systems are not readily comparable with point data, and the operation of the remote sensing systems is susceptible to problems due to atmospheric visibility and interferences.

Thus, the active sampling and automatic monitoring methods, despite having standard procedures and high accuracy, are expensive. The good data of ambient concentrations of pollutants are very important for controlling air pollution. The concentrations of air pollutants vary greatly from one location to another. Therefore, there is a need to measure the air pollutants in several locations for getting good data. It may not be feasible to have several sampling sites with these two methods because of the high cost. The passive sampling can provide a best alternative since it is cheaper and well suited to spatial coverage and can be used to identify "hot spots" in wide areas.

## 1.3: An introduction to passive samplers

The development and use of passive samplers originated in the field of occupational exposure monitoring (Kirby *et al*., 2000). In recent years, however, diffusion sampling techniques have been further developed and proven to be useful for ambient air quality monitoring (Seethapathi *et al*, 2008). Passive sampling method for monitoring of gaseous pollutants, such as $SO_{2,}$ $NO_2$ , and $O_3$, has been proven not only to be the technique of high resolution spatial monitoring, but also is light, cheap, robust, easy to operate, can be transported to other laboratories, stored for several weeks, and can be left unattended during sampling (Cadoff and Hadgeson, 1983; Cox, 2003). In addition on-site power and pumping of air are not needed as well (Krochmal and Kalina, 1997). Hence these samplers are low cost and could be a choice for developing countries like Nepal for air pollution monitoring, where active continuous air quality monitoring is a challenge due to high cost in terms of energy use, instrumentation and requirement of qualified man power.

Passive samplers are generally designed either in a tube-type configuration with one end open (so-called “Palmes tubes”); or in a shorter badge-type configuration, where the open end is protected by a membrane filter or other wind screen (Cox, 2003). In either case, the closed end contains an absorber for the gaseous species to be monitored. Several different types of commercial diffusion tubes are there in market in recent time. All of these samplers were developed basically from the above mentioned two types of diffusion tubes. Some of these are shown in figure. 1.6.

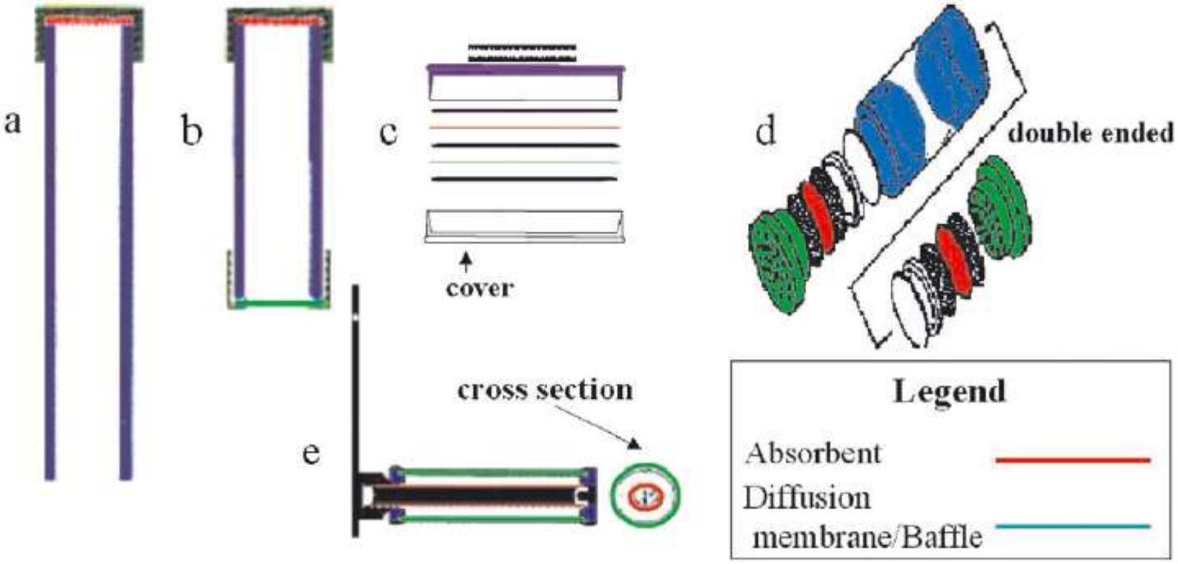


Figure 1.6: Examples of different types of commercial diffusion tubes of different sampler configurations: (a) open-ended diffusion tube, (b) shorter diffusion tube with diffusion membrane at opening, (c) badge-type with diffusion membrane at opening, (d) double-ended badge with baffles at opening, (e) cylindrical badge with tubular diffusion membrane. (Adapted from Cox, 2003)

Recent theoretical and experimental evaluations of diffusive samplers are considered to show that two important factors affect sampler performance (Harper and Purnell, 1987). First, the geometry of the device, principally the ratio of area to length, controls the uptake rate, the response-time and the effect of variations in the face velocity (Harper and Purnell, 1987). Second, the physical and chemical nature of the sorbent determines the efficiency of sampling and desorption and the magnitude of the effects of sample retention and interferences. Combined, these factors control the maximum permissible sampling range in terms of exposure time and concentration (Harper and Purnell, 1987). Careful considerations of geometry and sorbent enables selection of the most appropriate device for any situation.

## 1.4: Operational principle of passive samplers

The basic principle on which diffusion tube samplers operate is that of molecular diffusion, with molecules of a gas diffusing from a region of high concentration (open end of the sampler) to a region of low concentration (absorber end of the sampler) (Gair *et al.*,1991 and Palmes and Gunnison, 1973; Palmes et al, 1976). The movement of molecules of gas (1) through gas (2) is governed by Fick's first law, which states that the rate of diffusion, expressed as flux, is proportional to the concentration gradient:

$$F = -D\left(\frac{dc}{dx}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Where, F is the flux (mol $m^{-2}$ $s^{-1}$),

D is the diffusion constant ($m^{-2}$ $s^{-1}$),

(dc/dx) is the concentration gradient (mol $m^{-2}$ $s^{-1}$),

c is the concentration (mol $m^{-3}$) in the tube, and

x is a variable describing the length (m) of the tube.

The negative sign in the expression is placed simply to make F positive in case if the concentration gradient is negative.

On the basis of Fick's law the quantity (Q) of a particular gas transported from the surrounding air to the bottom of the tube is:

$$Q = F (\pi r^2) t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where, Q is in mol

t is the time of exposure (s)

r is the radius of the tube (m)

Putting value of F from equation 1 in equation 2,

$$Q = D\left(\frac{dc}{dx}\right)(\pi r^2)t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

Assuming uniform concentration gradient it can be expressed as:

$$\left(\frac{dc}{dx}\right) = \left(\frac{c_1 - c_0}{l}\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

Where, $c_1$ is the concentration (mol $m^{-3}$) in ambient air

$c_0$ is the concentration (mol $m^{-3}$) just above the absorber

l is the length of the tube (m)

Thus the number of moles of Pollutants ($NO_2$/ $SO_2$/ $O_3$) collected is:

$$Q = D\frac{c_1 - c_0}{l}(\pi r^2)t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(5)$$

Assuming the sorbent is 100% efficient and thus $c_0 = 0$, equation (5) becomes,

$$Q = D\frac{c_1}{l}(\pi r^2)t$$

or $$c_1 = \frac{Ql}{D(\pi r^2)t}$$

**NO$_2$**

The diffusion coefficient for $NO_2$ in ambient air is 1.54 x $10^{-5} m^2 s^{-1}$ .

Assuming the sorbent is 100% efficient and thus $c_0 = 0$, Palmes et al, 1976 expressed the concentration of $NO_2$ in ambient air with Q as the amount of $NO_2$ (µg) in the tube as:

$$c_1 = \frac{Ql}{1.54x10^{-5}(\pi r^2)t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(6)$$

= µg/$m^3$ of $NO_2$

(UNEP/WHO/GEMS/AIR, 1994; Shakya, 2004)

**$SO_2$**

The diffusion coefficient for $SO_2$ in ambient air is 1.27 X10 $^{-5}$m$^2$ s$^{-1}$.

Assuming the sorbent is 100% efficient and thus $c_0 = 0$, the concentration of $SO_2$ in ambient air is:

$$c_1 = \frac{Ql}{1.27x10^{-5}(\pi r^2)t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots. (7)$$

= µg/m$^3$ of $SO_2$

Here, Q is the amount of $SO_2$ (µg) which is obtained from $SO_4^{-2}$ (µg) in the tube by multiplying with 64/69. (UNEP/WHO/GEMS/AIR, 1994; Shakya, 2004)

**$O_3$**

The diffusion coefficient for $O_3$ in ambient air is 1.77 X10 $^{-5}$m$^2$ s$^{-1}$.

Assuming the sorbent is 100% efficient and thus $c_0 = 0$, the concentration of $O_3$ in ambient air is:

$$c_1 = \frac{Ql}{1.77x10^{-5}(\pi r^2)t} \quad \ldots\ldots\ldots\ldots\ldots\ldots. (8)$$

= µg/m$^3$ of $O_3$

Here, Q is the amount of $O_3$ (µg) which is obtained from $NO_3^-$ (µg) in the tube.

(Koutrakis *et al*., 1993; UNEP/WHO/GEMS/AIR, 1994)

## 1.5: Passive samplers for specific species

Different samplers are appropriate for different gaseous species. Table 1.1 shows the summery of passive samplers methodologies used for NOx, $SO_2$ and $O_3$. Passive samplers have also been developed for CO, and others; $NH_3$, $HNO_3$, $Cl_2$, formaldehyde and acetic acid, which have rather more specialist applications.

Table 1.1: Passive sampler methodologies for $NO_2$, $SO_2$ and $O_3$

| Pollutant | Reagent absorbant | Product of reaction | Analysis | Comments | References |
|---|---|---|---|---|---|
| $NO_2$ | Triethanolamine (TEA)<br>NaI + $Na_2CO_3$ | Nitrite | IC or Spectrophotometry | IC expensive and also measures sulphate | Palmes *et al.*,1976<br>Mulik *et al*.., 1989<br>Ferm, 1991 |
| $SO_2$ | TCM-West-Gaeke<br>TEA + glycol<br>KOH + glycerol<br>$Na_2CO_3$+ glycerine<br>TEA + $Na_2CO_3$ | Sulphite<br>Sulphite<br>Sulphate ($H_2O_2$ is added)<br>Sulphate | Spectrophotometry (Pararosaniline)<br>,,<br>Spectrophotometry (barium ions +DMSA)<br>IC<br>Thorine method after ion exchange | Disposal problems<br>IC preferable for analysis | Reiszner and West, 1973<br>Hangartner *et al*.., 1989<br>Hargreaves and Atkins, 1988<br>Ferm, 1991 |
| $O_3$ | 1,2,-di-(4-pyridyl)ethylene (DPE)<br>Indigocarmine<br>$NaNO_2$ + $Na_2CO_3$ + glycerine<br>KI (buffered to pH 9) | Aldehyde<br>Nitrate<br>I complex | Spectrophotometry<br>Reflectance<br>Spectrophotometry or IC<br>Spectrophotometry | Reaction light sensitive | Monn and Hangartner, 1990<br>Groslean and Hishan 1992<br>Koutrakis *et al*.. 1990, Mulik *et al*.,1989<br>Alexander *et al*.., 1991 |

### 1.5.1: Passive sampler for nitrogen dioxide

The most widely used passive sampler for nitrogen dioxide ($NO_2$) is a diffusion tube sampler using triethanolamine (TEA) as absorber, called Palmes-tube (Palmes *et al*, 1976). Such tubes have been used in a wide variety of large-scale urban and rural monitoring studies (Kirby *et al*., 2000; Krochmal and Kalina, 1997; Cox 2003; Bush *et al*., 2001; Glasius *et al*, 1999). Stainless steel mesh discs are coated with the absorber by either dipping into a solution of TEA and acetone before assembly of the tube or direct injection of a small quantity of this solution into assembled tube (Santis *et al*., 1997). Care must be taken to ensure that the procedure is undertaken in a clean atmosphere in order to ensure minimal contamination due to atmospheric $NO_2$. The open end of the tube is sealed and the tube stored prior to exposure.

After exposure, the tubes are analyzed by the addition of a solution of sulphanilamide in orthophosphoric acid and N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) solution, to form an azo dye, which is analyzed on a spectrophotometer at 540nm (Palmes *et al*, 1976, Atkins *et al*., 1986). The spectrophotometer is calibrated against standard nitrite solution, to allow the total $NO_2$ (as nitrite, $NO_2^-$) collected in the tube for determination.

$NO_2$ diffusion tubes have been shown to have a lower detection limit of about 200 ppb/h, which is adequate for urban area monitoring and to be unaffected by typical outdoor wind conditions and ambient temperatures (Atkins, *et al*., 1986). Good agreement has been found by Atkins and others between diffusion tubes and chemiluminescent monitors (Atkins, *et al*., 1986). However recent work conducted by Campbell *et al*. has shown a systematic difference between diffusion tube samplers and active monitors over a long period and a range of sites. The study suggests that diffusion tubes may cause overestimation of $NO_2$ concentrations (Campbell *et al.*, 1994). This looks consistent with a possible effect of wind turbulence on the tube but the cause of the discrepancy has, as yet, not been positively identified. Some practical solutions to these meteorological factors are suggested by Plaisance and colleagues on the basis of their study (Plaisance *et al*, 2002).

Diffusion tubes can be used for measurement in rural areas, where concentrations are much lower, but considerable care is required (Campbell, 1988). Increasing “blank” values with the storage of the tubes are reported (Gair *et al.*, 1991). For the most precise measurements, the storage period should be as short as possible, and that a freezer should be used. In addition it has been recommended that ion chromatography be used to increase the sensitivity of sample analysis for tubes exposed in very low concentration areas (Miller, 1984; Gair *et al*., 1991). The detection limit of ion chromatography is lower than that of the spectrophotometric analysis.

At the present time, there are at least five reasonably well developed badge-type passive sampling methods for determination of $NO_2$ in addition to the Palmes tube method: the Yanagisawa and Nishimura method (Yanagisawa and Nishimura, 1982), the modified Amaya-Sugira method (Amaya-Sugira, 1983; Krochmal and Gorski, 1991 a, b), the Cadoff and Hodgeson method (Cadoff and Hodgeson, 1983), the Lewis and Mulik method (Lewis *et al*., 1985; Mulik *et al.*,1989), and the Ferm method (Ferm, 1991). Badge-type samplers with a high sampling rate have, however, a lower detection limit than that of diffusion tubes.

### 1.5.2: Passive sampler for sulphur dioxide

Two absorbers have been utilized in Palmes type diffusion tubes for the determination of $SO_2$. Hargreaves and Atkins used mesh discs impregnated with potassium hydroxide (an absorbent for $SO_2$) and glycerol (a humifactant). Exposed tubes were analysed using di-methyl sulphanazo III (DMSA) to form blue barium DMSA complex which is estimated spectrophotometrically at 653 nm (Hargreaves and Atkins, 1988). Standard solutions of Sulphate in potassium hydroxide were used for calibration. The analytical technique is reported to be highly sensitive to pH and the presence of other ionic species and recommends that ion chromatography should be considered as an alternative. Validation of $SO_2$ diffusion tubes was not found to be entirely satisfactory.

Campbell *et al*., after detailed field and laboratory tests of measurements by $SO_2$ sampler without protecting membrane reported that the open tube samplers over-predicted relative to an ultraviolet fluorescence instrument (UVF) as a result of wind effect. Whereas membrane-protected tubes under-predicted relative to UVF for reasons which were not entirely understood (Campbell *et al*., 1992).

Hangartner *et al*. (1989) used $SO_2$ diffusion tubes of the same design as Hargreaves and Atkins (1988), but used a triethanolamine (TEA)/glycol mixture as the absorber and stabilizer for sulphite, and adopted the pararosaniline method of analysis (ISO 6767, 1990). The result of the $SO_2$ diffusion tubes with other measurements was again not good. Possible causes for this were cited as back-diffusion, humidity, and oxidation of sulphite.

Ferm described yet another method using badge-type sampler with carbonate impregnated filter to trap $SO_2$ and analyzed as sulphate using ion chromatography (Ferm *et al*., 1991, 1997, 1998).

### 1.5.3: Passive sampler for ozone

Monn and Hangartner developed a passive sampler for $O_3$ (Monn and Hangartner, 1990). The absorber used was 1,2-di-(4-pyridyl)-ethylene (DPE), which forms an aldehyde upon exposure to ozone (Hauser and Bradely, 1966). The aldehyde formed was determined spectrophotometrically with 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) at 442 nm. The formation of aldehyde by ozone is not stoichiometric and hence the samplers must be calibrated against an independent ozone monitoring technique. In addition, the reaction is light sensitive and Monn exposed the tubes inside a screen, which was carefully designed to eliminate light, yet allow a free flow of air to the sampler. The tubes were shown to be successful and correlated well with an UV absorption monitor. The samplers have been used for $O_3$ monitoring at altitude locations in Switzerland (Monn and Hangartner, 1990).

Detailed investigation of three samplers based on the Monn and Hangartner design confirmed the utility of the sampler in field measurements, with the proviso that it must first be calibrated in the field by comparison with continuous monitor (Campbell *et al.*, 1992). Further investigations are in progress using the palmes type tube and also with badge type samplers fitted with a protective membrane. Recent results are proven to be most encouraging.

A new sampler type, based on a colorant (indigo carmine), which fades on exposure to ozone, has also been reported (Grosjean and Hisam, 1992). This technique has the advantage that direct on-site measurements are possible, since the color change can be readily determined by on-the-spot reflectance measurements. The use of indigo paper as a basis for ozone passive samplers has been discussed in detail by Werner (Werner, 1992). In brief, several methods have been developed to determine ambient ozone by passive sampling using various sampling reagents, including 1,2-di-(4-pyridyl)ethylene (DPE) (Monn and Hagartner, 1990; Hangartner *et al.*, 1996), indigo carmine (Grosjean and Hisham, 1992; Hangartner *et al.*, 1996; Zhou and Smith, 1997; Lee and Tsai, 2008); potassium iodide (Hangartner *et al.*, 1996) and nitrite ion (Zhou and Smith, 1997; Lee and Tsai, 2008). However, there were drawbacks of the methods mentioned above. For example, the sampling time needed for currently used methods was relatively long due to the limited sensitivities, since either spectrophotometer or ion chromatography is used as the analytical instrument for most of the currently available ozone passive samplers. Besides, organic solvents were usually used for the sample desorption. This process is relatively time consuming.

## 1.6: Pros and cons of passive sampling

Despite the simplicity, possibility of easy handling and reliability of diffusion tubes passive samplers for air pollutants monitoring, they also have some limitations in determination of absolute concentrations. Passive samplers have relatively low sampling rates requiring long sampling times at low concentrations. This, however, favors estimation of only time-weighted average (TWA) concentrations of the analyte. The TWA concentration gives the long-term exposure action of the compound, which help the overall assessment of the pollutant impacts on human health (Zabiega *et al*. 2002), forest damage, agricultural crop damage, regional air quality and ecosystem studies (Grosjean and Hisham, 1992). Therefore passive samplers which offer a simple, cost-effective means of measuring air pollutants have been performed for the monitoring of ambient concentration levels worldwide (Chan and Wu, 2005; Sanz *et al.*., 2007; Grosjean and Hisham, 1992).

There is no standard method or validation for diffusion tubes. The results can be obtained only as average concentrations of the exposure period but short-term peaks are not obtainable. Some researchers have questioned about reliability of diffusion tubes (Cornwall air quality forum, 2000). The tube-type passive samplers have low diffusive transport rates, not allowing the resolution times lower than one week even in a moderately polluted environment (Santis *et al.*, 1997). A comparison of passive sampling with reference methods like active sampling sometimes indicate over or underestimation in passive sampling. The same studies also showed that these interferences could still be corrected with precautions to avoid the effects like turbulence, rainfall, direct sunlight, *etc*. The following review elaborates some studies on passive sampling including over or underestimation, and meteorological effects on passive samplers.

### 1.6.1: Overestimation by passive sampling

Campbell used Palmes diffusion tubes with triethanolamine as the absorbent to measure $NO_2$ concentrations (Campbell *et al.*, 1994). The mean ratio of $NO_2$ concentration obtained by diffusion tubes over a chemiluminescence monitor was found to be 1.26. In an experiment conducted in laboratory conditions, the shortening of diffusion paths by the wind-driven mixing of air in the mouth of the tube, was found to be responsible for this overestimation. To minimize this effect, a highly porous membrane was used to cover the mouth of the sampler. Gair and Penkett exposed diffusion tubes of varying length in the laboratory (indoor) and the university roof (outdoor) for measuring $NO_2$ (Gair and Penkett, 1995). The results gave a near-constant $NO_2$ concentration of 5 ppbv in laboratory exposure. A significant increase in $NO_2$ concentrations was observed with decreasing diffusion tube length indicating overestimation. In a repeated experiment, they attempted to prevent air being transported up the tube by exposing diffusion tubes with screens. There was no significant difference between $NO_2$ concentrations for each tube length after protection with a screen (Gair and Penkett, 1995). Thus, the previous reduction in diffusion length for unprotected samples was due to air turbulence.

The same authors also found a relationship between the reduction in molecular diffusion length and wind speed to be highly variable, showing the need for further research in this area. Heal and Cape measured $NO_2$ concentrations in urban and rural air by using passive diffusion samplers with triethanolamine (TEA) as absorbent (Heal and Cape, 1997). The interferences from peroxyacetyl nitrate (PAN) and others were observed to be small for British conditions. The systematic error of within-tube chemistry was also known to be responsible for overestimations of $NO_2$ by diffusion samplers, which was previously thought to be only due to the wind effects. They found passive sampling to be more efficient for measuring $NO_2$ concentrations in rural air compared to urban air. The combined error due to effect of wind on path length and chemical effects, within cities was found to cause up to 70% overestimation of $NO_2$ (30% chemistry, 30-40% tube length).

The results obtained by the use of passive diffusion sampling for the measurement of $SO_2$ and $NO_2$ in ambient air gave precision of 5-10% for $NO_2$ at ~15 ppbv and 10-25% for $SO_2$ in the range of 0.5-5 ppbv (Ayers *et al.*, 1998). Good agreement ($r^2>0.85$) was observed for $NO_2$ and $SO_2$ measurements between active and passive sampling. These good results were obtained with the use of teflon membrane screen, which served to suppress turbulent transport within the passive diffusion sampler body thus helping to reduce overestimation of gas mixing ratios. Their experiment also supported the results of Heal and Cape, which showed the increase in measured $NO_2$ mixing ratio with increasing tube length, up to about 30% increase at 70 mm tube length in summer (Heal and Cape, 1997). Heal *et al*. exposed acrylic, foil-wrapped, and quartz passive diffusion tubes (PDT) for four weeks concurrently with one week to measure $NO_2$ in urban air at three sites equipped with continuous analyzers. The comparison of the results with chemiluminescence analyzers showed an overestimation of 27% by standard acrylic PDT for one week exposure (Heal *et al*., 1999). They did not find any significant difference between standard and foil-wrapped acrylic tubes, while the mean ratio of 1.06 was observed between quartz tubes and chemiluminescence analyzers. They also obtained a decrease in net effective $NO_2$ uptake with exposure time showing lower $NO_2$ concentrations in four weeks of exposure compared to the average of one week parallel exposures. Good agreement and the overestimation of less than 10% were found between measurements of $NO_2$ with passive samplers and chemiluminescence (Glasius *et al*., 1999). They related their good results with the use of a mounting device.

### 1.6.2: Underestimation by passive sampling

Kasper-Giebel and Puxbaum using polyethylene tube as diffusion samplers and triethanolamine as an absorbent, found approximately 50% lower $NO_2$ concentrations than nearby chemiluminescence monitors (Kasper-Giebel and Puxbaum, 1998). The measurements by placing two grids into the diffusion tube had shown to correct the underestimation of $NO_2$ concentrations. They extracted the sampler with eluent and did not find any significant difference of this extraction procedure with routine extraction procedures. A strong interference in the determination of $SO_2$ was observed from wall deposition of $SO_4^{2-}$ aerosols in both polyethylene and acrylic tubes. They recommended equipping diffusion tubes with windshield, or badge-samplers to overcome these interferences from $SO_4^{2-}$- aerosols. Santis *et al.* found underestimation of $NO_2$ measurements by Palmes diffusion tubes in comparison to chemiluminescence monitor. (Santis *et al.*, 2003). They related the problems of underestimation with photo degradation of $NO_2$-TEA adduct and incomplete extraction of nitrite. To reduce errors, they recommended the careful extraction procedure, the use of a stainless steel mesh at the entrance of the tube and the use of non- transparent plastic.

## 1.7: Problem statement

Air pollution is a growing threat to health throughout the world. Nepal is no exception. The high pace of urbanization together with the rise in numbers of vehicles posed a tremendous increase in air pollution at the urban centers of Nepal, especially Kathmandu Valley.

Currently, Kathmandu, the capital city of Nepal, is a rapidly growing urban center. The population growth rate percentage in the valley has increased from 4.2 to 4.7% during the period from 1991 to 2011 (CIA, 2011). Each year more than 13,000 vehicles are added into already growing volume of traffic in Kathmandu valley (ITDG, 2002). There was addition of 38803 vehicles in 2006/07 alone (DoTM, 2006/07). The figure has changed to around 55000 registered vehicles for 2011, (DoTM, 2010/2011). These vehicles are responsible for the emission of complex mixture of gaseous; carbon monoxides (CO), oxides of nitrogen (NOx), oxides of sulfur ($SO_2$), hydrocarbons, lead and other solid pollutants.  These pollutants reduce the quality of air we breathe by limiting the availability of oxygen. Besides, city dwellers are forced to breathe in substances that are harmful to lungs. The consequences are the acute effects such as irritation of eyes, nose, throat, headache, difficulty in breathing followed by chronic effects like; emphysema, bronchitis, chronic cough and asthma. Children are most prone to pollution related affliction as they have underdeveloped biological defense mechanism. The elderly people are also affected due to the enhancement of preexisting respiratory diseases (Gold *et al.*, 1999). Several studies showed the rise in respiratory diseases in Katmandu (State of environment 2001; ITDG, 2002; KVEO, 2007).

Wide spread and effective air quality monitoring programs are very essential to develop air quality management plans and to have better control plans for air pollution in order to reduce risks from it (Langgons, 2004). However, Monitoring of air quality in cities of the third world is a formidable challenge owing to the high cost of automated monitoring equipment. With the establishment of six Ambient Air Quality Monitoring stations at different locations of Kathmandu valley in 2002, MOPE under a DANIDA supported project ESPS/MOPE started to gather the air pollution data. Since then TSP, $PM_{10}$, $NO_2$, $SO_2$, CO, Benzene are being monitored. The National threshold limits for these pollutants also being enacted as NAAQS by government of Nepal (Appendix IX). According to the latest monitoring result, TSP, $PM_{10}$ and $PM_{2.5}$ exceeded the NAAQS value except in monsoon season while NOx, $SO_2$, CO, HCs were higher in roadside stations than the NAAQS for the Kathmandu valley (MOPE, 2003/4). However, due to power failure and other constraints these monitoring stations were continuously disturbed. Furthermore, the monitoring data have not yet been precisely used in assessment and air quality management planning within the country.

Several other urban cities of the country as, Birgunj, Biratnagar etc are also experiencing higher air pollution level with increasing number of vehicles and industries. The TSP level at Birgunj and Pokhara were also found to exceed the NAAQS (NHRC, 2004). Apart from this, the studies of air pollution data for these cities are almost nonexistent. This indicates the need for ambient air quality monitoring system in these cities as well. The simple low cost method for monitoring is always choice- of- priority for Nepal like any other developing countries. Passive sampling method for monitoring of $SO_2$ and $NO_2$ has been proven to be the technique of high resolution spatial monitoring, which can yield better information about the distribution of air born pollutants over an urban territory (Carmichael *et al.*, 2003).

Passive sampling has many advantages. The equipment is light, cheap, robust and easy to operate. It can be transported to other laboratories, stored for several weeks, and can be left unattended during sampling (Krochmal and Kalina, 1997). They are small, soundless and reusable. On-site power and pumping of air are not needed. Moreover, most passive sampling techniques require little or no solvents, and they have simple sample pretreatment, thus supporting so-called "green analytical chemistry" (Gorecki and Namiesnik, 2002). It is very appropriate for large scale monitoring. These benefits favor air quality monitoring by passive sampling to have sufficient number of sampling sites. In other words, the use of passive sampling can save money, energy, labor, and is also less hazardous to environment. Despite having many advantages, passive sampling technique has still not been used in routine analysis. Very few works have been carried out in developing countries, which could have taken more benefit from this technique. This study is one of such attempts to develop and use the locally available tubes as passive sample for sampling ambient $NO_2$, $SO_2$ and $O_3$. In this regard, hardly any studies have previously been attempted in Nepal.

Additionally, all the three selected pollutants are the ubiquitous pollutants found in the ambient air which exhibit documented adverse effects on health and welfare. $NO_2$ and $SO_2$ are primary pollutants while $O_3$ is a secondary pollutant. Though all of these criteria pollutants are well below the NAAQS value, they are in increasing- trend in recent time for the valley. This study examines the spatial distribution of $NO_2$, $SO_2$ and $O_3$ as well.

## 1.8: Research objectives

The overarching goal of this work was to find the affordable low cost passive samplers logistically feasible and technically suitable to use for ambient $NO_2$, $SO_2$ and $O_3$ monitoring in Kathmandu valley in other to create self sustainable monitoring unit of longer life-span.

To accomplish this goal, locally available polyethylene tubes were developed as diffusion tubes for ambient passive sampling. These tools were then applied to assess the spatial variability in $NO_2$, $SO_2$ and $O_3$ across the Kathmandu valley. This work was divided into the following objectives.

The main objectives of this research project are to:

1. Develop a low cost locally available diffusion tubes for passive sampling analysis of $NO_2$, $SO_2$ and $O_3$.

2. Use the developed passive sampling diffusion tubes for the assessment of $NO_2$, $SO_2$ and $O_3$ concentrations in ambient air of Kathmandu valley.

3. Produce spatial concentration maps of the pollutants $NO_2$, $SO_2$ and $O_3$ from intensive passive monitoring in Kathmandu.

# Chapter 2: Literature review

## 2.1: Passive sampling methodologies

A passive sampler for gaseous species is defined as a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static layer or permeation through a membrane, but which does not involve the active movement of air through the sampler (Brown *et al.*, 1981). The older generation passive sampling methods, like lead peroxide candle method, Liesegang methods or Fukui method, employed absorbing surfaces exposed directly to the air without a diffusion path (Kristensson, 2009). The results of such measurements were strongly dependent on meteorological conditions. The modern concept of passive sampling was developed independently by Palmes and Gunnison (diffusion type) and Reiszner and West (permeation/diffusion type) in 1973 (Palmes and Gunnison, 1973; Reiszner and West, 1973). Table 2.1 list review of different development stages of passive sampling devices and application.

## 2.2: Air quality surveys with passive samplers

### 2.2.1: An area- comparability study using passive samplers

Campbell *et al.*, 1994 describe a national study of $NO_2$ undertaken by the Warren Spring Laboratory, throughout the UK. This study has repeated a similar study undertaken in 1986 (Bower *et al.*, 1991a). These studies provided a coherent and comprehensive set of measurements enabling the UK cities to be ranked in terms of $NO_2$ concentrations. The diffusion tube dataset allowed cities with the highest $NO_2$ concentrations to be readily selected for compliance monitoring with respect to the Directive (Bower *et al.*, 1991a).

## Table 2.1: Review of stages in development of passive sampling devices

| No | Author/s | Publication year | Emphasis | Reference |
|---|---|---|---|---|
| 1 | Gordon and Lowe | 1853 | First use of passive exposure for ozone | Namie´snik *et al*, 2004 |
| 2 | | 1927 | U.S. patent of a diffusive sampler for CO. | Kristensson, 2009 |
| 3 | Plantz *et al*. | 1968 | Diffusive sampler for hydrazine. | ‘’ |
| 4 | Palmes | 1973 | Exposure monitoring of gaseous contaminant | Palmes and Gunnison |
| | ,, | 1976 | Personal sampler for Nitrogen dioxide | ,, |
| 5 | Tompkins and Goldsmith | 1977 | Gasbadge sampler for organic compounds using activated charcoal. | Ferm, M, 1979 |
| 7 | Ferm M | 1979 | Ferm dosimeter, Badge passive samplers | |
| 8 | Saunders | 1981 | Workplace exposure measurements | Saunders,1981 |
| 9 | Fowler | 1981 | Theory and fundamentals of passive vapor sampling applied to both permeation through membrane and diffusion through static air. Also discussed the effects of temperature, pressure, face velocity and sampler response time | Fower,1982 |
| 10 | Rose and Perkins | 1982 | State-of-the-art of the technology, practical aspects and various commercially available passive samplers at the time | Perkin,1982 |
| 11 | Namie´snik *et al*. | 1984 | Quantitative and statistical aspects of commercially available passive samplers applied to inorganic and organic gases and vapors | Namie´snik *et al*.,1984 |
| 12 | Harper and Purnell | 1987 | Theory and practical evaluation of the performance of diffusive samplers with the emphasis on the geometry and sorbent efficiency | Harper and Purnell, 1987 |
| 13 | Berlin, Brown and Saunders | 1987 | Collection of articles presented at international symposium on diffusive sampling in workplace air monitoring | Berlin, 1987 |
| 14 | Brown | 1993 | Technical report on the use of diffusive sampling for monitoring ambient air | Brown. 1993 |
| 15 | Levin and Lindahl | 1994 | Application of diffusive sampling for reactive compounds | Levin and Lindahl, 1994 |
| 16 | Kozdro´n-Zabiegała *et al*. | 1995 | Application of passive samplers for indoor and outdoor air applied to volatile organic compounds | Kozdro´n-Zabiegała *et al*., 1995 |
| 17 | Ferm M. and Rodhe H., | 1997 | Badge type diffusive samplers for $SO_2$, $NO_2$ and $NH_3$ | Ferm M. and Rodhe H., 1997 |
| 18 | Ferm M. and Svanberg | 1998 | | |
| 19 | Brown | 1999 | Environmental factors affecting the performance of passive samplers in ambient air, and European Union initiatives towards standardization | Brown,1999 |
| 20 | Kot *et al*. | 2000 | Long-term monitoring of environmental pollutants in environments using passive samplers | Kot *et al*., 2000 |
| 21 | Lu *et al*. | 2000 | Background and applications of semi permeable membrane devices | Lu *et al*., 2000 |
| 22 | G´orecki and Namie´snik | 2002 | Application of passive samplers in air, water and soil analysis, as well as bio-monitoring | G´orecki and Namie´snik, 2002 |
| 23 | Cox | 2003 | Equilibrium passive sampling devices | Cox, 2003<br>Mayer, 2003 |
| 24 | Mayer | 2003 | | Ferm *et al* l., 2005 |
| 25 | Ferm *et al* | 2005 | Application of Passive samplers for nitric acid in study of corrosion | |
| | | 2006 | Application of Passive samplers for PM in corrosion studies | Ferm *et al* 2006 |
| | Ferm *et al* | | | |
| 26 | | | | |
| 27 | Namie´snik *et al*. | 2005 | Passive sampling techniques for environmental analysis with special emphasis on solid-phase microextraction devices | Namie´snik *et al*. , 2005 |
| 28 | Partyka *et al*. | 2007 | Monitoring organic constituents in air with emphasis on analytical methods required for the release and quantification of the analytes from the sorption media | Partyka *et al*. , 2007 |
| 29 | Mills *et al*. | 2007 | Application of passive samplers for the monitoring of pharmaceutical and personal care products in the environment | Mills *et al*., 2007 |

Over 400 sites were included in 1986 and as many as possible sites from them are included again in 1991. The result indicated very similar spatial distribution of $NO_2$ in these two years, but concentrations were significantly higher in 1991. This was consistent with the overall estimated increase in emission of oxides of nitrogen from motor vehicles in the UK over the intervening period.

These studies demonstrate the feasibility of running large scale monitoring studies over wide geographical area by posting diffusion tubes to local operators for exposure, and returning to a central laboratory for analysis and collation of results. This approach enables large-scale survey of $NO_2$ to be implemented in a very cost effective and efficient manner. The success of these studies has resulted in a long-term 1200 site $NO_2$ survey of the UK being initiated in 1993.

Recent investigations have shown that even though the diffusion tubes provide integrated average concentrations over one month, it may also be possible to use the results to obtain estimates of exceedences of short-term air quality guidelines. These are estimated using appropriate scaling factors derived from a longer-term database (Carless *et al.*, 1994). The factors derives are applicable to the UK, but may also be useful in other parts of the world.

### 2.2.2: An area-intensive study using passive samplers

An Area-Intensive Study for spatial distribution of $NO_2$ concentration using Passive samplers has been carried out in and around Gatwick Airport. Annual average concentrations were interpolated between sites by a computer package to produce a counter plot of $NO_2$ concentrations throughout the study area and showed the highest concentrations observed close to the central terminal area (GEMS/AIR, 1994).

Similar area- intensive study using Badge-type samplers have been carried out in the centre of Cracow city, Poland. A network of 120 measuring points was established over an area of 12 $km^2$. The modified Amaya-Sugiura method (Amaya and Sugiura, 1983; Krochmal and Gorski, 1991a.b) was used to carry out 24 hour measurements of $NO_2$ concentrations. Three projects, each of one year were performed between 1983 and 1990. About 150 maps of spatial distribution of $NO_2$ concentrations were plotted. By combining this information with meteorological data it was possible to identify major sources of $NO_2$ in the area. It was reported that during summer season the $NO_2$ distribution pattern was similar to the layout of the main traffic routes, whereas in winter the main source of $NO_2$ pollution was domestic heating systems.

Similar studies were performed in several other cities in southern Poland. One of such studies was carried out in the Tatra mountains and adjacent city, Zakopane, to investigate the effect of city air pollution on the quality of air in the National Park. Weekly determinations of $NO_2$ in the National park were below 5ppb, indicating that for $NO_2$, city air pollution had no significant effect on the quality of the mountain air.

### 2.2.3: Studies of background levels at different locations using passive samplers

The Swedish Environmental Research Institute used passive samplers in a six month survey of the geographic distribution of $NO_2$ and $SO_2$ in background areas surrounding Swedish cities (IVL, 1992). The results showed a high correlation between increasing latitude and decreasing concentrations of $NO_2$ and $SO_2$. It was concluded that long range transport makes a substantial contribution to average $NO_2$ and $SO_2$ concentrations in southern Swedish cities.

Ferm reported the investigation for the repeatability of the techniques under different geographic and cultural conditions from the similar Swedish diffusion tube samplers for $NO_2$, $SO_2$ and $NH_3$. One year period survey was carried out at urban sites of China and at sites in Southeast Asia to represent regional background. Accordingly, the best results were obtained with the $SO_2$ samplers. Repeatability was very good in the whole concentration range (0.1-76 ppb). The average relative standard deviation for all measurements was 7.7% (Ferm, 1992).

Problems were encountered with $NO_2$ samplers. Initially, $NO_2$ values were abnormally low. It seemed that the reagent was being consumed by ozone, present at higher levels than in Sweden where the samplers were developed. The problem was resolved by improving the formula for the impregnation solution. The new samplers were found to have high repeatability in an acceptable range of concentration.

The initial value for reproducibility of the ammonia samplers was also poor (SD 31.1%). Evaporation of ammonia from particles deposited on the wind screen, followed by absorption by the sampler, was identified as a possible cause of the problem. A change in protocol requiring the wind screen to be replaced with a solid lid before mailing improved repeatability considerably (to SD 15.4%, concentration range 0.07 to 37 ppb).

The results indicated the importance of evaluating passive samplers under different climatic, geographic and cultural conditions before they are used in wide-scale surveys. Minor adjustments to the sampler or the handling protocol might be necessary when conditions differ from those under which the sampler was initially tested. The samplers were being tested under a wide range of conditions in 11 different countries: Bangladesh, China, Hong Kong, India, Indonesia, Korea, Malaysia, Nepal, Taiwan, Thailand, and

Vietnam. The samplers were provided from Sweden and analyze in IVL (Carmichael *et al.*, 2003).

### 2.2.4: Inter comparison of passive samplers in Alps

In 1992, the ARGE Alp (Association of Alpine Countries) performed a six month inter comparison of passive samplers for ozone and $NO_2$ at six different sites in the Alps (Kirchner *et al.*, 1994). The study was part of a long-term project on the presence and effects of photo oxidants, in particular ozone, in the alpine region. The primary aim was to identify a method which could be used to measure vertical distribution profiles of ozone at a range of mountain locations. Different passive samplers for $NO_2$ were inter compared at the same time. The study was co-ordinated by the GSF Research Centre for Environment and Health, Neuherberg/ Munich, Germany. Five alpine sites were chosen at different heights, together with one heavily polluted urban site for comparison. All sites have continuous analysers operating. A total of 16 different passive samplers from 10 organizations in Germany, Austria, Italy, Switzerland and the UK were exposed in parallel, and exchanged at intervals of one or two weeks (depending upon sampler specifications) throughout the test period. Samplers were returned to the organizations from which they came for analysis. The results from the different sampler measurements were compared with the results from the continuous analyzers.

The measured values of the majority of the ten samplers tested for $NO_2$ showed significant correlation coefficients with the corresponding averages from the continuous analyzers when compared across all six sites (>0.9), although measurements at the two high altitude stations, with very low concentrations of $NO_2$, showed only a poor correlation. The differences between samplers based on similar principles were small.

Although at low concentrations of $NO_2$ the samplers could not replace measurements with continuous analyzers, they did provide a good indication of $NO_2$ concentrations and could usefully be employed in a variety of studies.

Of the six ozone samplers tested, two (a diffusion tube exposed for one week and an indigo paper sampler exposed for two weeks) showed a significant correlation coefficient (>0.8) with the values measured by the continuous analyzers. The results indicate that meteorological factors should also be taken into account when interpreting the results from the ozone passive samplers. Although, the samplers could not be used to measure precise ozone concentrations, they did provide a useful indication of trends over time and could be recommended for certain studies at the mountain sites.

In the second phase of this study, the two ozone samplers selected on the basis of the results of the inter comparison test were used to investigate the vertical distribution profiles of ozone in different areas within the Alps.

## 2.3: Other studies in passive sampling

Krochmal and Kalina used a badge-type passive sampler with Whatman 1 Chr filter paper impregnated with 0.1 ml of 20% (m/m) TEA aqueous solution to collect $NO_2$ and $SO_2$ in ambient air (Krochmal and Kalina, 1997). They found suppressed ion chromatography to have a lower determination limit of 0.08 µg /ml compared to 0.4 µg/ml of $SO_4^{2-}$ (Krochmal and Kalina, 1997). Good agreement was observed between passive sampling and automated methods. They got a precision of 6% for $NO_2$ determination and 14% for $SO_2$ determination at concentrations above 20 µg for one month exposures (Krochmal and Kalina, 1997). The results from their experiment didn't show any significant difference between samplers stored at $-10^0$C, $0^0$C and $20^0$C. The results obtained from measurements of $NO_2$ and $SO_2$ in background and urban air showed a difference of 15% between passive and active sampling techniques (Ferm and Svanberg, 1998). They also concluded that the design of the sampler can be changed to fit the requirements in passive sampling. They observed the losses of $NO_2^-$ with the use of TEA as absorbent for more than one month exposure and later used a mixture of potassium iodide and sodium arsenite as absorbents.

Brown mentioned the importance of choosing a sorbent with high sorption capacity and low vapor pressure of the sorbed material (Brown, 2000). He also mentioned about the effects of several environmental factors like temperature and pressure, humidity, transients, and air velocity. High humidity can alter the sorption behavior of the exposed inner wall of diffusion tubes. The low air velocity and high speed has minimal effect on tube type samplers if protected with a draught shield. Bush *et al*. exposed diffusion tubes at 17 urban background monitoring sites equipped with chemiluminescence $NO_2$ monitors for one year (Bush *et al*., 2001). The differences between the diffusion tube and chemiluminescence measurements were found to be within 10%. They also observed the reduction of uncertainty on the average difference from + 24 to 38% for individual diffusion tube measurements to + 10 to 18% for annual averages. Plaisance *et al*. evaluated the performances and application of tube type sampler to determine $NO_2$ and $SO_2$ in ambient air (Plaisance *et al*., 2002). They found a relative standard deviation of 5% for $NO_2$ and 12% for $SO_2$ when gases were collected using TEA as absorbent and extraction from tubes were analyzed by ion chromatography. Comparison of passive samplers with continuous monitor data for $NO_2$ and $SO_2$ showed high degrees of linearity (>0.8). They also obtained an increase in correlation coefficient for the diffusion tubes with a protective device showing a decrease of wind velocity effects on the diffusion tubes.

## 2.4: Status of air pollution in the Kathmandu valley

### 2.4.1: Air pollution studies in Nepal

Numerous theoretical and empirical studies on ambient air quality were existed in sporadic form. Significant of them are from ENPHO,1993; RONAST, Sharma et al., 1992; Devkota, 1993; Sharma, 1997; Otaki et al., 1995; NESS,1999; KVVECP, 1993; Leaders, 1998, ADB-URBAIR, 1999). Almost all of these studies were done for Kathmandu valley using active sampling methods (Appendix i: The list of the air pollution studies in Nepal).

MOPE/ ESPS had been monitoring the ambient air quality in Kathmandu valley from six permanent monitoring stations: Putalisadak and Patan hospital (road side stations), Thamel (Residence area), Kirtipur and Bhaktapur (valley background), Matshya gaon (control site) since September, 2002. The stations had been set up according to the campaign monitoring results from the organization carried out during 2001.The parameters being monitoring from mentioned six permanents stations are TSP, $PM_{10}$, $NO_2$, $SO_2$, CO, and Benzene following the method as described in table 2.2.

Accordingly, the total suspended particles and $PM_{10}$ values observed at different sample sites in the valley were found to be higher than the WHO guideline values (TSP- 120 $\mu g/m^3$ and $PM_{10}$-70 for 8 hours) at all except residential and control sites (SOE, 2001). The other pollutants, $SO_2$, NOx, HCs, were below the WHO guideline values. The highest value for TSP occurred during April/May, where as lowest were in July (DHM, 1999). Similar trend was observed for following years, 200-2004, but larger amount

(Gautam, 2004.). However the exceed in the concentration level greater than NAQG threshold limits for $NO_2$ and $SO_2$ values at several incidences especially during dry season at road side stations has been frequently reported (Gautam, 2004; MOE, 2006, 2007). Ozone has monitored only in campaign basis.

Table 2.2: Description of the parameters monitoring by MOPE

| Parameter | Method | Frequency |
|---|---|---|
| TSP | Active | 24 hr average once a week in two road side stations |
| $PM_{10}$ | Active | 24 hr average continuous in all stations |
| PM2.5 | Active | 24 hr average campaign basis |
| $NO_2$ | Passive | Weekly average continuous in all stations |
| $SO_2$ | Passive | Campaign basis in all stations |
| CO | Passive | Campaign basis in roadside stations |
| Benzene | Passive | Weekly average continuous in all stations |
| PAH | Passive | Campaign basis in all stations |

*Source: Gautam, 2004.*

Sporadic studies carried out at different times predict the ozone pollution existed in the valley with average annual concentration ranges between 40- 60 ppb (Neupane, 1994; Dhakal, 2001; Carmichal *et al*., 2003, Pudasainee. 2004, Pandey, 2006; Neupane, 2006) Studies on diurnal variation of ozone during days indicated high ozone- concentration during several incidences with respect to 8hr WHO standard guidelines (Pudasainee *et al*., 2010, Pandey, 2006; Neupane, 2006)

### 2.4.2: Use of passive samplings in Nepal

Very few ambient air pollution studies had been carried out in Nepal. Out of which, almost all of these studies had been done for Kathmandu valley using active sampling methods. First detailed air quality study of Kathmandu valley was carried out by the World Bank in 1997 under URBAIR (Urban Air Quality Management Strategy in Asia). The report was based on 1993 data taking the revision and utilization of following data sources:

- Surendra Raj Devkota (1992) “Energy Utilization and Air Pollution in Kathmandu Valley”, MS Thesis, Asian Institute of Technology, Bangkok.
- “Study of Kathmandu Valley Urban Road Development” by Japan International Cooperation Agency (JICA, 1992).
- Ram Manohar Shrestha and Sunil Malla (1993) “Energy Use and Emission of Air Pollutants: Case of Kathmandu Valley”, Asian Institute of Technology, Bangkok.
- H.B. Mathur (1993) Final Report on the “Kathmandu Valley Vehicular Emission Control Project” (Mathur-KVVECP), HMG/UNDP.
- Nepal Environmental and Scientific Services- NESS (1995) “Assessment of the Applicability of Indian Cleaner Technology for Small Scale Brick Kiln Industries of Kathmandu Valley”, Thapathali, Kathmandu.

The report focused on the development of an air quality management system for Kathmandu Valley and the resulting action plan.

This study reported the growth in population for Kathmandu valley by 26% from 1970-1980 and another 44% between1980-1990, while in 1992 out of total population of

1,060,000, 56% was urban. Increase in vehicles, brick industries and the Himal cement factory were reported to be the major sources of air pollution. The report also cited the increase in consumption of coal and automotive fuel.

Substantial decrease in visibility in the valley was depicted. The number of days with good visibility (greater than 8,000 meters) around noon had decreased in the winter months from more than 25 days per month in the 1970s to about 5 days per month in 1992/93. Air pollution measurements showed that particulate pollution was the most significant problem in Kathmandu valley. Total TSP emissions per year amounted to 16,500 tons and that of PM emissions were 4,700 tons/year. WHO air quality guidelines (AQG) for TSP and PM were often substantially exceeded. The study reported that the total impact in health in monetary terms was worth about NRs 200,000 million.

ESPS update in 2001 based on the same emission factors as URBAIR study and found substantial increase TSP and PM concentrations with the increase in both mobile and stationary sources of air pollution in the valley. TSP increased from 16575 tons (URBAIR, 1997) to 19884 tons (ESPS, 2001) and PM 4712 tons (URBAIR, 1997) to 7580 tons. More significant increase in pollution had been reported due to mobile sources, which accounted increase from 2100 tons (URBAIR, 1997) to 8979 tons (ESPS, 2001) and 970 tons (URBAIR, 1997) to 5081 tons (ESPS, 2001) for TSP and PM respectively (Gautam, 2004).

The continual trend in increase of TSP and PM has been reported for following years, 2002, 2003 and 2004. 2005, 2006 and 2007, amount of $NO_2$ exceeded at the Annual National Ambient Air Quality Standard values (NAAQS) at heavy Traffic area. $SO_2$ was reported at residential area. Amount of $SO_2$ in Patan and Bhaktapur area during

Feb/March (dry season) exceeded the Annual National Ambient Air Quality Standard values (Gautam, 2004, MOE, 2008).

The ambient ozone in the Kathmandu valley became a matter of serious concern in recent past due to the typical physiographic characteristic together with the anthropogenic activities especially in the increase in total VOC emission which is estimated of 73,009 tons for the year 2003 (Shrestha, 2004). Few ground level ozone monitoring studies were existed for Kathmandu and they were carried out for short term and in sporadic form.

As mentioned earlier most of the studies for air pollutants were carried out by using active sampling method. Monitoring of NOx, $SO_2$ and $O_3$ concentrations in Kathmandu using Passive sampling device was carried out in 1997/1998 (Silwal *et al.*, 2001). Samplings were carried out at eleven sites including heavy traffic city centers, semi-industrialized areas, residential areas and remote areas. The passive samplers were prepared and analyzed in Japan (Silwal *et al.*, 2001).

Leaders Nepal 1999/2000 used Amaya-Sugiura passive diffusion sampler for NOx from Japan. After the 24 hour exposure of the samplers with TEA as absorber, was immediately tested using Saltzman's solution. Colour intensity was measured by using NOx analyzer that give a concentration of NOx in ppm, equivalent to the intensity of the color developed (NESS, 2001).

Monitoring stations established by ESPS/ MOPE also uses passive samplers, the Rediolle from Italy for measurement of $SO_2$, $NO_2$, Benzene, PAH. After sampling they were sent to different private laboratories namely, ENPHO, SOIL Laboratory, Dilhi bazaar, for further analysis. The sampler itself cost about Euro 30. Similarly other commercially available passive samplers cost in different rate according to manufacturer.

For example, Gradko tubes cost £5-25 per sampler; Ogawa, Japan cost > $100. Thus, these commercially available passive samplers are still costly for a developing country like Nepal. In addition, due to power failure and other constraints these monitoring stations are continuously disturbed and not functioning since March 2009. Furthermore, the monitoring data had not yet been precisely used in assessment and air quality management planning within the country.

Hence it is in pertinent to have a sampler which is affordable and logistically feasible to be sample and analyze in our environment. In this line this study attempted to use locally available polyethylene tubes with triethanolamine coated filter paper to use as ambient $NO_{2;}$ $SO_2$ and nitrite coated filter paper as $O_3$ sampler and monitoring. These, locally developed diffusion tubes for passive sampling could be useful for long run, self sustained monitoring.

# Chapter 3: Study area

## 3.1: Geographical settings and climate of Kathmandu valley

Kathmandu valley is situated in the central development region of Nepal. It lies between latitudes 27°32’13” and 27°49’10” north and longitudes 85°11’31” and 85°31’38” east at 1,300 masl. It has unique topography with extreme climatic variation. The temperature ranges from below 0°C in winter to near above 30°C in summer (Kathmandu Valley Environment Outlook, 2007). The westerly and southwesterly winds dominate in the valley throughout the year (Sapkota, 2004). A temperate climate prevails in Kathmandu valley. There are three dominant seasons in the valley; winter, spring, summer and autumn; with three months each season and December is the harbinger of winter. The rainy season is from June to September when 80% of the rainfall occurs. The annual rainfall of the valley is around 1300mm (Gautam, 2006).

The valley comprises of five municipalities and 114 Village Development Committees (VDCs). The five municipalities are Kathmandu, Lalitpur, Bhaktapur, Madhyapur and Kirtipur. According to the self governance act, 1999 urban classification, these municipalities are classified as Kathmandu metropolitan city, Lalitpur sub-metropolitan city and Bhaktapur, Madhyapur and Kirtipur municipalities (Figure 3.1).

Thus, Kathmandu valley forms a basin of approximately 30 x 30 kilometers. It encloses the entire area of Bhaktapur district, 85% of Kathmandu district and 50% of Lalitpur district (KVEO, 2007). It is surrounded by the Mahabharat mountain range on all sides. There are four hills acting as forts of the valley, Phulchowki in the South East, Chandragiri/ Champa

Devi in the South West, Shivapuri in the North West, and Nagarkot in the North East. The highest altitudes of the peaks are 2,166m in Bhaktapur, 2,732m in Kathmandu, and 2,831m in Lalitpur. The city is especially vulnerable to air pollution due to its bowl-shaped topography which restricts wind movements and retains air pollutants in the atmosphere during thermal inversions (Gautam, 2006; KVEO, 2007; Sapkota, 2004).

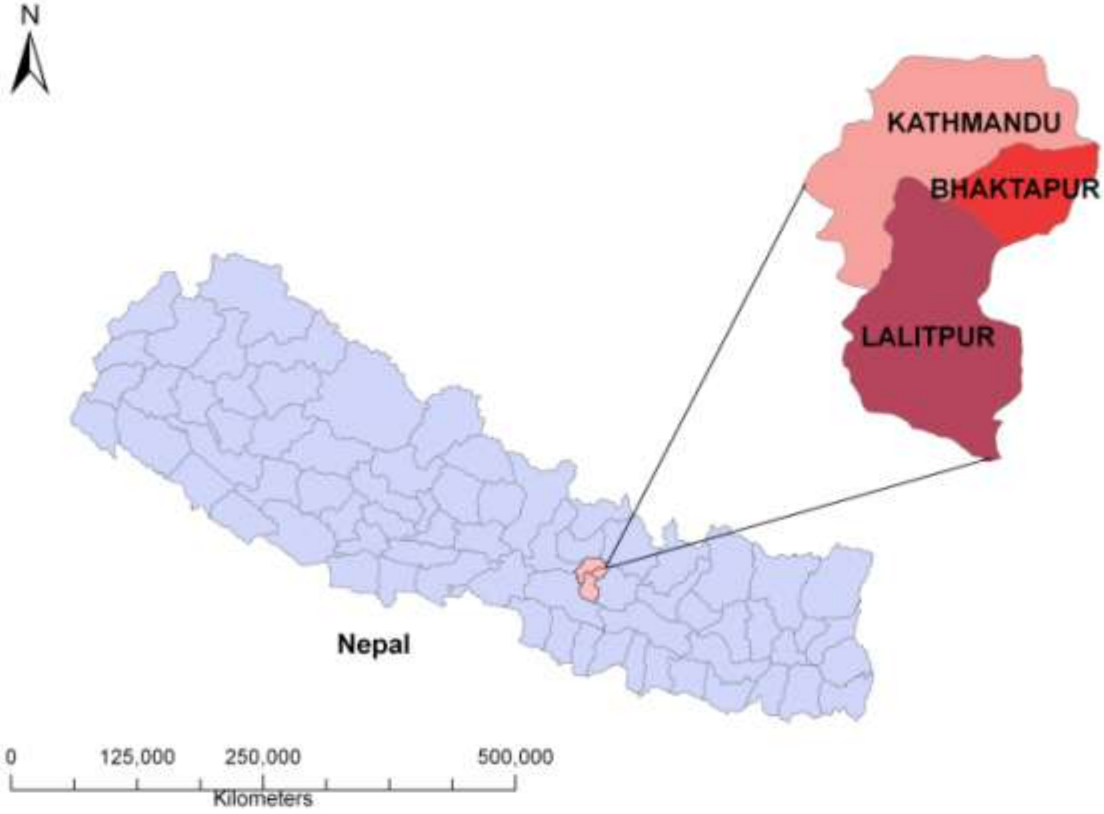


Figure 3.1: Location of Kathmandu Valley in Nepal.

As Kathmandu City is a part of Kathmandu valley, every aspect of air pollution in the city is linked with the Kathmandu valley as a whole.

## 3.2: Population and urbanization of Kathmandu valley

Over the past 30 years, Kathmandu valley has witnessed a substantial change in population dynamics due to the increased economic, political and social activities including employment, educational and career opportunities. Currently, it is estimated that the valley alone accommodates nearly 1.6 million people out of 20.2 million people living in Nepal (CBS, 2001). According to 2001 census, the urban population is increasing at a rate of 6.65% where as the annual national growth rate stands only at 2.3%. By 2050, 46.34% of people will be living in cities, compared to 8.85% in 1990. The urban population growth rate in Kathmandu valley is 4.06% (CBS2003b). The main reasons for this rapid rate of urbanization are the migration of people from villages to the larger cities in search of better opportunities. According to recent census, with an estimated population of 29,391,883 (July 2011 est.), Nepal is the 41st most populous nation in the world. The rate of urbanization is 4.7% (CIA, 2011). The population density of Nepal is 157.3 (person per sq. km.) at a growth rate of 2.25% per annum (CBS, 2009).

## 3.3: Traffic volume and road network

With industrial and economical development, transportation has become an important requirement in urban Kathmandu. The number of vehicles in this city is ever increasing, and in the 1990s alone, the number of vehicles increased by 4.2 fold (LEADERS Nepal, 1999). According to the Department of Transport Management, the number of vehicles in the Bagmati zone has increased to 171,678 by the end of fiscal year 2001/02 which is a very high number considering the small road network in Kathmandu Valley. In Nepal it is not precisely known what percentage of registered vehicles is actually operated (Adhikari, 1999). However, it appears that almost all the vehicles in Bagmati zone run on the streets of Kathmandu (CEN, 2001) and of the total number of vehicles registered in Nepal, almost 60% ply inside valley. According to the latest registration record from DOTM till mid july 2007/2008, the total number of registered vehicles for all categories was 7, 03,044. Thus about 421826 vehicles were running inside the Valley. Over the last 7 years, the Bagmati zone alone accounted for 56.2 percent of the total vehicles registered in the country. (Figure 3.2)

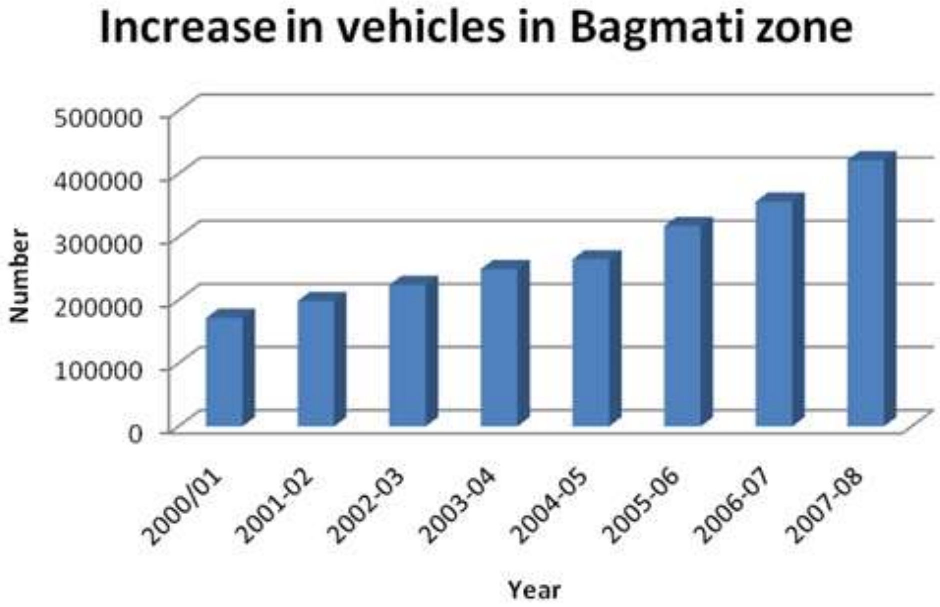


Figure 3.2: Vehicle Registration Data of Bagmati Zone.

*Source: Department of Transportation Management (2005/06)*

The large number of vehicles and their movement has caused adverse impacts on the air quality of the Kathmandu Valley. A study done by the Society for Legal and Environmental Analysis and Development Research (LEADERS Nepal) has concluded that vehicles are responsible for the increased concentration of respirable particulate matter at different traffic intersections (LEADERS Nepal, 1999). Approximately 36.5% of the vehicles running in the streets of Kathmandu valley failed to comply with the emission standards set by His Majesty's Government of Nepal (Bastola, 1998). Despite the increasing number of vehicles, the total length of road networks in Kathmandu Valley is only 1202 kilometers of which 596 km is black top, 290 km is gravel, and 316 km is earthen road (Table 3.1, DoR, 2004 and Kathmandu Valley Environment Outlook, 2007).

Table 3.1: Road Status in Three Major Districts in Kathmandu Valley

| District | Major Urban center | Road Type | | | Total Km |
|---|---|---|---|---|---|
| | | Black topped | Graveled | Earthen | |
| Kathmandu | Kathmandu | 499.29 | 175.61 | 137.93 | 812.83 |
| Lalitpur | Patan | 14 | 64.47 | 129.64 | 208.11 |
| Bhaktapur | Bhaktapur | 82.62 | 50.5 | 48 | 181.12 |
| Total in Valley | | 595.91 | 290.58 | 315.57 | 1202.06 |

*Source: DoR 2004 and Kathmandu valley Environment Outlook, 2007.*

The roads in urban Kathmandu have not been maintained regularly to accommodate the increasing number of vehicles. Thus, most motorable roads in Kathmandu are too narrow for the dense traffic with only 3.65 m per vehicle (Pokherel, 2002). This figure is for the total urban road network. However, if only black top surfaced road is considered, per vehicle road space is only 2.81 m (LEADERS Nepal, 2000). Since Kathmandu has an insufficient and sub-standard road network, the transport or the vehicle-related air pollution has been linked not only with types and condition of vehicles, but also with the infrastructure to accommodate them properly (Adhikari, 1999). In addition, the increase in vehicle number is also associated with the increase in the demand for vehicle fuel (Figure 3.3). Accordingly, the total energy consumption in the country is increased by about 2.4% annually during the period of 2000/01 to 2008/09 (WECS, 2010). Of which, about 63% of the total petroleum consumption is occurred in the transport sector. Hence, though the average annual change in the petroleum consumption is very low just about 0.7% as mostly the transport vehicles use this fuel, most of this is consumed in Kathmandu.

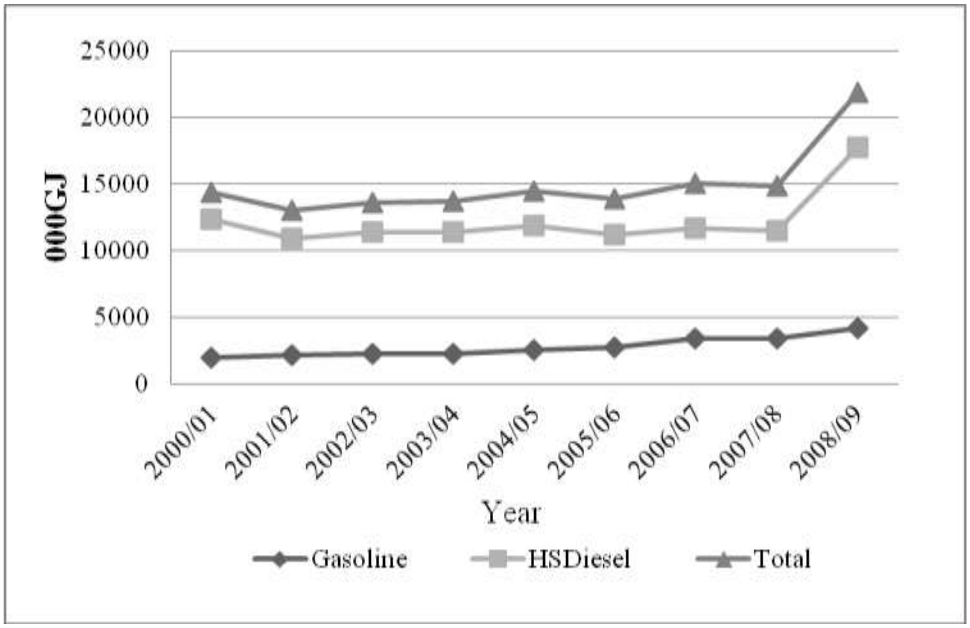


Figure 3.3: Consumption of Vehicular fuel in Nepal for the years 2000/01-2008/09.

***S**ource:(WECS, 2010)*

## 3.4: Industrial growth

Urbanization has helped the city to diversify the economy by facilitating the growth of the industrial base. But at the same time these industries are a major source of pollutant emissions in the Kathmandu Valley. Industrial development has been growing at a rapid rate in the last decade. In 2001 the valley was the host for about 25% of the total units of the industries in the country (UNEP, 2001). This figure increases with time. Currently, Kathmandu Valley accommodates 38% of the total units of the industries in the country (KVEO, 2007). According to the Department of Cottage and Small industries Kathmandu valley has 14,791 industries of which 10,527 are in Kathmandu; 2,933 in Lalitpur; and 13,331 in Bhaktapur (KVEO, 2007). These industries are responsible for generating stack and fugitive emissions primarily responsible for air pollution.

Out of 125 industries identified as point sources for the pollution in the country, 105 industries have air pollution problems (NECG, 1990). According to a study done to estimate total amount of air pollutants, 3156 industries were found to be in the category of air polluting industries, out of which Kathmandu Valley accommodates 47.5 percent of them (Devkota and Neupane, 1994). The brick and cement industries are pinpointed as the main industrial polluters (Devkota and Neupane, 1994; URBAIR, 1996). However, the cement industries have been closed. According to the previous air pollution inventories the industrial pollutants are mainly particulate dust, carbon monoxide and sulphur dioxide (Gautam, 2006).

### 3.5: Air pollution and its impact on health

Air pollution is a major environmental health problem, affecting both developed and developing countries around the world, and Nepal is no exception. Increasing amounts of potentially, harmful gases and particles are emitted into the atmosphere at high scale, resulting in damage to human health and the environment. Air pollution is associated with increase in outpatient visits due to respiratory and cardiovascular diseases in hospital admissions and in daily mortality. Recent estimates in daily mortality shows that on the global scale 4-8% (about 5,37,000) of premature deaths are due to exposure to particulate matter in ambient and indoor environments (WHO,2002). Around 20-30% of all respiratory diseases appear to be caused by air pollution (WHO, 2000).

High concentrations of lower atmospheric pollutants pose a threat to the health of the residents of the Kathmandu Valley, especially during dry winter months (LEADERS Nepal 1998; LEADERS Nepal, 1999). Though, the potential threats to human health, due to this high level of lower atmospheric pollution across the urban area of Kathmandu have been a focus of Nepalese scientists and local government agencies over the past decade, very few studies on the impacts of Kathmandu valley’s air pollution were carried out. While long term epidemiological studies are almost non existence (KVEO, 2007), a citizen’s report published by LEADERS Nepal in 1998 indicates a rise in incidence of respiratory disorders, the reporting of eye, throat and skin problems, and incidence of cardiovascular related problems among people living in Kathmandu. A preliminary study has shown that urban residents exceed the number of respiratory-related cases treated in hospitals, compared to that from the rural areas in Kathmandu. One possible reason for the increased numbers could be linked with the deteriorating ambient air quality (LEADERS Nepal, 1999).

Acute respiratory disease (ARI) is one of the top five diseases reported in Nepal (UNEP, 2001). In Kathmandu, Lalitpur and Bhaktapur (the three major municipalities inside the Kathmandu Valley) 16.5% (156,483 patients) of all hospital visits during 1996-97 were reported to be for respiratory problems (Pokhrel, 2002).

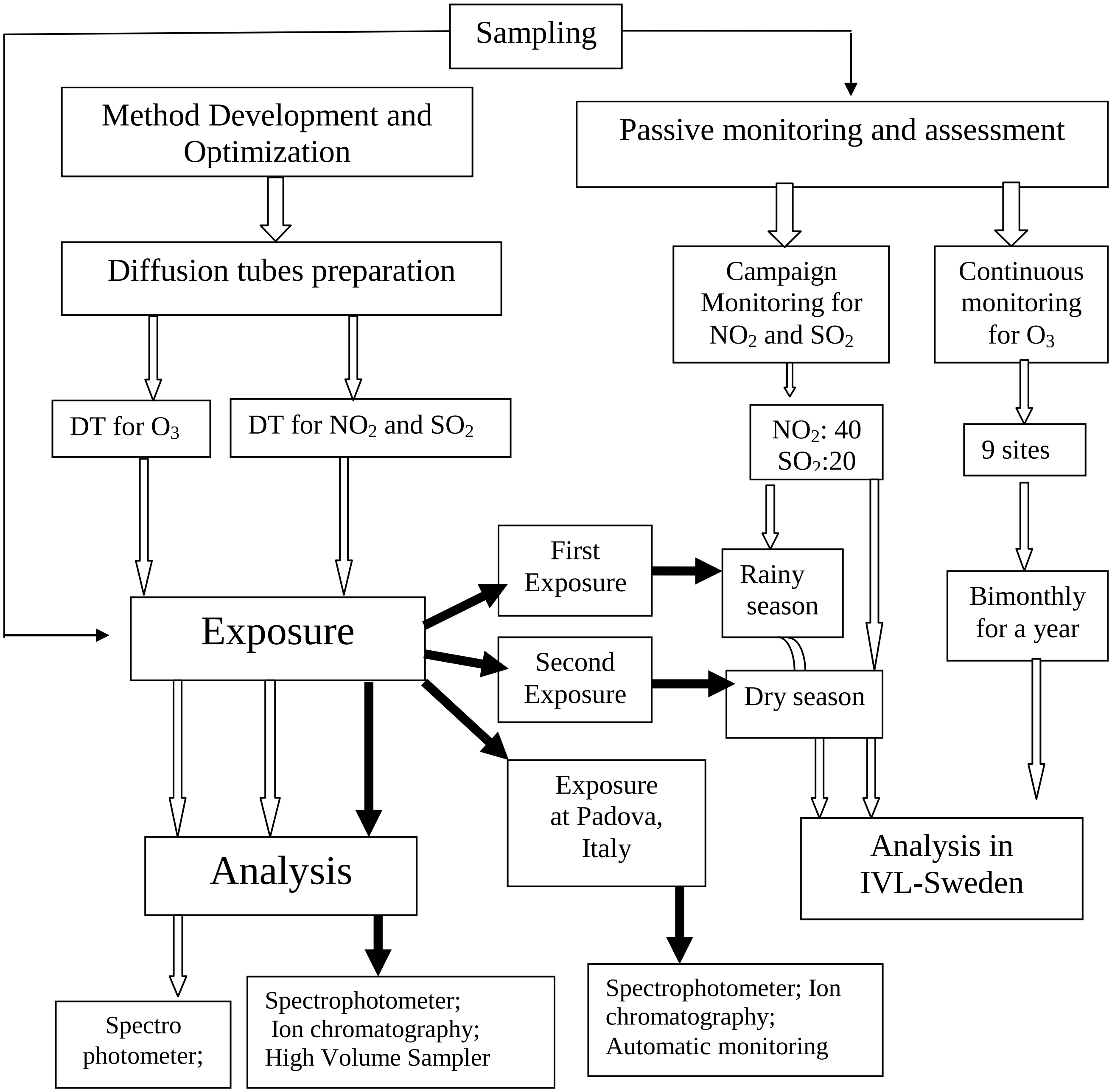
According to the estimates of the Ministry of Environment, Science and Technology for 2005, the ambient air pollution has been made responsible for the premature deaths of 1600 people per year in Kathmandu valley. Clean Energy Nepal/ Environment and Public

Health Organization (CEN/ENPHO), 2003 estimated that about NRs.30 million of hospital costs every year could be saved by reducing Kathmandu’s $PM_{10}$ level to meet WHO guideline values (CANN, 2008).

# Chapter 4: Materials and methods

## 4.1: Research design

Detail research design is presented in the following flow-chart (Box2). Its component will be discussed in following sections.



Box 2: Flow chart representing experimental set up.

## 4.2: Sampling

### 4.2.1: Selection of sampling sites

Two intensive monitoring were carried out. One comprised of monitoring of $NO_2$ and $SO_2$ in the year 2006/ 2007 as campaign monitoring. Two campaign monitoring were carried out, one for rainy season and another for dry season. Another was carried as continuous monitoring of $O_3$, $NO_2$ and $SO_2$ from November 2006 to November 2007. Neither of the campaign monitoring was run simultaneously with continuous monitoring. Both of these monitoring were supported by UNEP and carried out in collaboration with IVL and ICIMOD.

For the campaign monitoring and assessing the air quality of Kathmandu valley forty sampling sites were selected. The selection of sampling sites was done with view to represent the different sectors of the emission sources in Kathmandu, such as road side, residential area, industrial area, cultural sites. Forty sampling sites were classified into rural site, urban background, intermediate road side, near road side and industrial site, similar to the sampling manual from Gradko, UK (Gradko, 2010). Among the 40 sites selected, two were rural sites, eight were urban back ground, nine were intermediate road sides, and twenty were near road sides and one industrial site. Total of eighty 80 diffusive $NO_2$ samplers (40 sampling sites X 2 seasons) from IVL-Sweden were exposed. Within these sites, twenty $SO_2$ exposure sites were selected and used for sampling of $SO_2$ using samplers from IVL- Sweden as well. Total of 40 diffusive $SO_2$ samplers (20 sampling sites X 2 seasons) from IVL-Sweden were exposed (Figures 4.1, 4.2 and Appendix II).

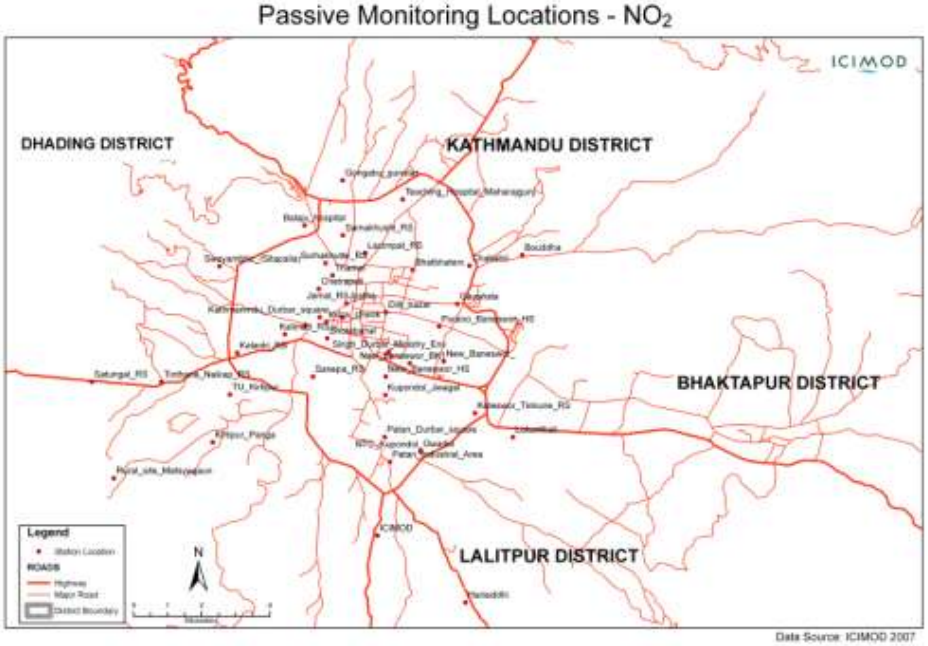


Figure 4.1: Sampling sites of $NO_2$

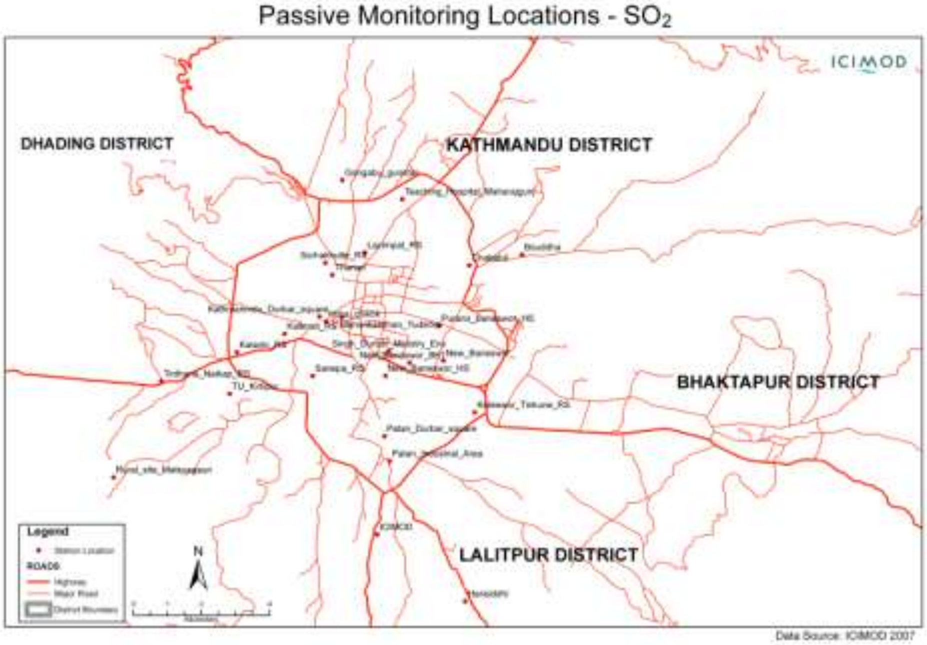


Figure 4.2: Sampling sites of $SO_2$

Samplers were exposed for two seasons, rainy and dry in these sites guided by pattern of pollution scenario observed in the valley predicted from the previous monitoring results (MOEST, 2006). Measurement of both the samplers were made simultaneously. The IVL samplers were of badge type, 10 mm long and 20 mm internal diameter. A membrane was mounted at the inlet to prevent them from wind-induced turbulent diffusion. The membrane was protected from mechanical damage by a stainless steel mess (Figure 4.3). These samplers were normally mounted under a metal disc (rain shield) attached to an aluminum arm (Figure 4.4).

Figure 4.3: Passive samplers from IVL, Sweden.

Three of the forty sites, namely, Thamel, Putali sadak and Patan were the sampling sites of the Ministry of Environment Science and Technology (now Ministry of Environment) as well. They used the High volume sampler, active monitoring for measuring particulates and passive samplers from Italy for measuring $NO_2$.

Figure 4.4: Exposure of Passive samplers mounting with metal disc as rain shield at Thamel.

Among these forty sampling sites, five ( sites I-V) were selected for exposure of prepared test-passive sampler sites so as to compare them with IVL-ferm samplers for first exposure and eight (sites I-VIII) for second exposure (Table 4.1and Figure 4.5).

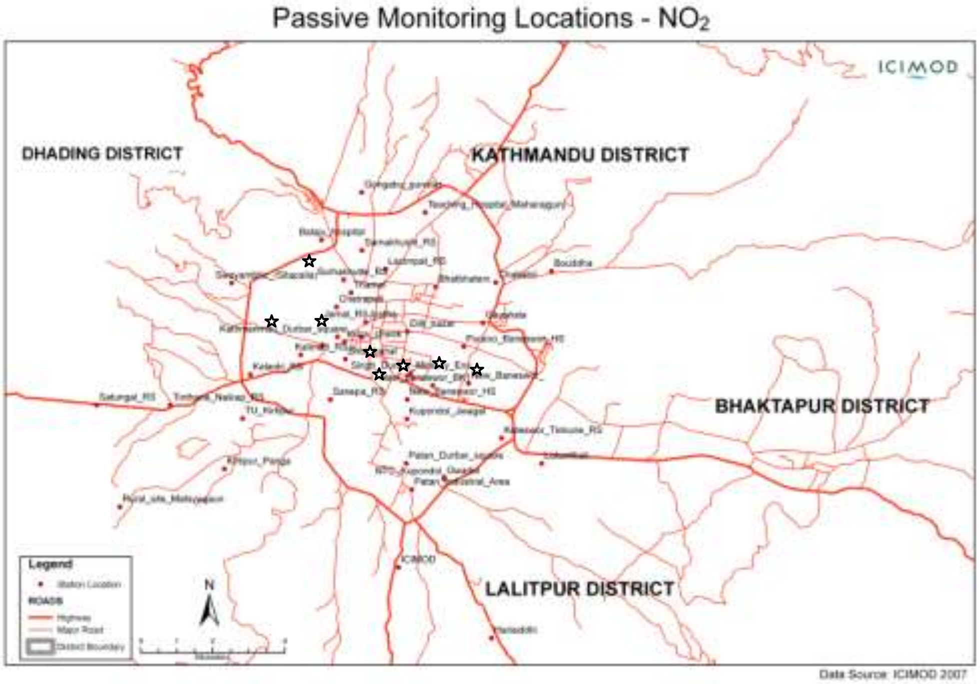


Figure 4.5: Test passive sampler exposure sites

Table 4.1: Description of sampling sites

| **Exposure Station sites** | **Latitude (ºN)** | **Longitude (ºE)** | **Altitude (m)** | **Remarks** |
|---|---|---|---|---|
| I. Bijuli bazaar RS | 27.6795 | 85.3245 | 1304 | High volume sampler sampling station |
| II. New Baneswor HS | 27.6885 | 85.3253 | 1311 | Road side + high slope |
| III. New Baneswor RS | 27.6925 | 85.3407 | 1316 | Intermediate site (Road side with less traffic) |
| IV. Maitighar RS | 27.6934 | 85.3216 | 1304 | High traffic |
| V. Indra chwok RS | 27.7029 | 85.3096 | 1303 | Market center |
| VI. Thamel, MOEST | 27.7152 | 85.3113 | 1321 | Urban Residential , Ministry’s monitoring station |
| VII Kalimati RS | 27.6996 | 85.2987 | 1443 | High traffic road intersection |
| VIII. New BaneswörUBK | 27.6920 | 85.3317 | 1310 | Inside residential area<br>Urban Background site |

*Note: RS = Road side monitoring sites; UBK = Urban Back ground monitoring sites; HS = High slope road side monitoring sites.*

*MOEST = Continuous monitoring stations of Ministry of Environment,*

Continuous monitoring of $O_3$, $NO_2$ and $SO_2$ at nine sites for a year was carried out inside Kathmandu valley. In this continuous monitoring programme bi-monthly average concentration of $NO_2$, $SO_2$ and $O_3$ were measured using diffusive samplers from IVL between November 2006 and November 2007. This was part of RAPIDC-corrosion project carried out by ICIMOD. The sites were therefore selected near buildings with cultural heritages. Detail information about these monitoring locations were collected (Appendix III).

Neither of the two intensive campaigns was run simultaneously along with the continuous monitoring at 9 stations. The samplers were analysed in the IVL-Sweden.

## 4.3: Experimental setting

### 4.3.1: Materials and Chemicals

All the materials and chemicals used in the current research were of analytical grade. (Appendix VI)

## 4.4: Method development

### 4.4.1: Method selection from literature

Following methods were selected for sampling and analysis of selected air pollutants; $NO_2$, $SO_2$ and $O_3$, for current research (Table 4.2)

Table 4.2: Methods for current study

| Pollutant | Method (Test Methods) | Advantage | Disadvantage |
|---|---|---|---|
| Passive sampling of $NO_2$ | Modified Griess-Saltzman Method for analysis using TEA as absorber | -Requires simple inexpensive instruments and preparation<br>- Lower detection limit 200ppb<br>-precision reported 9%<br>wide range of temperature stability tested ( 0- +400)<br>-Numerous studies carried out regarding field comparison and validation<br>- ISO 6768 (1985) | |
| Passive sampling of $SO_2$ | TEA/Water as absorber and pararosaniline method of analysis using spectrophotometer. | -simple and specific to $SO_2$<br>- ISO 6767, 1990 method | Safe use and handling and proper disposal of toxic reagent. |
| Passive sampling of $O_3$ | Nitrite/carbonate-water as absorber and Azide Modified Sodium salicylate method using spectrophotometer. | Simple and inexpensive | Rapid analysis is necessary |

These selected method referred as “test method” in this document now on.

### 4.4.2: Passive or diffusive samplers

Passive samplers used in this work were tube types which were developed as follow.

#### 4.4.2.1: Selection of diffusion tubes:

Three types of polyethylene tubes with following specification (Table 4.3) from the local market were chosen for use. The tubes were shown in figure 4.6.

Table 4.3: Specification of three polyethylene tubes

| Tube | Length | Diameter |
|---|---|---|
| Tube-1 | 5 cm | 1.2cm |
| Tube-2 | 5 cm | 1.0 cm |
| Tube-3 | 8 cm | 0.8 cm |

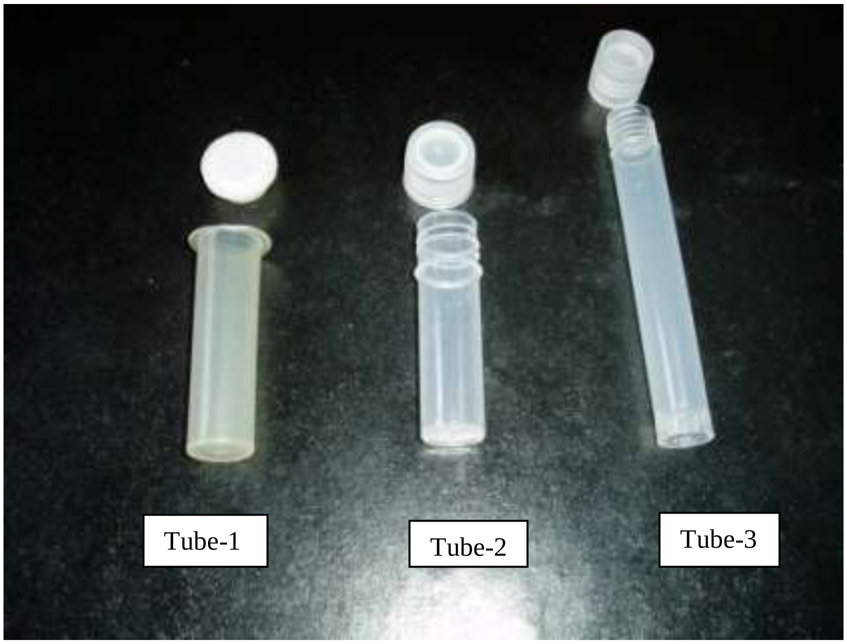


Figure 4.6: different types of tubes from local market to be test as diffusive sampler.

### 4.4.2.2: Preparation of diffusion tubes:

The filter papers were cut into circle with the diameter equal to the inner diameter of the tube. These filter papers were soaked overnight with double distilled (dd)- water. They were air dried and with the help of plastic forceps, placed inside the tube allowing it to reach at the bottom of the tube (Figure 4.7).

Absorbents were added on the same day of installation on all occasions of exposure.

Different concentrations of absorbents were used to test and make for choice of the more suitable to be use. Precaution was taken during tube preparation so that all the absorbents were put on the filter paper and not at the sides of the tube. The tubes were then covered with a cap immediately and labeled properly.

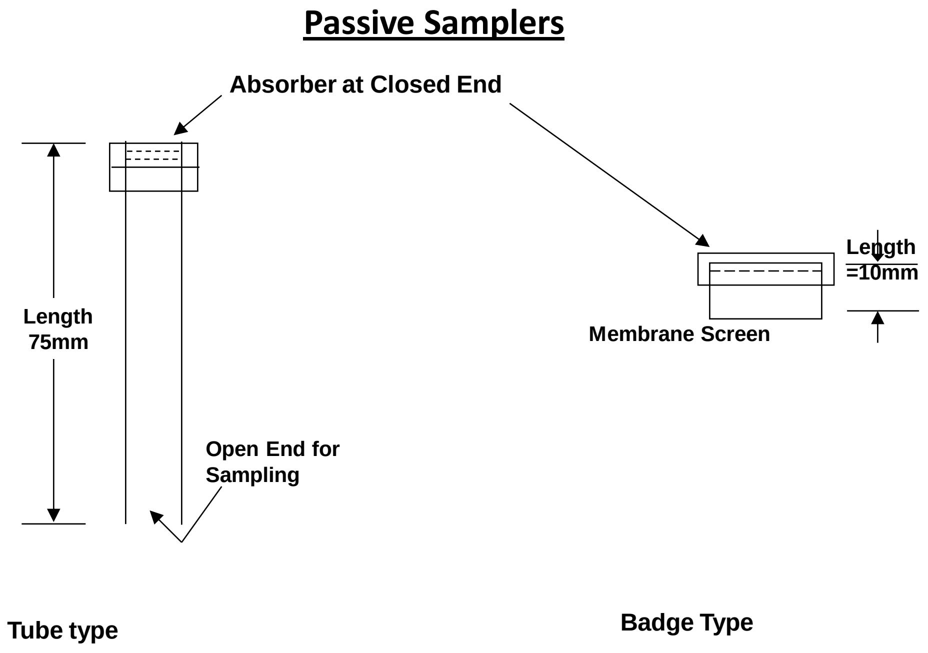


**Figure 4.7: Diffusion tube preparation**

Recommendations from previous researches had been considered for the exposures. Installations of blanks, storage of samplers in a refrigerator, analysis of pollutants by ion chromatography (Gair et.al, 1991) were considered. The samplers were exposed inside shields to protect them from wind, sunlight, rain, and draught (Kasper-Giebl and Puxbaum, 1999; Krochmal and Kalina, 1997; Brown, 2000).

#### 4.4.2.3: Filter paper to be use for absorbent:

Throughout the study Whatmann GF/A was used as absorbing medium for the preparation of diffusion tubes. Three types of filter papers, Whatmann GF/A, Whatman no. 40 and Whatmann Qualitative 5 were considered for comparison as absorbent medium in the current study.

### 4.4.3: Sample analysis

All the chemicals used were of analytical grade and Kathmandu based analysis were carried out in CEMAT-Water Lab, Bijulibazar.

## Part I: Analysis of $NO_2$ and $SO_2$

#### 4.4.3.1: Determination of nitrite ($NO_2^-$) by spectrophotometer

After exposure to definite time period, the tubes were collected and closed with caps. The time of collection was noted. The tubes were stored in a refrigerator till the time of analysis.

(a) Preparation of reagents

Reagent-1 was prepared by dissolving 10.75 g sulfanilamide in 28 ml concentrated phosphoric acid, and diluting with deionised water up to 500 ml.

Reagent-2 was prepared by dissolving 0.152 g N-1 napthyl ethylendiamine dihydrochloride and diluting to 100 ml with deionised water.

Both reagents were stored in a refrigerator till the time of analysis. Immediately before analysis, 10 ml of reagent–2 was mixed with 100 ml of reagent-1.

(b) Preparation of nitrite standards

$NO_2^-$ stock standard (1,000 µg/ml) was prepared by dissolving 1.50 g $NaNO_2$ and diluting to 1 liter with deionised water. The $NaNO_2$ was previously dried overnight at $105^0$C. This stock standard was used for 3 months and stored in a refrigerator. The $NO_2^-$ stock standard of 100 and 10 µg/ml was also prepared from the main stock standard (1,000 µg/ml). These stock standards were prepared monthly.

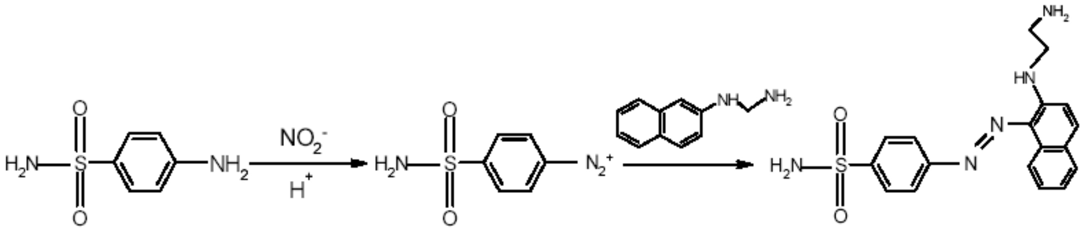
Only one stock standard either 10 or 100 µg/ml was used to prepare different concentration ranges for a calibration curve. The working solutions were prepared daily.

(c) Extraction of samplers

To the diffusion tubes collected after exposure of prescribed time period weeks, 1 ml of dd water was added. The tube was left for 15 minutes for extraction of all the $NO_2^-$ present on the filter paper, and the tube was closed. The tubes were shaken occasionally to increase the extraction process.

(d) Analysis by spectrophotometer

To 1 ml of $NO_2^-$ standard solutions, 2 ml of the mixture of reagent–1 and reagent–2 were added. The same proportion of reagent mixtures was added to the diffusion tubes after extraction. These solutions were left for 10 minutes to allow the reaction to complete. The stable red-violet color obtained was measured by sphectophotometer at 540 nm. Before taking the measurements, spectrophotometer was zeroed against the reagent blank solution to avoid the interferences from impurities in the reagents. The reactions involved are shown as follows (BCH 5112, 2003):



Azo dye, $\lambda_{max}$ = 543

### 4.4.3.2: Determination of sulphate ($SO_4^{2-}$) by spectrophotometer

(a) Preparation of reagents

P-rosaniline Hydrochloride solution:

About 0.20 gm of P-rosaniline was dissolved in 100 ml of distilled water and filtered the solution after 48 hours. 20 ml of this was pipette into a 100 ml volumetric flask. 6 ml of Hydrochloric acid was added in it and allowed to stand for 5 minutes, and then dilute up to the mark with distilled water.

Formaldehyde solution:

Five ml of 40 % formaldehyde solution was diluted to 1 liter with distilled water, prepared weekly.

(b) Preparation of sulphate standards

Sodium Metabisulphite solution:

Six hundred forty (640) mg of sodium metabisulphite (assay 65% as $SO_2$) was dissolved in 1 litre of distilled water. This yields solution of approximately of 0.4mg%/ml as $SO_2$. The solution was standardized by titration with standard 0.01N iodine with using starch as indicator and adjusted to 0.0123N.

(c) Extraction of samplers

To the diffusion tubes collected after exposure of two weeks, 2 ml of double distilled water was added. The tube was left for 15 minutes for extraction of all the $SO_4^{2-}$ present on the filter paper, and the tube was closed. The tubes were shaken occasionally to increase the extraction process.

(d) Analysis by spectrophotometer

One ml each of p-rosaniline and formaldehyde solutions were added to each of these 2ml of extract and shaken well. 2 ml reagent blank was taken similarly in tube without adding sulphite solution.

After 30 minutes the absorbance of the standard samples was measured with a spectrophotometer at 560 nm.

Calibration curve was plotted with absorbance against concentration μl/ml of $SO_2$. A linear relationship was obtained.

### 4.4.3.3: Calculation of nitrogen dioxide ($NO_2$) and sulfur dioxide ($SO_2$) in ambient air

The $NO_2$ and $SO_2$ concentrations in ambient air in the unit of microgram per cubic meter (μg/m$^3$) were calculated from the value of $NO_2^-$ and $SO_4^{2-}$ in diffusion tubes (Appendix IV).

### 4.4.3.4: Determination of nitrite ($NO_2^-$) and sulphate ($SO_4^{2-}$) by ion chromatography

The tubes exposed for two and four weeks for simultaneous analysis of $NO_2^-$ and $SO_4^{2-}$ were collected and were closed with caps immediately. The time of collection was noted. The tubes were stored in a refrigerator till the time of analysis.

(a) Preparation of eluent

Stock solution (180 mM $Na_2CO_3$/ 170 mM $NaHCO_3$) was prepared by dissolving 1.9078 g $Na_2CO_3$ and 1.4282 g $NaHCO_3$ in milli-Q water and diluting the resulting solution to 100 ml.

The eluent of 1.8 mM $Na_2CO_3$/ 1.7 mM $NaHCO_3$ was then prepared by pipetting 10 ml of the above stock solution and diluting to one liter with milli-Q water. The solution was filtered through a 0.45 µm cellulose acetate membrane (Millipore) to remove micro-particles. This solution was degassed in an ultrasonic bath for 15 minutes to remove dissolved gases every day before use.

(b) Preparation of mixed nitrite and sulphate standards

The $NO_2^-$ stock standards were prepared for the spectrophotometric analysis were used for this analysis also. The stock standards of 10 and 100 µg/ml ($SO_4^{2-}$) were prepared from the $SO_4^{2-}$ stock standard (1000 µg/ml). These standards were prepared monthly. From these stock standards, two ranges of mixed standards with low and high concentrations of $NO_2^-$ and $SO_4^{2-}$ were prepared for the calibration curve. The working standards were prepared daily.

(c) Optimization of ion chromatograph conditions

The conditions recommended yielding better sensitivity and resolution for ion chromatograph were checked using a mobile phase 1.80 mM $Na_2CO_3$/ 1.70 mM $NaHCO_3$ (Na-Chiangmai, 1997). The effects of eluent flow rates, varying from 1.0- 2.0 ml/minute, were studied by injecting a mixed standard of 1 µg/ml, each of $NO_2^-$ and $SO_4^{2-.}$

(d) Analysis of samples

To the diffusion tubes collected after exposure of two weeks, 2 ml of milli-Q water was added. The tube was shaken 2-3 times to increase the extraction process. 1.0 ml of the extract from the tubes of first exposure was mixed with 1.0 ml of 0.15% $H_2O_2$ (Krochmal and Kalina, 1997). The diffusion tubes were extracted with 2 ml eluent and mixed with 9.5 µl of 35% $H_2O_2$ (Plaisance *et al.*, 2002) from the second exposure onwards.

The mixed standard solutions of different concentrations were injected three times into the ion chromatograph. The calibration curve was prepared from the average value of peak areas from these measurements. The samples were then injected two times. The retention time and peak areas from the integrated chromatogram were noted.

## 4.5: Sample exposure design and set up

### 4.5.1: Diffusion tubes preparation for $NO_2$ and $SO_2$

**(i)First exposure**

(a) Polyethylene tubes of T-1 were prepared as diffusion tubes for first exposure. 20 µl of 20% TEA in milli-Q water and 50% TEA acetone were put on the filter paper in these tubes for Kathmandu.

(b) Exposure at Padova, Italy

Diffusion tubes for $NO_2$ and $SO_2$

Polyethylene tubes of T-1 were prepared as diffusion tubes for exposure in Padova as well. Same tubes those used in Kathmandu were used for sampling of $NO_2$ and $SO_2$ respectively after proper cleaning and drying.

Diffusion tubes for $NO_2$

Six tubes each were used for 10 µl of 50% TEA water, 20 µl of 50% TEA water, 15 µl 20% TEA water and 20 µl TEA water respectively for $NO_2$ sampling. Of the 6 tubes 4 (2 duplicates, one blank and one laboratory blank) were for Spectrophotometer analysis and two for ion chromatographic analysis.

Diffusion tubes for $SO_2$

Similar set were prepared for $SO_2$ as well.

**(ii) Second exposure**

All the three kinds of tubes were prepared for collecting samples in dry season. Different concentrations of TEA, 20%, 30%, and 50% TEA water absorbent were used. Similarly three types of filter papers were used.

## 4.6: Exposure of diffusion tubes

### 4.6.1: First exposure

For the first exposure, the prepared diffusion tubs were installed on October 7, 2007 for four weeks at five sites using sample holder made of plastic boxes (Figure 4.8).

Total of ninety samplers were exposed at five sites on first exposure for four weeks on October 7, 2007 to November 4, 2007. Each site had 6X3 sets of samplers. Two sets of six, (one each for 20% aqueous TEA and 50% TEA acetone) were for spectrophotometer analysis and one for chromatographic analysis. Of the six samplers three (one blank +2 replicates) were for $NO_2$ analysis and other three were for $SO_2$. Except site one, rest of the sites were the sampling sites for air quality monitoring and assessment by using standard passive samplers from IVL, Sweden. Site one was the CEMAT-water lab where sampling were carried out using High Volume sampler, during the exposure time. The detail layout of the samplers of the sampling is shown in following table (Table 4.4). These test samplers were co-exposed with Ferm-IVL-sampler inside plastic sample holder so as to prevent from rain (Figure 4.7).

Total of sixty badge type diffusive samplers, forty $NO_2$ and twenty $SO_2$ diffusive samplers from IVL-Sweden were also exposed on July to September 2007 for rainy season.

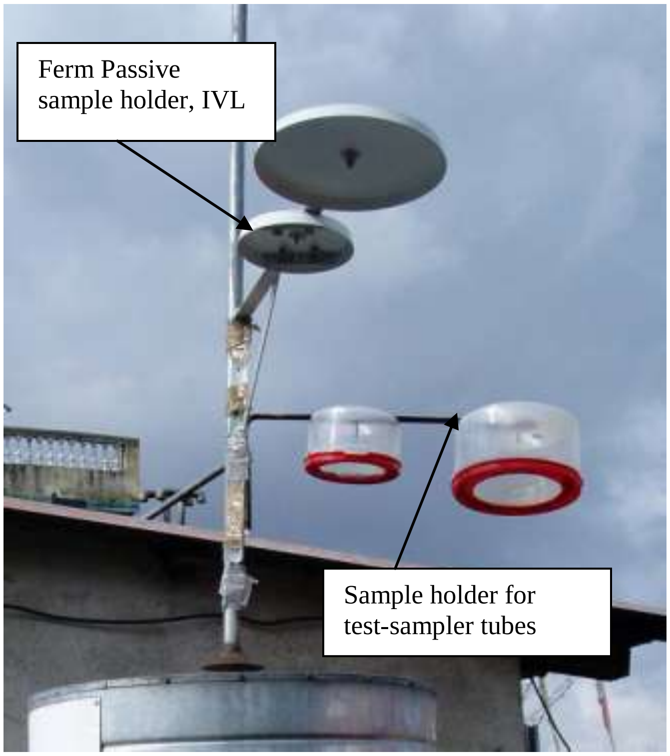


Figure 4.8: Co-exposure of Test-samplers and Ferm-passive sampler from IVL

### 4.6.2: Exposure at Padova, Italy

Similar sampler development, exposure and analysis were carried out in the University premises of Padova University, Venice, Italy as well. The samplers were installed under plastic boxes and analysed during November-December, 2007 (Figure 4.9).


University premises, PADOVA, Venice, Italy

Figure 4.9: Test exposure analysis at Padova University, Italy.

### 4.6.3: Second exposure

Total of 120 Test samplers exposed at eight sites for dry seasons from March to April 2008. Similarly, total of 60 badge type diffusive samplers, forty $NO_2$ and twenty $SO_2$ diffusive samplers from IVL-Sweden were also exposed on March to May, 2008 (Table 4.4).

Caps of the tubes were opened at the sampling sites. The field blanks were placed at the sampling sites without opening the caps of the tubes. The laboratory blanks were placed in the laboratory at room temperature without opening the caps. Diffusion tubes were put inside an airtight plastic box during transportation to the sampling sites and also after collection from the sampling sites.

Table 4.4: Total test-sampler exposure

| **Exposure time** | Diffusive passive sampler used | Total sites | Analysis method | Analysis performed Laboratory |
|---|---|---|---|---|
| First exposure/ Rainy season (June-Oct./07) | Test sampler | 5 | Spectrophotometer | CEMAT Water Lab, Nepal |
| | | | Ion chromatography | Dep. Env. Engineering, Padova university, Venice |
| | Ferm-IVL-sampler | 40 ($NO_2$)<br>20 ($SO_2$) | IVL- Sweden | |
| Exposure at Padova (Nov.-Dec./07) | Test sampler | 1 | Spectrophotometer | Dep. Env. Engineering, Padova university, Venice |
| | | | Ion chromatography | Dep. Chemistry, Padova university |
| Second Exposure/Dry season (March-May/08) | Test sampler | 8 | Spectrophotometer | CEMAT Water Lab, Nepal |
| | Ferm-IVL-sampler | 40 ($NO_2$)<br>20 ($SO_2$) | IVL- Sweden | |

The tubes were protected from sunlight, wind, rainfall or drought by placing inside a transparent plastic box, made as sampler holder as shown in figure 4.8. The diffusion tubes were fixed inside polyethylene box with adhesive tape.

### 4.6.4: Comparison between absorbents: 20%, 30% and 50% v/v aqueous TEA

Five sets of triplicates of three different absorbent concentrations; 20% v/v TEA-$H_2O$; 30% TEA- $H_2O$ and 50% TEA- $H_2O$, using 20 µl diffusion tubes were prepared using Tube-1 and were co-exposed randomly at different sites for two weeks and tested.

### 4.6.5: Comparison between absorbents volumes:

Five sets of triplicates of two different volumes of 10µl, and 30 µl of 20%, 30% and 50% v/v aqueous TEA were tested for tube one for two weeks exposure.

### 4.6.6: Comparison between three types of tubes:

Triplicates of three diffusion samplers from each type of tubes were co-exposed for two weeks and analyzed.

### 4.6.7: Comparison of filter papers (GF filter paper, Whatmann 40 and Quantitative- 5 filter paper) as absorbent base:

Samplers were prepared with GF filter paper, Whatmann 40 and Quantitative- 5 filter paper as absorbent base and exposed simultaneously for same duration and analyzed.

## 4.7: Statistical analysis

### 4.7.1: Passive sampler validation

Precision was expressed as the coefficient of variation (CV), also referred to as relative precision by the US EPA, CV was calculated as the sample standard deviation divided by the sample mean times 100%. CV across sites or tests was done by taking the square root of the squared CV sets, which the US EPA refers to as the root mean square (rms).

Precision was determined by deploying the replication of diffusion tubes. For all the exposures, two to five replications of diffusion tubes were installed. The precision was determined both for the samples and the field blanks.

Accuracy of passive sampler was evaluated by comparing the measured results with the co exposed commercial validated passive sampler from Sweden, IVL- badge diffusion samplers.

The accuracy of passive sampler was also evaluated by comparing results of $NO_2$ and $SO_2$ with active sampling measurements and ion chromatography carried out in Padova University Italy both from first exposure and exposure at Padova. The active sampling data at Padova were obtained from pollution control department (PCD), Padova, Italy, where for the active sampling, $SO_2$ and $NO_2$ were measured by continuous fluorescent $SO_2$ analyzer, model 100, and chemiluminescence NOx analyzer, model 200, Advanced Pollution Instrumentation Inc., respectively.

A linear regression was performed with pollutants $NO_2$ and $SO_2$ measured with the passive samplers as the dependent variable and that measured with the other co-exposed standard sampler as the independent variable. The slop, intercept, and Pearson correlation coefficient from this regression was compared to the criteria established by the US EPA and EU for acceptable performance of equivalent methods.

Pair t- test and an ANOVA analysis were performed for performances from three different tubes and different absorbent concentrations.

### 4.7.2: Uncertainty analysis

**Detection limit and minimum detectable quantity**

For this research, two kinds of detection limit (DL) were calculated. The first DL was for the analytical equipment, spectrophotometer and ion chromatograph. The second DL was for the entire sampling method of $NO_2$ and $SO_2$ for two and four week exposure of tubes (Appendix 3).

The DL for the spectrophotometer was calculated from a calibration curve with the help of equation 9 (Miller and Miller, 1984). The detection limit (Y) is the analyte concentration that gives a signal equal to the blank signal (YB) plus three standard deviations of the blank, SB.

$$Y = YB + 3SB \text{ -- } (9)$$

The DL for the ion chromatograph was calculated from the signal twice the standard deviation of the noise level with the help of equation 10 (Kanokkarn, 2003). For this, 25 µl volume of mixed standard solution each 0.01 µg/ml of $NO_2^-$ and $SO_4^{2-}$ was injected into the ion chromatograph at the output range 1 µS.

$$DL = \frac{2nm_x}{R} \quad \ldots\ldots\ldots..(10)$$

Where, DL = detection limit

R = peak signal response

n = noise level

$m_x$ = amount of compound injected

In practice, the noise level is obtained from integrating the zoomed baseline of chromatogram of each ion. The minimum detectable quantity (MDQ) was calculated by a peak signal with two times the noise level (equation 11).

$$MDQ = DL * W_{1/2} \text{-- } (11)$$

Where, $W$ = width at half height (seconds)

IUPAC (2000) defines lower detection limit as "the minimum concentration of a compound in an air sample which can be determined by an analytical method with a given statistical probability". It is expressed as three-times the standard deviation of the noise of an analytical method under the assumption that its distribution is Gaussian. The detection limit for the passive sampling method was calculated by multiplying the standard deviation of blank values with one-tailed t-value (degrees of freedom at 99% confidence level). The equation is given below.

$$DL = SB * t_{(á,\ n-1)} \text{ -- } (12)$$

Where,

SB = standard deviation of blank values

$t_{(á,\ n-1)}$ = critical value of t-distribution with n-1 degrees of freedom and a significance level of á (0.01 level).

### 4.7.3 Field blank test

Field blanks, each twelve set of duplicates, for $NO_2$ and $SO_2$ diffusion tubes co exposed at different sites for two weeks period were analyzed and investigated by calculation of coefficient of variation (CV).

### 4.7.4 Comparison between different exposure periods (1-4 week)

Two-Four sets of five diffusion tubes- duplicates field blanks and three for sample in each (Total 20) were exposed at two sites and collected a set in each week and analyzed.

## 4.8: Outlier removal

An outlier in a set of data may be defined as an observation (or subset of observations) which appears to be inconsistent with the remainder of that set of data (Barnett and Lewis, 1978). Though outliers are removed as a means to eliminate observations from a data to avoid disturbance, they may be interesting in themselves because of the probability of obtaining hints about certain structures in the data or about special events during the sampling period. Thus, one should be careful in outlier removal. There are many methods to detect outliers. In this experiment, the scatter plot diagram with the help of SPSS version 10.0 and Grubb's test (equation 13) were used to remove the outliers (NIST, 2003).

$$G = \frac{max[Y_i - \bar{Y}]}{S} \quad \ldots\ldots\ldots\ldots.(13)$$

Where,

$Y_i = suspected\ outlier$

$\bar{Y}$ = sample mean

$S = standard\ deviation$

Two sets - Triplicate 2-week and triplicate 4-week, normal diffusion tubes were co-exposed at different sites randomly. The precision of measurements for these exposure types were investigated by calculation of the CV of each triplicate (11 triplicates in total for 2- week and 10 for 4 -week)

## Part II: Analysis of $O_3$

### 4.9: Diffusion sampler preparation

Polyethylene tubes of 5cm long with 1.2 cm cross section with one end open from local supplier were used for sampling. Filter paper (GF/A) cut into the circular equal to the inner cross section of the tube dipped into dd water for 24 hrs followed by air drying was placed into the closed end of the tube. Twenty µl of solution of sodium nitrite and potassium carbonate in ethylene glycol/glycerin ($NaNO_2$ + $K_2CO_3$ ethylene glycol/glycerin) was fed in each diffusion tube as trapping solution on GF/A filter paper as absorbent base.

### 4.10: Sampler exposure

Ten sets of diffusion tubes each containing five tubes ( one blank + 4 replicates) were prepared and exposed at New Baneswor (urban background) during month of March 2009 for different duration; 24 hrs, 2 days, 5 days, 1 week and two weeks. During the same time two sets of diffusion tubes covered outside with brown paper, and a badge type IVL- sampler from Sweden were co exposed as well. IVL sampler been used for several past studies (Ferm *et al*., 2005 and 2006).

### 4.11: Sample extraction

To the diffusion tubes collected after exposure of prescribed time period weeks, 5 ml of dd water was added. The tube was left for 15 minutes for extraction of all the $NO_3^-$ present on the filter paper, and the tube was closed. The tubes were shaken occasionally to increase the extraction process.

## 4.12: Analysis

Standard nitrate solution and Extracted samples were analyzed for nitrate using Azide Modified Sodium salicylate method spectrophotometrically at 415 nm.

All the chemicals used were of Analytical grade. The research was carried out in CEMAT/Water laboratory. IVL-sampler was analyzed at Sweden.

## 4.13: Statistical analysis

### Method validation

Precision was expressed as the coefficient of variation (CV), also referred to as relative precision by the US EPA, CV was calculated as the sample standard deviation divided by the sample mean times 100%.

Accuracy of passive sampler was evaluated by comparing the measured results with the co exposed commercial validated passive sampler from Sweden, IVL- badge diffusion samplers.

Pair t- test were performed for comparison of covered and uncovered exposure tubes.

### Uncertainty analysis

### Detection limit and minimum detectable quantity

For this research, two kinds of detection limit (DL) were calculated. The first DL was for the analytical equipment, spectrophotometer and second DL was for the entire sampling method of $O_3$ for different exposure of tubes. The DL for the spectrophotometer was calculated from a calibration curve with the help of equation 9 (Miller and Miller, 1984).

The detection limit for the passive sampling method was calculated by multiplying the standard deviation of blank values with one-tailed t-value (degrees of freedom at 99% confidence level) using equation 12.

# Part III: Air quality monitoring and Assessment of Kathmandu valley

## 4.14: Monitoring and assessment of $NO_2$ and $SO_2$

Arc GIS 9.2 soft ware was used for the spatial data preparation and analysis to assess the air quality of Kathmandu. Image interpretation was done using a mosaic consisting of Quick bird images from January 2006. On screen digitization was applied for all the monitoring points/ sites selected using detail information recorded from GPS (Figure 4.10).

The concentrations measured in these sites were spatially disaggregated for both the campaign monitoring.

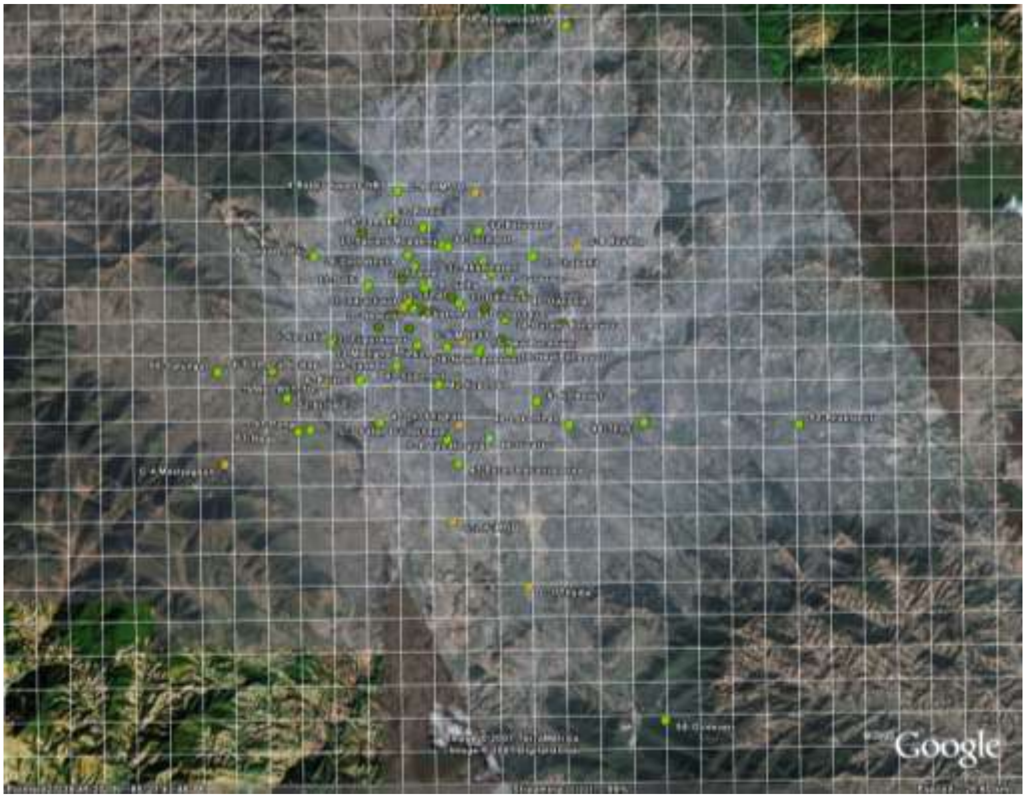


Figure 4.10: Passive monitoring sampling sites for assessment of air quality in Kathmandu

## 4.15: Monitoring and assessment of $O_3$

Assessment of ozone in Kathmandu was carried out from continuous bi monthly passive monitoring for one year from November 2006- November 2007.

# Chapter 5: Results and discussion

## Part I: Passive sampling of $NO_2$ and $SO_2$

### 5.1: Determination of $NO_2$ and $SO_2$ concentration by spectrophotometer

This research work was based on an inexpensive method of passively measure ambient $NO_2$ and $SO_2$ with the use of locally available polyethylene tubes. Passive measurement includes development of these tubes into diffusive tubes using triethanolamine (TEA) as absorbent. After extraction with water, modified Griese-Saltzmann method and West-Gaeke method were used for analysis of nitrite and sulphate adduct respectively formed due to reaction of $NO_2$ and $SO_2$ respectively using spectrophotometer. These methods were selected in view of the ease of chemical analysis and feasibility under the existing facilities in the laboratory. In addition, these methods were already used in previous studies and were proven of standard test analysis. (Palmes *et al*., 1976, Mulik *et al*., 1989, Ferm, 1991; Reiszner and West, 1973)

Two ranges of $NO_2$ standards with low and high concentrations were prepared for calibration curves and subsequent analysis of blanks and exposed tubes were carried out. This same standard curve is used for the calculation of detection limits as well (Figure. 5.1 and Figure 5.2). Similarly, the standard curves for $SO_2$ measurements were also prepared (Figure 5.3 and 5.4).

Average values of $NO_2$ and $SO_2$ from the exposed tubes after subtraction from that of the blanks at the corresponding sites was used in equations 6 and 7 to determine $NO_2$ and $SO_2$ in $\mu g/m^3$ concentration in ambient air respectively (Appendix IV).

Detection limits for the current methods were calculated of 0.09 μg/m$^3$ and 0.05 μg/m$^3$ for $NO_2$ and $SO_2$ respectively.

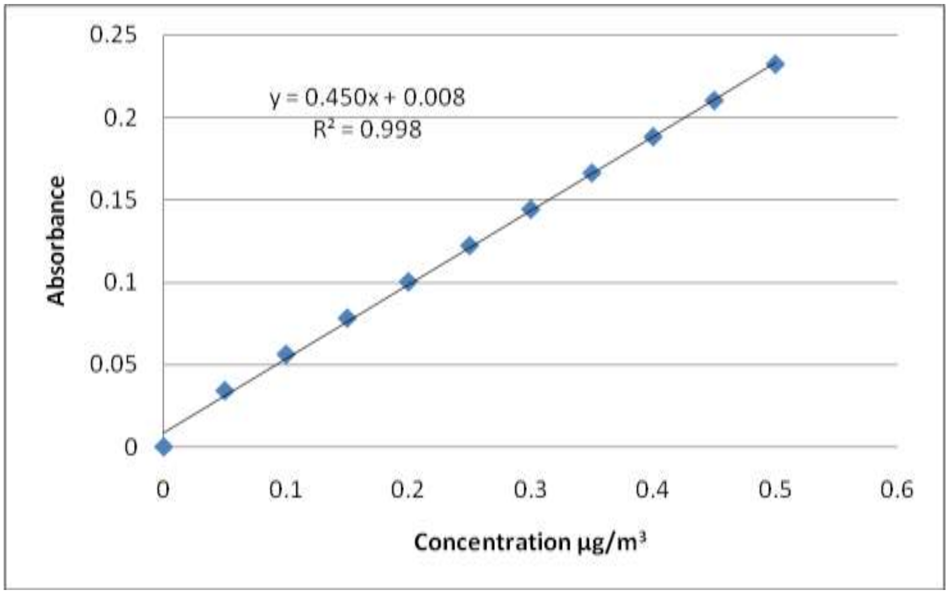


Figure 5.1: Calibration curve of $NO_2^-$ (0.05-0.5 μg/m$^3$).

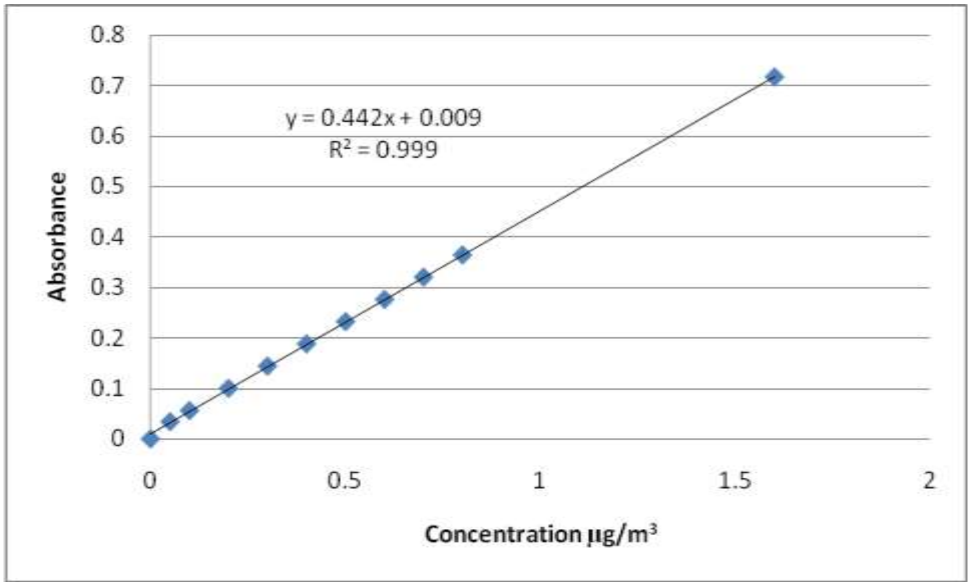


Figure 5.2: Calibration curve of $NO_2^-$ (0.05-1.6 μg/m$^3$).

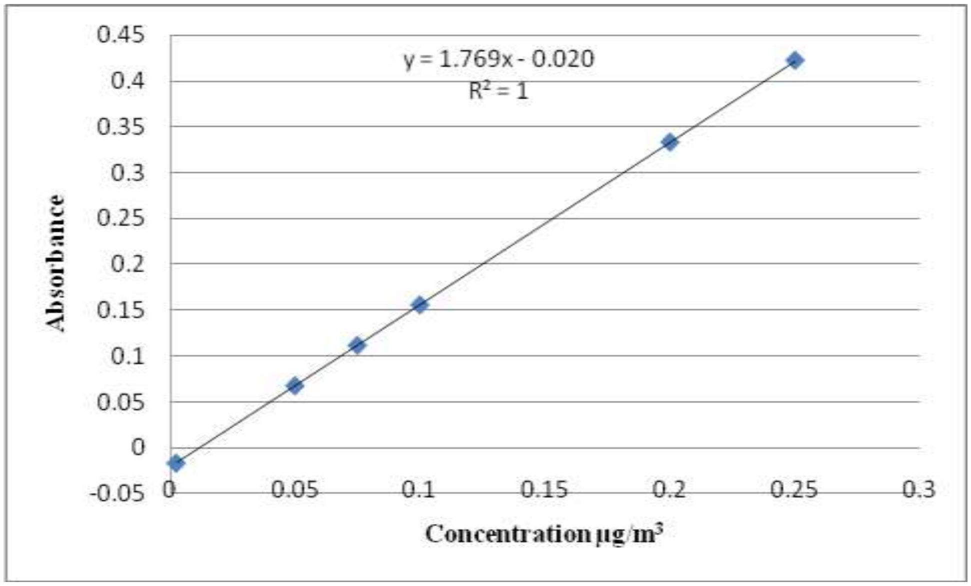


Figure 5.3: Calibration curve of $SO_2^-$ (0.05-0.25 µg/$m^3$).

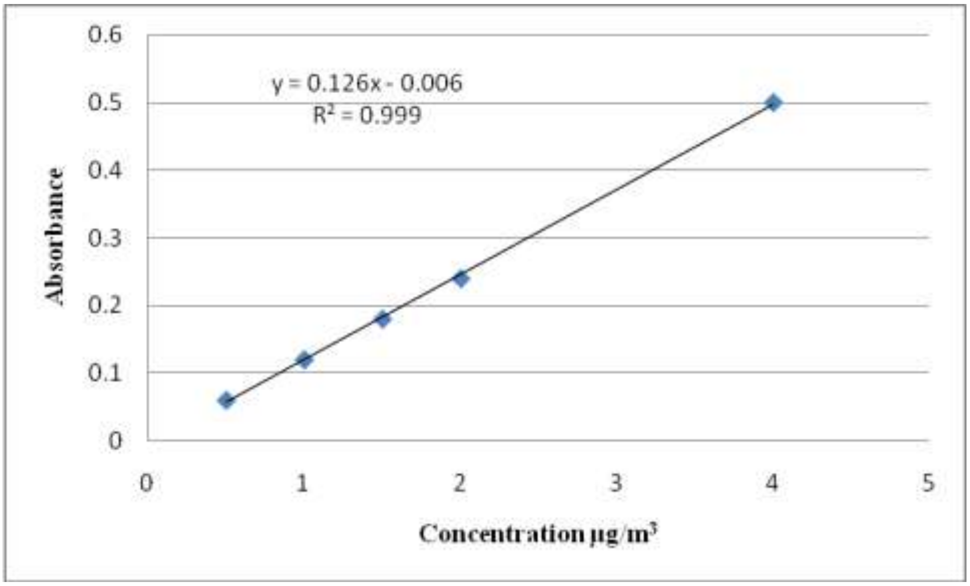


Figure 5.4: Calibration curve of $SO_2^-$ (0.5 – 4.0µg/$m^3$).

Apart from the chemical factors, passive analysis of the pollutants depends on the several physical factors such as; diffusion samplers size, mounting directions and conditions, and local meteorological conditions. This study was undertaken in confined with the test of three types of tubes which were easily available from the local market as to be used as diffusive samplers rather than manufacturing the passive samplers. Season wise two exposures analysis was conducted. First exposure used only one type of tube; Tube-1 was carried out in rainy season. The first exposure was aimed as a trial to test the method developed and the second exposure was carried out with the improvement and modification based on the results of first exposure analysis. Only five sites were used for the first exposure trial and three more sites were added for the second one with the use of all three types of tubes. Except the site 1, Ferm badge samplers from IVL, Sweden were deployed in the rest of the sites 2, 3, 4, 5, 6, 7and 8 . High volume sampler analysis was carried out in Site I during the exposure period and site 6 was the monitoring site of MOEST.

The first exposure analysis for $NO_2$ and $SO_2$ concentrations provided results for the rainy season (Tables 5.1 and 5.2) and the second exposure analysis provided information for dry season (Tables 5.3 and 5.4). The results of all location provide a reliable ambient $NO_2$ and $SO_2$ passive sampler with good precision, quite capable of comparison to the other samplers. The precision of $NO_2$ measurement for two week- exposure- period was found to be 21.4%, which was well within the acceptance criterion (25%) of the US National Institute of Safety and Health (NIOSH) for field performance of passive sampler applications in air (Seethapathy *et al*, 2008).

Table 5.1: Result of $NO_2$ µg/m$^3$ for rainy season exposure

| Sampling site | **$NO_2^-$ Concentration** | | | | | |
|---|---|---|---|---|---|---|
| | 20% TEA aqueous | | | 50% TEA aqueous | | |
| | Blanks | (µg/tube) | $NO_2$ in ambient air (µg/m$^3$) | Blanks | (µg/tube) | $NO_2$ in ambient air (µg/m$^3$) |
| I | 0.022 ± 0.001<br>% rsd = 2.66 | 0.134 ± 0.031<br>% rsd = 22.8 | 1.6 | 0.053 ± 0.001<br>% rsd = 2.66 | 0.141 ± 0.026<br>% rsd = 18.50 | 1.7 |
| II | 0.022 ± 0.001<br>% rsd = 2.66 | 0.07 ± 0.056<br>% rsd = 80.1 | 0.8 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.151 ± 0.039<br>% rsd = 25.60 | 1.8 |
| III | 0.022 ± 0.001<br>% rsd = 2.66 | 0.153 ± 0.006<br>% rsd = 4.20 | 1.8 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.033 ± 0.010<br>% rsd = 29.50 | 0.4 |
| IV | 0.095 ± 0.050<br>% rsd = 5.40 | 0.26 ± 0.090<br>% rsd = 37.08 | 3.1 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.224 ± 0.011<br>% rsd = 5.22 | 2.7 |
| V | 0.022 ± 0.001<br>% rsd = 2.66 | 0.246 ± 0.080<br>% rsd = 32.61 | 3.0 | 0.022 ± 0.001<br>% rsd = 2.66 | 1.51 ± 0.290<br>% rsd = 19.30 | 15.3 |

Table 5.2: Result of $SO_2$ µg/m$^3$ for rainy season exposure

| Sampling site | **$SO_2^-$ Concentration** | | | | | |
|---|---|---|---|---|---|---|
| | 20% TEA aqueous | | | 50% TEA aqueous | | |
| | Blanks | (µg/tube) | $SO_2$ in ambient air (µg/m$^3$) | Blanks | (µg/tube) | $SO_2$ in ambient air (µg/m$^3$) |
| I | 0.022 ± 0.001<br>% rsd = 2.66 | 0.037 ± 0.060<br>% rsd = 1.66 | 0.6 | 0.053 ± 0.001<br>% rsd = 2.66 | 0.053 ± 0.007<br>% rsd = 13.20 | 0.8 |
| II | 0.022 ± 0.001<br>% rsd = 2.66 | 0.085 ± 0.010<br>% rsd = 12.00 | 1.3 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.087 ± 0.005<br>% rsd = 5.40 | 1.3 |
| III | 0.022 ± 0.001<br>% rsd = 2.66 | 0.054 ± 0.040<br>% rsd = 7.27 | 0.8 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.055 ± 0.010<br>% rsd = 18.00 | 0.8 |
| IV | 0.095 ± 0.050<br>% rsd = 5.40 | 0.095 ± 0.050<br>% rsd = 5.40 | 1.4 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.075 ± 0.005<br>% rsd = 6.40 | 1.1 |
| V | 0.022 ± 0.001<br>% rsd = 2.66 | 0.164 ± 0.010<br>% rsd = 6.30 | 2.5 | 0.022 ± 0.001<br>% rsd = 2.66 | 0.136 ± 0.001<br>% rsd = 0.63 | 2.0 |

Precision of $SO_2$ measurements in all the locations were found to be <15%, which was comparable to the USEPA acceptance criterion (15%) for field performance of federal equivalent methods.

Table 5.3: Result of $NO_2$ µg/m$^3$ for dry season exposure

| Sampling site | $NO_2^-$ amount (µg/tube) | | $NO_2$ in ambient air (µg/m$^3$) |
|---|---|---|---|
| | Blanks | Samples | |
| I | 0.022 ± 0.001<br>% rsd = 2.66 | 0.502 ± 0.080<br>% rsd = 16.40 | 22.7 |
| II | 0.044 ± 0.009<br>% rsd = 19.68 | 0.323 ± 0.070<br>% rsd = 23.50 | 15.9 |
| III | 0.06 ± 0.001<br>% rsd = 1.60 | 0.257 ± 0.060<br>% rsd = 24.50 | 10.5 |
| IV | 0.032 ± 0.001<br>% rsd = 3.125 | 0.539 ± 0.030<br>%rsd = 6.30 | 24.6 |
| V | 0.032 ± 0.002<br>% rsd = 4.80 | 0.889 ± 0.035<br>%rsd = 3.99 | 21.1 |
| VI | 0.032 ± 0.002<br>% rsd = 6.61 | 1.078 ± 0.022<br>%rsd = 2.04 | 25.5 |
| VII | 0.034 ± 0.001<br>% rsd = 5.60 | 1.14 ± 0.030<br>%rsd = 3.37 | 52.1 |
| VIII | 0.023 ± 0.006<br>%rsd = 2.60 | 0.270 ± 0.039<br>%rsd = 14.77 | 12.3 |

Table 5.4: Result of $SO_2$ µg/m$^3$ for dry season exposure

| Sampling site | $SO_2^-$ amount (µg/tube) | | $SO_2$ in ambient air (µg/m$^3$) |
|---|---|---|---|
| | Blanks | Samples | |
| I | | Na | |
| II | 0.044 ± 0.009<br>% rsd = 19.68 | 0.317 ± 0.090<br>% rsd = 23.50 | 19.8 |
| III | 0.06 ± 0.001<br>% rsd = 1.60 | 0.343 ± 0.033<br>% rsd = 9.70 | 20.6 |
| IV | 0.032 ± 0.001<br>% rsd = 3.13 | 0.251 ± 0.040<br>%rsd = 18.20 | 15.1 |
| V | 0.032 ± 0.002<br>% rsd = 4.80 | 0.094 ± 0.010<br>%rsd = 10.86 | 8.6 |
| VI | 0.032 ± 0.002<br>% rsd = 6.61 | 0.265± 0.011<br>%rsd = 4.29 | 7.9 |
| VII | 0.034 ± 0.001<br>% rsd = 5.60 | 0.333 ± 0.010<br>%rsd = 3.37 | 10.0 |
| VIII | 0.023 ± 0.006<br>%rsd = 2.60 | 0.264 ± 0.002<br>%rsd = 0.90 | 15.8 |

In each station the concentration of both $NO_2$ and $SO_2$ were higher for second exposure period, as expected. The range of $NO_2$ as measured was 0.8 to 15.3 $\mu g/m^3$ for rainy season and 10.5 to 52.2$\mu g/m^3$ for dry season. Similarly, ranges of $SO_2$ were 0.6 to 2.5$\mu g/m^3$; and 7.9 to 20.6$\mu g/m^3$ for rainy season and dry season exposures, respectively.

The number of samples presented in Table 5.1 and 5.2 are lower than the number of exposed tubes installed and analyzed. Some of the field blanks and the exposed tubes gave negative absorbance values. The filter papers dropped out from some of the tubes at site 1, 4 and 5. The dropped out were more for NaOH plus NaI absorbent tubes. The damage or wreckage was less in second exposure.

A repeated test for repeated measures of both $NO_2$ and $SO_2$ for two exposures implied significant difference for five sampling sites (Site 1 –5) and also for first and second exposure periods. As mentioned earlier second exposures were carried out during the month of February-March with the additional three more sites (eight in total) sites 1 to 8. The concentration of $NO_2$ was highest at the site 7, Kalimati, a road side site with high traffic intensity. Site 8 was a residential site and indicated lowest concentration of $NO_2$. In other words, the vehicles could be the one of the major sources of $NO_2$ in Kathmandu. However, the $SO_2$ concentration at the sites 2, 3 and 8 (the Baneswor sites), were greater than in the sites 4, 5, 6 and 7, the city centers sites. The major sources of $SO_2$ in Kathmandu are the fuel use in cooking and industrial use.

Laboratory blanks were used to identify sources of contamination. As field blanks include both contributions from transport and exposure as well as chemical analysis and preparation, only the field blank values at the respective sampling sites were subtracted from the exposed tubes.  Data of the field blanks analysis for $NO_2$ and $SO_2$ concentration by using test method were analyzed. (Figures 5.5 and 5.6).

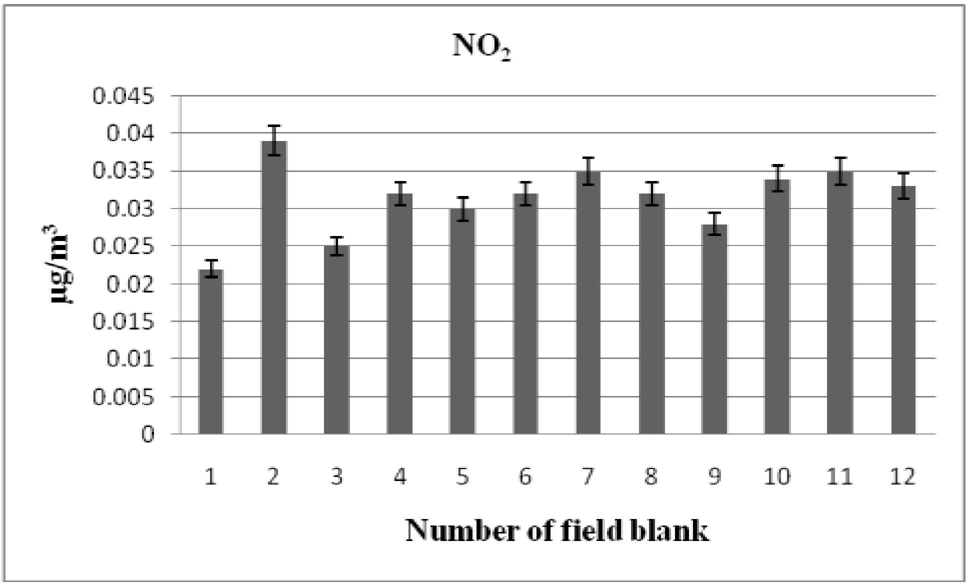


Figure 5.5: Field blanks of $NO_2$ analysis for test method. Error bar showing percentage.

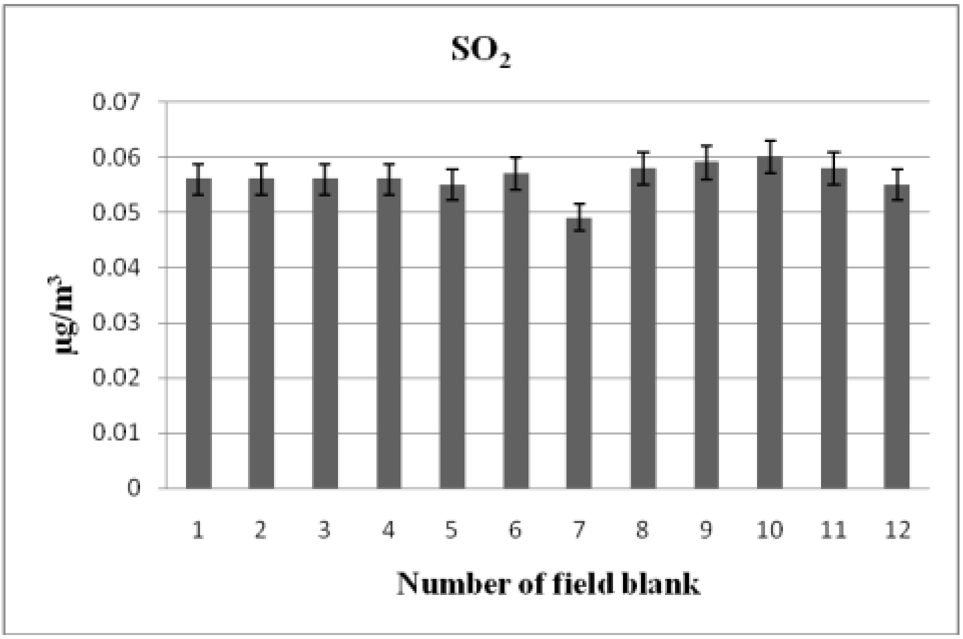


Figure 5.6: Field blanks of $SO_2$ analysis for test method. Error bar showing percentage.

Blank absorbance for unexposed tubes was found to be equivalent to mean nitrite mass of 0.03µg/m$^3$ for diffusion tubes using aqueous TEA solution. The blank values indicated the status of preparation of diffusive sampler and sampling methods. In this study the CV of blank tubes were found to be of 14.7% with standard error of the mean.0.0014 (figure5.5) for $NO_2$ and the CV of 4.9% and with standard error of the mean. 0.008 for $SO_2$ (figure 5.6).

There was considerable variation in blanks compared to the exposed tubes. This might be due to improper fittings of caps of the diffusion tubes. Some of the caps were later made air tight by using parafilm as a sealant. The values in all these tubes were lower than the tubes without parafilm. The variation in field blanks was also reported for the sampling of $NO_2$, $SO_2$, and other gases (Krochmal and Kalina, 1997; Ayers *et al.*, 1998; Tate, 2002). Tate (2002) reported the field blank values to be higher and more variable than in the exposed tubes. He inferred this to the contamination in the Ogawa passive samplers used for the collection of $NH_3$. He used new cleaning procedures to reduce the blank variations, but the blank problems could not be fully solved by these cleaning procedures. The blank values were also found to be strongly dependent on the analyte concentration in ambient air (Krochmal and Kalina, 1997). The source of contamination in blanks was also reported to be due to the permeation of $SO_2$ and $NO_2$ in polythene bags and plastic parts of samplers. Thus, the collected tubes were put inside the air tight plastic box during transportation and were stored in a refrigerator till the time of analysis. The tubes were not stored for more than three weeks. Gair *et al*. strongly recommended storing the samplers in a refrigerator (Gair *et al*., 1991). Their results also showed the variability in sample contamination. Krochmal and Kalina also found an increase in the mass of $NO_2^-$

for blanks storage of unexposed samplers with Whatmann 1 chromatographic paper (Krochmal and Kalina, 1997). They did not find any significant difference between samplers stored at -10$^0$C, 0 $^0$C and 20$^0$C.

### 5.1.1: Absorbent test

A study was conducted to compare between two absorbents for $NO_2$ and three absorbents for $SO_2$. No significant difference was found between two kinds of absorbents used for $NO_2$ (Table 5.5), still high percentage of drop out were observed for NaOH + NaI as an absorbent for ambient air $NO_2$ sampling.

Table 5.5: Results of $NO_2$ (μg/m$^3$) from exposure analysis using TEA and NaOH plus NaI (July, 2007)

| Sampling site | Tube-1 with TEA | Tube-1 with NaOH plus NaI |
|---|---|---|
| II | 3.99 ± 0.62 | 4.15 ± 0.68 |
| IV | 4.59 ± 0.98 | 4.15 ± 0.38 |
| V | 17.52 ± 17.00 | 15.08 ± 13.72 |

*Note: no significance difference between absorbents at $p \leq 0.05$.*

Variable results were obtained for three kinds of absorbents used for $SO_2$ (Table5.6). The study was conducted for only one exposure and more studies are necessary to draw definite conclusions. Due to damage or wreckages, only few numbers of tubes were remained for analysis, hence standard deviations are not presented in the table 5.6.

Table 5.6: Results of $SO_2$ ($\mu g/m^3$) from exposure analysis (March, 2008)

| Sampling site | $SO_2$ ($\mu g/m^3$) from Tube-1 with absorbents | | |
|---|---|---|---|
| | TEA | NaOH | $Na_2 CO_3$ |
| II | 18.20 | Na | 3.40 |
| III | 22.72 | 2.42 | 3.50 |
| IV | 15.40 | Na | 2.00 |

Na = not available due to dropped out of filter paper from tubes.

*Note: Significant difference between exposed tubes with absorbents between, TEA and NaOH, TEA and* $Na_2 CO_3$ *at* $p \leq 0.001$ *level but no significance difference between NaOH and* $Na_2 CO_3$ *absorbents at* $p \leq 0.05$.

There was also a large interference peak in the chromatogram using NaOH as the absorbent. Another problem was unsuitability to use other absorbents except TEA in these filter papers, as the filter papers tended to drop out. The absorbent might be required to make viscous so as to avoid the dropping of filter papers. The absorbent are often added to make it viscous by adding wetting agents such as Brij 35 (Plaisance *et al.*, 2002). The performance of a passive sampler is critically dependent on the selection and the use of a sorbent with high sorption efficiency (Brown, 2000). Reverse diffusion can also occur if the vapor pressure of the analyte at the sorbent surface is greater than the external concentration. He recommended to use an absorbent with high absorption capacity and low vapor pressure of the absorbed material or of the reaction product formed by a reactive sorbent

Thus, the selection of absorbent has an important part in passive sampling. Though there are other absorbents described in the literature such as NaI + $Na_2CO_3$, NaI + NaOH, KOH + glycerol, $Na_2CO_3$+TEA etc, TEA was good and more popular as the absorbents for both $NO_2$ and $SO_2$ measurements. Some problems had also been reported with using TEA as the absorbent. The losses of $NO_2$ were observed by using TEA for long-term sampling (Ferm and Svanberg, 1998). $NO_2^-$ TEA adduct is prone to photodegradation while exposing the tubes in sun (Santis *et al.*, 2003). It was recommended to find out the best absorbent for passive sampling of $NO_2$ and $SO_2$ measurements according to the local environment.

Not only the type of absorbent but their volume and concentration also were the integral part of the passive sampling. Five exposure sets were deployed to determine whether the aliquot volume used on the diffusion tube also contributed to differences in $NO_2$ uptake by the samplers (Comparison of aliquot volume). Five sets of triplicates of two different volumes of 10µl, and 30 µl of 20%, 30% and 50% v/v aqueous TEA were tested for Tube one for two weeks exposure and compared. Twenty µl TEA volumes compared with these from comparison of concentration test exposure and the results were analyzed (Figure 5.7).

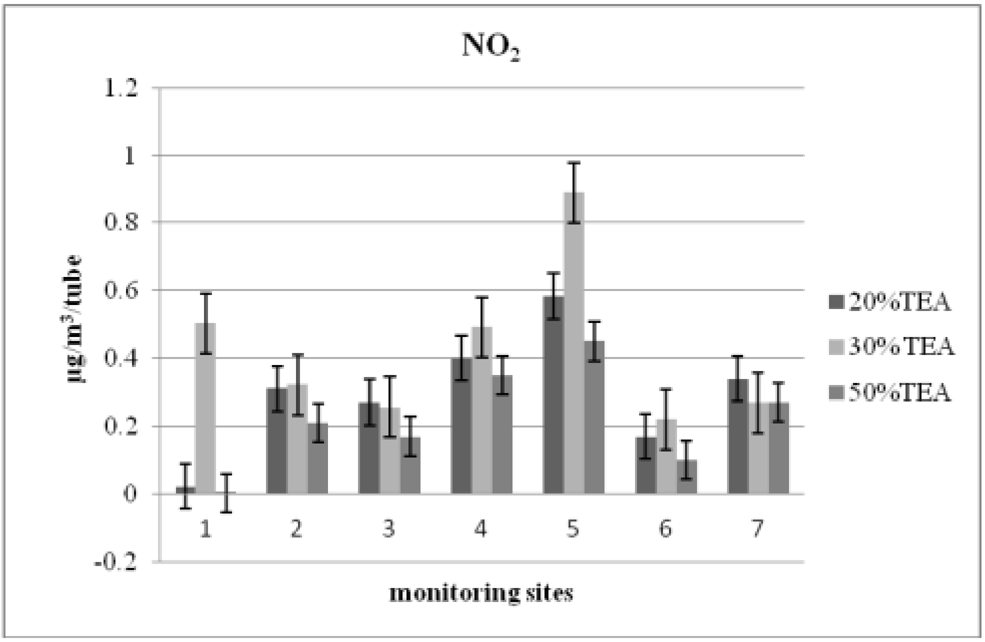


Figure 5.7: Comparision between TEA concentrations for ambient $NO_2$ sampling using test sampler. Error bars represent standard error.

Pair t-tests showed no difference between compared sampler means, indicating that $NO_2$ uptake was equivalent for samplers prepared using aliquot volumes in the range 10-30 µl. However for the samplers with aliquot volume 10 µl, there was higher rate of drop out. Further exposure sets compared for three different concentrations of TEA, 20%, 30% and 50% using 20 µl of aliquot volumes showed no significant different between the TEA concentrations at the tested environment using ANOVA at $p \leq 0.05$ confidence level for the first exposure set in rainy season, while a significant difference between the three different concentrations and highly significant different between the sites were observed for the dry season samples exposure. (Figure 5.7 and Appendix Va)

Absorbent solution of 50% v/v/ TEA in deionized water impedes the absorption of $NO_2$ gas and subsequent conversion to nitrite (Kirby *et al*, 2000). The reason for this behavior was associated with TEA basicity. In aqueous solution, TEA acts as a weak base: pKb = 7.77 at 25$^0$C, measured at/ extrapolated to indefinite dilution. There may be insufficient water molecules available in a solution of 50% v/v TEA to achieve equilibrium dissociation. The absorption of the acidic $NO_2$ gas as nitrite may be incomplete if complexation between nitrite ions and TEA is restricted by lack of hydroxyl ions in the solution, resulting lower accumulation of nitrite ion than for other lower concentrated solutions (Kirby *et al*, 2000). The earlier study by Palmes and Johnson mentioned that the hydration of TEA is necessary for conversion of $NO_2$ to nitrite (Palmes and Johnson, 1987). In the same study the mole ratio of $NO_2$ to TEA for a polluted environment (50 ppb of $NO_2$) suggests a presence of very large excess of TEA, 1:1000 for 2 weeks and 1:500 for 4 weeks exposure periods. This favors the current tested result of no significant difference between the 20%, 30% and 50% TEA v/v absorbents during rainy season and significant different for dry season at $p\leq 05$ and $p\leq 01$ level of confidence respectively. It was because the concentrations were higher during dry season.

Similar exposure analysis for $SO_2$ also showed the insignificant difference among the concentration and volume of the aliquot of TEA as absorbent at 20%, 30% and 50% v/v TEA at $p \leq 0.05$ confidence level.

### 5.1.2: Comparison between absorbent bases (GF filter paper, Whatmann 40 and Quantitative- 5 filter paper as absorbent base)

A comparative study was conducted to find out the efficiency of sampling mediums by using three types of filter papers, GF filter paper, Whatmann 40 (What-40) and

Qualitative-5 (Q-5) filter papers for analysis of $NO_2$ and $SO_2$. The study was conducted at site 3 and site 7 for $NO_2$ and $SO_2$ respectively during March 24, 2010. The results were analyzed (Figure 5.8). For each exposure set, details, regarding, number of samplers, mean $NO_2$ and $SO_2$ concentrations and RSD are presented. (Appendix Vb)

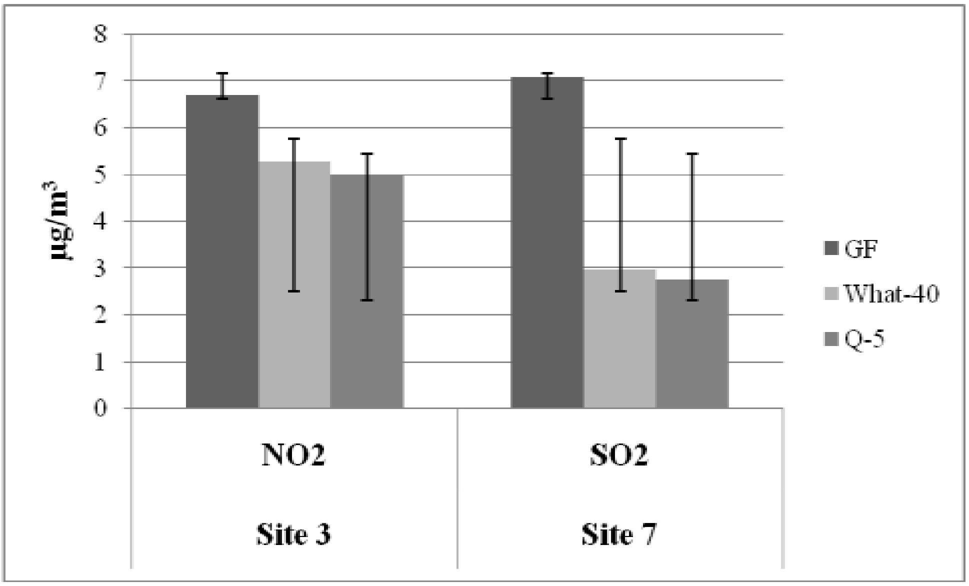


Figure 5.8: Comparison between three types of filter paper as absorbent for test method analysis of ambient $NO_2$ and $SO_2$ (exposure: March, 2008).

*Note: In Figures 5.8 -5.10 error bars represent standard deviation.*

Two –sample Student's t-tests (two-tailed) were used to estimate the level of significance of any differences in $NO_2$ and $SO_2$ measurements by the compared absorbent bases. Sampler means are significantly different if the *p* value is ≤ 0.05 (95% confidence level), and very highly significantly different if *p* value is ≤ 0.01 (99% confidence level). A highly significant difference was observed between the GF-filter papers and Whatmann 40 and Quantitative 50 for both the pollutants. But, there was no significant difference between Whatmann 40 and Quantitative 5 filter papers. (Appendix Vb)

There were differences in $NO_2$ and $SO_2$ concentration uptake depending on the different types of the sampling medium used in the preparation of samplers as well. The filter papers used in this experiment were not very thick and absorbents soaked were less (8-20 μl). Thicker filter paper with the ability to absorb larger volumes of absorbent can have longer contact time with gases. Thick filter paper, Whatmann no. 17 was reported to be the best filter paper in terms of capture efficiency and recovery percentage (Axelrod and Hansen, 1975). The study was based upon the comparison between Whatmann no. 3, 4, 5, 17, 40, 42, and 50, filter papers, and Millipore blotter paper, to measure $SO_2$ concentrations. An investigation on the efficiency of filter papers is required to find out the best filter paper for sampling conditions.

### 5.1.3: Comparison between three types of tubes:

Sizes of the tubes are very important in the uptake of ambient $NO_2$ and $SO_2$. In other to find the most suitable locally available tubes for sampling of $NO_2$ and $SO_2$, a study was conducted among the three tubes, Tube- 1, Tube -2 and Tube-3. Triplicates of three diffusion samplers from each type of tubes were co-exposed for two weeks and analyzed for respective concentrations (Figures 5.9 and 5.10).

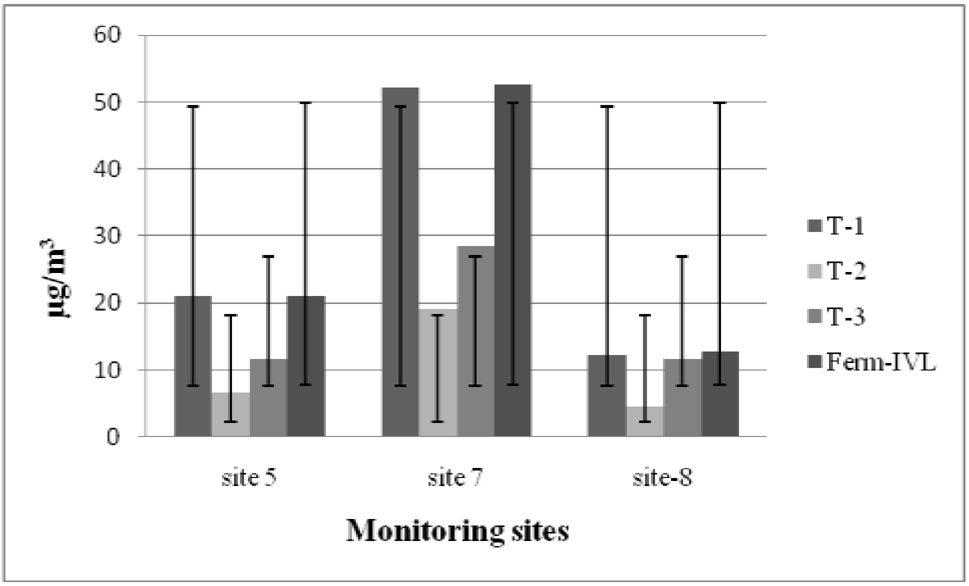


Figure 5.9: Comparison between three types of tubes for ambient $NO_2$ monitoring by test method (exposure: March, 2008).

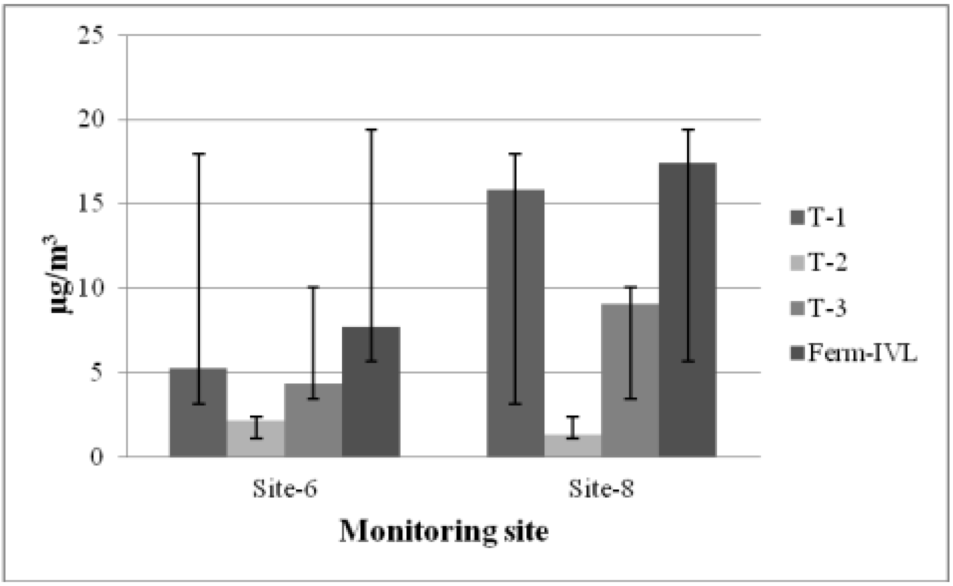


Figure 5.10: Comparison between three types of tubes for ambient $SO_2$ monitoring by test method (exposure: March, 2008).

One way ANOVA test shows significant different among the tested three different tubes at t= 0.05 for both the pollutants (Appendix Vc). Tube -2 showed the lowest sampling result. Transparency of the tube might be the reason for this lower efficiency.

In this study, transparent polyethylene tubes gave more underestimation of $NO_2$ measurements compared to less transparent T1 tubes. There might have been more photo degradation of $NO_2$-TEA adduct in T-3 tubes as it was exposed to sunlight. The precautions at every analytical step, investigation of the potential interferences, and following the recommendations of previous researches could help to reduce errors.

## 5.1.4: Comparison with other methods:

### 5.1.4.1: Comparison with Ferm IVL- passive sampler result

All of the test samplers are co-exposed with Ferm-Badge type sampler from IVL, Sweden. These were analyzed in IVL and the results of IVL-sampler for both seasons for $NO_2$ and $SO_2$ concentrations are presented (Table 5.7).

Table 5.7: IVL-sampler result for both exposure periods

| Site | $NO_2$ µg/m$^3$ | | $SO_2$ µg/m$^3$ | |
|---|---|---|---|---|
| | Rainy season | Dry season | Rainy season | Dry season |
| I | Na | | | |
| II | 12.4 | 18.9 | 1.1 | 17.9 |
| III | 10.3 | 15.4 | 0.8 | 20.3 |
| IV | 21.7 | 26.9 | 2.2 | 15 |
| V | 18.5 | 21.0 | 1.7 | 11.1 |
| VI | | 26.1 | | 7.7 |
| VII | | 52.6 | | 11.2 |
| VIII | | 12.8 | | 17.4 |

The site seven (road side) was the most polluted one amongst the eight sites studied for ambient $NO_2$. The lowest $NO_2$ concentration was observed in site eight, which was a background area. While, the sites 2, 3, and 8 were from the same area, New Baneswor, had higher concentrations of $SO_2$ than other sites irrespective to traffic intensity.

A linear regression analysis was performed for $NO_2$ and $SO_2$ measured with the current test passive samplers on the ferm-IVL passive sampler (Figures 5.11, 5.12, 5.13 and 5.14). Strong correlations were observed between the current test sampler and ferm-IVL sampler result for both the seasons (Figures 5.11 and 5.12). It confirmed the validity of the reliable ambient $NO_2$ and $SO_2$ test samplers with good precision, quite capable of comparison to the ferm-IVL sampler.

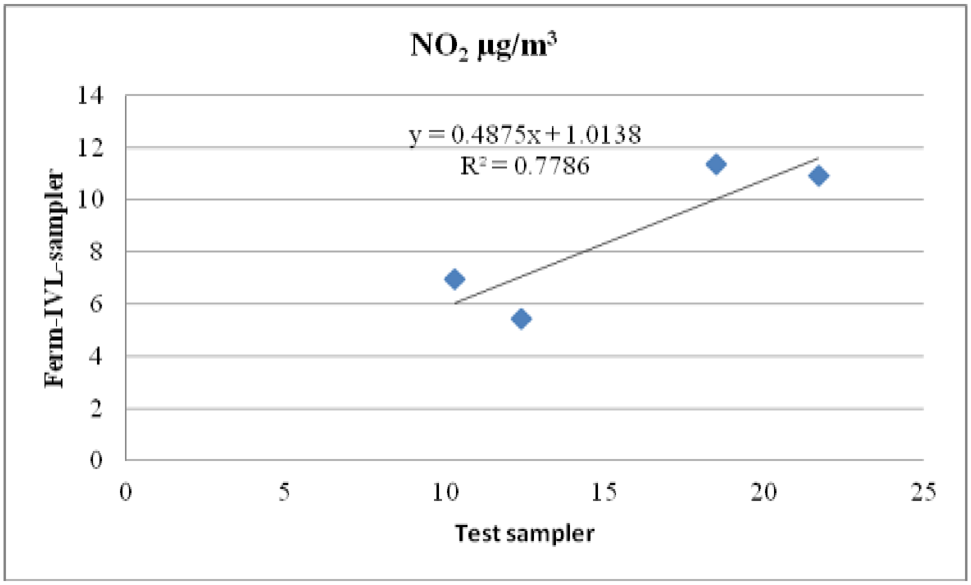


Figure 5.11: Corelation of $NO_2$ concentration between test-method with IVL-sampler for rainy season.

Accuracy, defined as the percent deviation of $NO_2$ measured by test passive samplers from the ferm-IVL samplers, was identified as over all under estimation of 18% for one week exposure and 96 % that for four week exposure for dry season, while it was 68% for first exposure-Rainy season. In simplest form, the test passive samplers underestimates the ambient $NO_2$ than Ferm-IVL samplers, though it did show an over estimation of 0.5%.

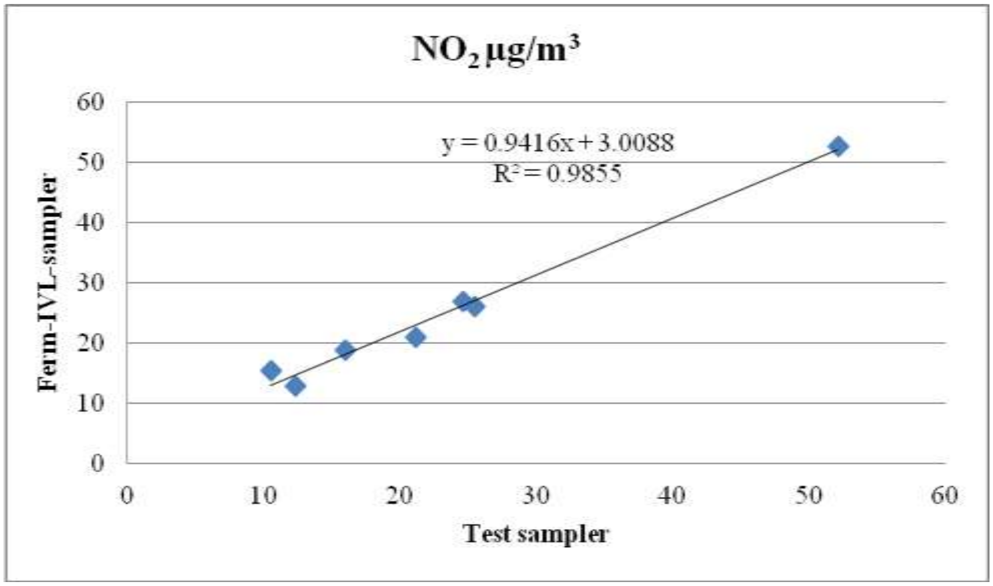


Figure 5.12: Corelation of $NO_2$ concentration between test-method with IVL-sampler for dry season.

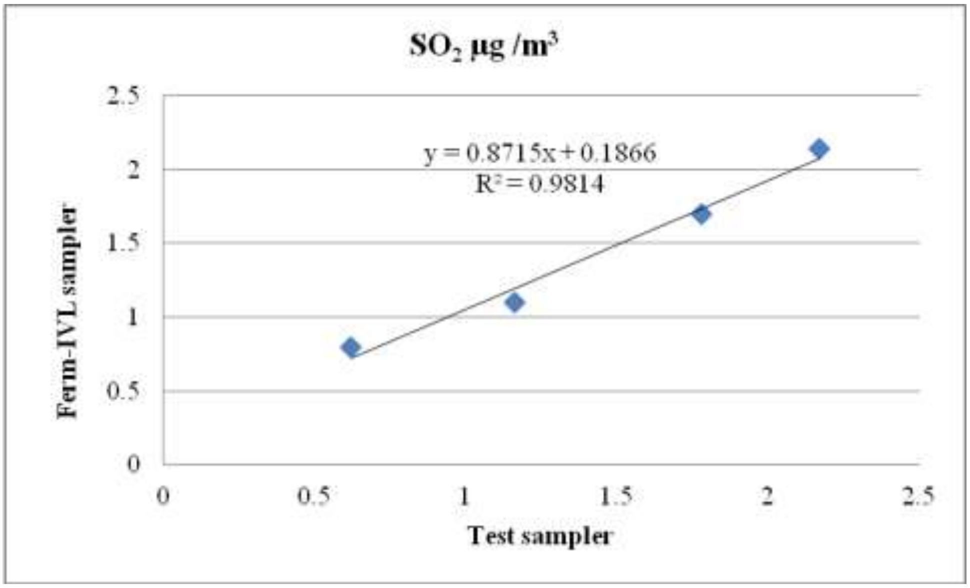


Figure 5.13: Corelation of $SO_2$ concentration between test-method with IVL-sampler for rainy season.

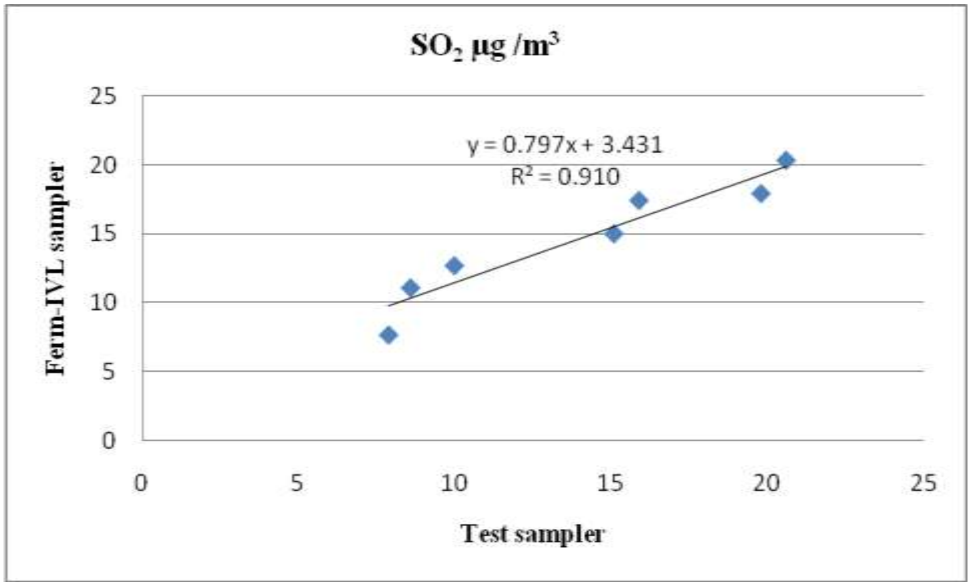


Figure 5.14: Corelation of $SO_2$ concentration between test-method with IVL-sampler for dry season.

Similarly, the percent deviation of $SO_2$ measured by test passive samplers from the ferm-IVL samplers, were identified as over estimation of 3.8% and underestimation of 18% for one week exposure for dry season. It was over estimation of 3.9% and underestimation of 22.5% first exposure-Rainy season. Several factors attributed to this deviation, notably the concentration and amount of absorbent medium, sampler size and the meteorological condition of monitoring period. During dry season, temperature inversion restricts the dispersion of the pollutants resulting elevated concentration in the Kathmandu valley. As a result the one week exposure analysis was sufficient and suitable for both ambient $NO_2$ and $SO_2$ monitoring during dry season. It is further revealed by the weekly variation result analyzed below. Saturations were observed during first week in dry season for both $NO_2$ and $SO_2$. Hence, time weighted average made underestimation for four week exposure result. Better results during second exposure analysis (Dry season) compared to the first exposure results attributed to the improvement in the sampler preparation and modifications undertaken.

The fact that $NO_2$ and $SO_2$ measured with the current test passive samplers correlated extremely well with that measured with the Ferm-IVL samplers and it further suggested that the bias was systematic. Such systemic bias might be attributed to the assumption made in calculating concentration with the passive samplers, volume and with chemical speciation capability of the absorbing medium. Alternatively, seasonal and /or site correction factors could be developed and applied to adjust passive sampler data (Ott, 2007). Regression analysis revealed the valid comparison since the parameters, slope, intercept and Pearson correlation coefficient, r; are within the tolerance set by US EPA's acceptance criterion Environment monitoring (Table5.8).

Table 5.8: Comparison of field measurements of test- method with IVL- sampler, to EPA acceptance criteria.

|  | $NO_2$ µg/m$^3$ |  |  | $SO_2$ µg/m$^3$ |  | EPA Acceptance Criteria |
|---|---|---|---|---|---|---|
|  | Rainy (4 weeks exposure) | Dry (1 weeks exposure) | Dry (4 weeks exposure) | Rainy (4 weeks exposure) | Dry (1week exposure) |  |
| Slope of Regression | 0.510 | 0.941 | 0.136 | 0.871 | 0.797 | 1 +/- 0.12 |
| Intercept of Regression | - 2.630 | + 3.008 | + 13.720 | 0.186 | 3.431 | -7 to 7 |
| $R^2$ | 1.660 | 0.985 | 0.104 | 0.981 | 0.910 | - |
| Pearson Corelation Coefficient, r | 0.408 | 0.993 | 0.323 | 0.991 | 0.954 | 0.946 |
| Precision (rms CV) | 20.70 | 2.02 | 14.97 | 0.10 | 1.40 | 15% |
| Significant two sample t-test difference, *P* value# | 0.04 | 0.05 | - 0.71* | 3.14 | 1.51 |  |

*Note: # $p \leq 0.05$ (significant), and $p \leq 0.001$ (very highly significant); *Significant difference*

The method comparison was further done by Pair t-test (TWO-tailed) to estimate the level of significance of any differences in $NO_2$ and $SO_2$ measurements by the compared two methods. Sampler means are significantly different if the $p$ value is $\leq 0.05$ (95% confidence level), and very highly significantly different if $p \leq 0.001$ (99.9% confidence level).

For all the exposure analysis, first exposure (rainy season) and second exposure (dry season) of both the parameters $NO_2$ and $SO_2$ under tested periods were not significantly different except for four week dry season exposure for $NO_2$. It was significantly different at $p \leq 0.05$ (95% confidence level).

### 5.1.4.2: Weekly variation analysis

The appropriate duration of exposure period is important in the passive sampling monitoring and analysis of ambient air quality. The combined factors including volume and saturation of absorbent solution, absorbent medium itself, ambient concentration and nature of the pollutant under measurement and local meteorology determined the suitable exposure duration in diffusive measurement. In order to find out the suitable duration of exposure for the test sampler in the Kathmandu valley was carried out (methodology section4.6.4). Weekly exposure analysis result of ambient $NO_2$ carried out at two sites 2 and 4 up to fourth week period and analyzed (Figure 5.15). For $SO_{2,}$ it was carried out at three sites, 2, 3 and 5 and analyzed (Figure 5.16).

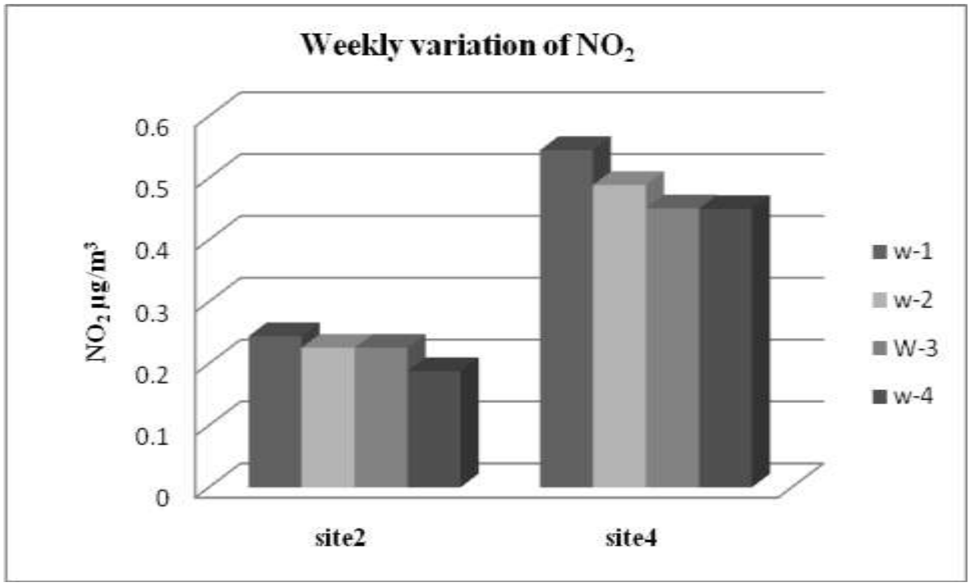


Figure 5.15: Weekly variation of ambient $NO_2$ µg/m$^3$ measurement per tube for test diffusion tube sampler (exposure: March 2008).

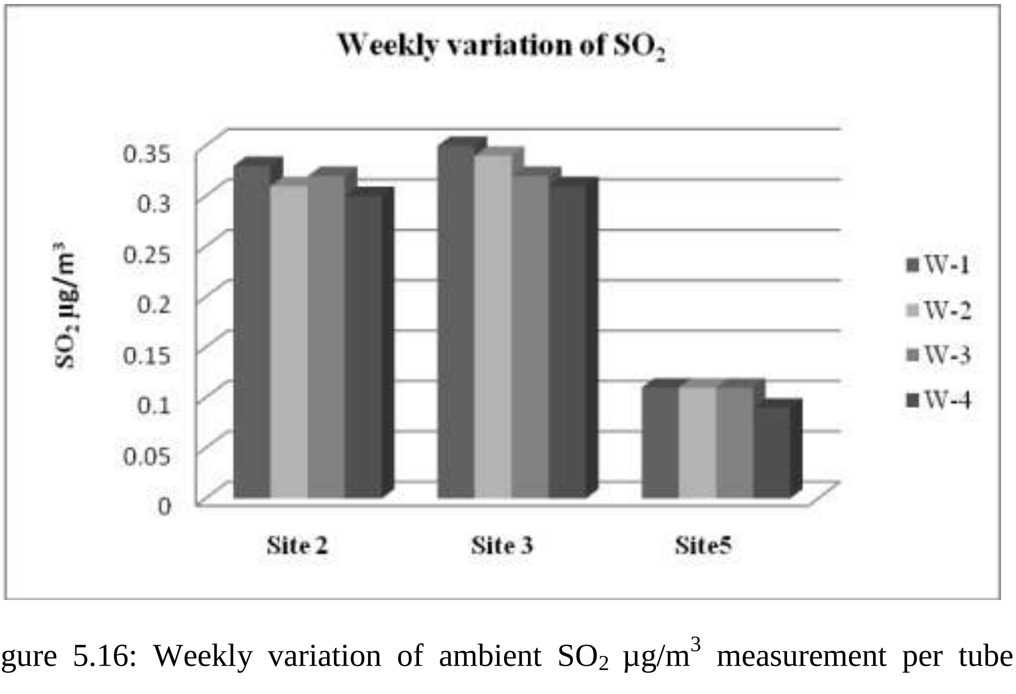


Figure 5.16: Weekly variation of ambient $SO_2$ µg/m$^3$ measurement per tube for test diffusion tube sampler (exposure: March 2008).

Saturations were observed during first week in dry season for both $NO_2$ and $SO_2$. Two way analysis of variance (ANOVA) for weekly variation of $NO_2$ showed that there were no significant different between the weeks at $p \leq 0.05$ (95% confidence level). There were significantly different between sites at $p \leq 0.05$ (95% confidence level) (Appendix Va).

Hence from the ANOVA test and the figure 5.15 it was evident that though there was no significant loss of $NO_2$ for four week exposure time, one week was sufficient and suitable for analysis of ambient $NO_2$ for dry season. Similarly it was suitable up to two weeks for ambient $SO_2$.

### 5.1.4.3: Comparison of test method with chromatographic analysis

Chromatographic analysis was carried out at Department of Environmental Engineering and Department of Inorganic Chemistry, Padova University, Italy. Thirty test samplers from first exposure were sealed and brought to be analyzed by ion chromatography. Similarly, diffusive test samplers were developed and exposed at Padova University premises for one and two weeks period during November-December, 2007 and analyzed by both spectrophotometer and ion chromatography for comparison.

**Analysis by ion chromatography to determine $NO_2$ and $SO_2$**

The exposed tubes after extraction with eluent and $H_2O_2$ were left for at least 15 minutes. The solution was then filtered and injected into an ion chromatograph under optimized conditions to determine $NO_2^-$ and $SO_4^{2-}$ concentrations.

**Ion chromatograph conditions**

Ion chromatograph conditions were optimized after checking the different eluent flow rates. The eluent flow rate of 1.5 ml/minute and eluent concentration of 1.8 mM $Na_2CO_3$/ 1.7 mM $NaHCO_3$ were selected for the experiment. The other optimized conditions

(Table 5.9) for ion chromatograph with IonPac AS4A were the conditions reported to give high sensitivity and good resolution (Na-Chiangmai, 1997).

Table 5.9: Optimized IC conditions

| **Operation** | **Optimal Conditions** |
|---|---|
| Eluent | 1.8 mM $Na_2CO_3$/ 1.7 mM $NaHCO_3$ |
| Eluent flow rate | 1.8 ml/min |
| Suppressor | Anion self-regenerating suppressor |
| Detector | Conductivity |
| Background conductivity | 0.4 X 10-2 µS |
| Working pressure | 1180- 11900 psi |
| Detector temperature compensation | 1.7% /$^0$C |
| Sample loop volume | 10 µl |
| Analysis time | 8 minute |

Table 5.10: Repeatability of $NO_2^-$ and $SO_4^{2-}$ determinations

| Run | $NO_2^{\ -}$ | | $SO_4^{\ 2-}$ | |
|---|---|---|---|---|
| | Retention time (min) | Peak area (*$10^5$) | Retention time (min) | Peak area (*$10^5$) |
| 1 | 1.413 | 2.4 | 3.62 | 3.4 |
| 2 | 1.413 | 2.5 | 3.62 | 3.0 |
| 3 | 1.413 | 2.2 | 3.62 | 1.1 |
| 4 | 1.413 | 3.4 | 3.63 | 1.1 |
| 5 | 1.407 | 2.0 | 3.62 | 1.1 |
| 6 | 1.407 | 2.2 | 3.62 | 2.6 |
| 7 | 1.403 | 3.1 | 3.60 | 2.6 |
| Mean | 1.409 | 2.5 | 3.60 | 2.1 |
| SD | 0.004 | 0.520 | 0.009 | 1.00 |
| %rsd | **0.29** | **20.30** | **0.25** | **47.00** |
| Error M | 0.0015 | 0.2000 | 0.0034 | 0.3800 |

The repeatability in the IC was checked by injecting a mixed standard solutions containing 1 µg/ml each of $NO_2^-$ and $SO_4^{2-}$ into IC system at the optimized conditions.

The ion chromatograph with IonPac AS4A in optimized conditions provided very good precision for $NO_2^-$ and $SO_4^{2-}$ determinations (Table 5.10). The % rsd of peak area obtained for $NO_2^-$ was better than for $SO_4^{2-}$, while it was the reverse for the retention time. The precision for retention time indicates that $NO_2^-$ was more sensitive to the chromatographic conditions than $SO_4^{2-}$. The precision obtained were suitable for determination of $NO_2^-$ and $SO_4^{2-}$.

**Determination of nitrogen dioxide ($NO_2$) concentration**

Nitrite ($NO_2^-$) in diffusion tubes was calculated with the help of calibration curve. Two ranges of $NO_2^-$ standards with low and high concentrations were prepared for the calibration curve. Blanks and exposed tubes were measured subsequently at optimized ion chromatograph conditions with background conductivity of 1 and 3 µS, respectively. The concentration of $NO_2$ in the exposed tube was subtracted from the field blank at corresponding sites. This value was then used in equation 6 to calculate the concentration of $NO_2$ (µg/m$^3$) in ambient air.

There was a problem in the analysis of $NO_2^-$ by ion chromatograph. A chloride peak next to the $NO_2^-$ peak tends to overlap with the $NO_2^-$ peak (figure 5.17 and 5.18). In only few cases, these peaks were separated, those were not clear enough for analysis. Different flow rates ranging from 0.5 to 2.0 ml/min and eluent concentrations in the ratio of 2.7 mM $Na_2CO_3$/0.3 mM $NaHCO_3$, 2.6 mM $Na_2CO_3$/3.3 mM $NaHCO_3$, and of 2.2 mM $Na_2CO_3$/2.8 mM $NaHCO_3$ were tested. These eluent concentrations were reported for the

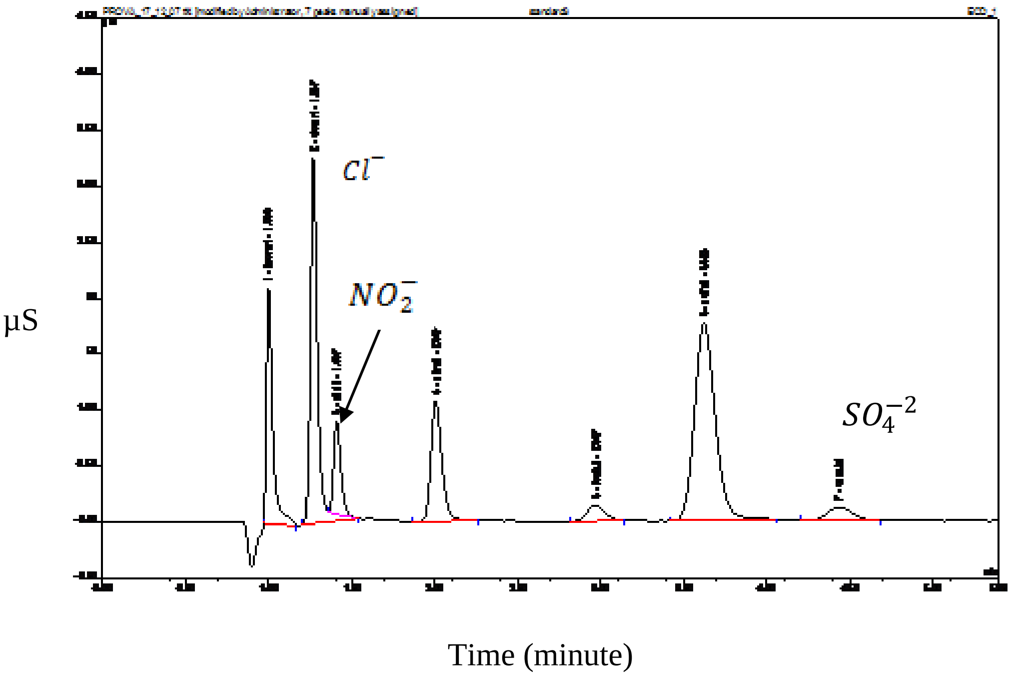


Figure. 5.17: Example Chromatogram presenting Standard sample run.

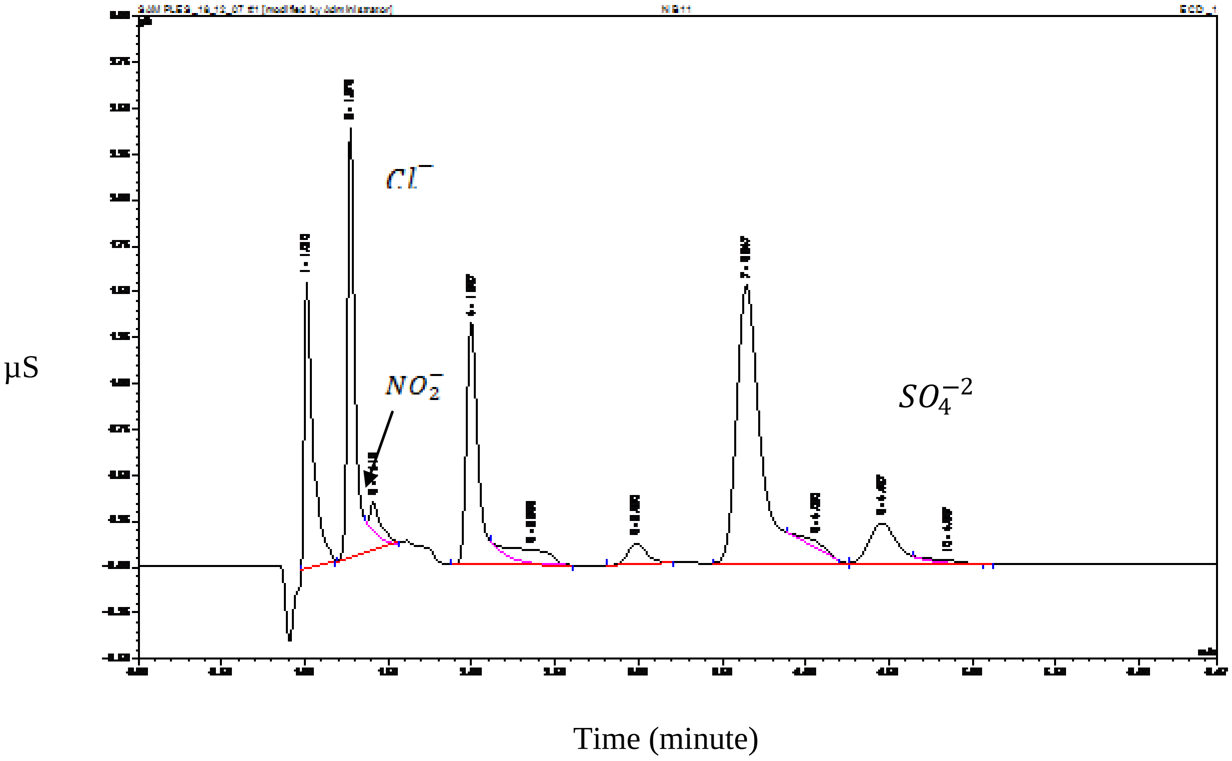


Figure 5.18: Example Chromatogram presenting sample run interference of chloride peak can be distinctly observed.

separation of $NO_2^-$ and $SO4^{2-}$ by ion chromatography (Santis *et al.*, 1997; Kasper-Giebl and Puxbaum, 1998; Small, 1989). The problem still persisted.

Thus, analysis of $NO_2^-$ by IC could not be accomplished with satisfactory results because of interference with $NO_2^-$ determination by a peak adjacent to it. In most cases, $NO_2^-$ peak was not separated. There was also a presence of $NO_3^-$ peak in chromatograms suggesting the possible oxidation of $NO_2^-$ to $NO_3^-$. Addition of $H_2O_2$ might have favored this oxidation process, as suggested by other researches (OSHA.1991; Shakya.2004). They mentioned of $NO_2$ concentration calculated from separated $NO_2^-$ peaks were lower than the results of $NO_2$ concentrations analyzed by the spectrophotometer. Lower measurements of $NO_2$ concentrations by IC also suggest the losses of $NO_2^-$ because of its oxidation to $NO_3^-$. Chloride peak was adjacent to $NO_2^-$ peak and because of the high chloride concentration it tended to overlap with $NO_2^-$ peak. Separate $NO_2^-$ peak can be obtained only for reduced chloride ($Cl^-$) concentration. At higher concentrations of $Cl^-$ in the sample (>5 μg/ml), $NO_2^-$ ion appears as a shoulder on the $Cl^-$ peak during IC analysis (OSHA, 1991). The IC conditions have to be optimized for the analysis of $NO_2^-$, or interferences, such as $Cl^-$ have to be reduced or removed before injection into the IC. The chromatogram with the overlapping $NO_2^-$ peak and the chromatogram with the separation of $NO_2^-$ peak were studied (Figure 5.17 and Figure 5.18).

Smith and Chang reported problems in $NO_2^-$ analysis by the IC (Smith and Chang, 1983). It was due to the similar affinity of the $NO_2^-$ and $Cl^-$ ions for resin, making it difficult to determine $NO_2^-$ in the presence of high $Cl^-$ concentrations. In this case, chemical pretreatment may help to remove high $Cl^-$ concentrations. $NO_2^-$ ion interacts with the anion suppressor resin, and the water dip is also a problem. Increase in peak height may be observed from repetitively injected $NO_2^-$ standards. It was recommended to improve sample dilution or pretreatment, use of different lengths or types of separator columns, use of different eluent strengths or types of separator columns, and use of different ion-separating mechanisms.. They also recommended the use of L-20 separator column to enhance $Cl^-$ and $NO_2^-$ separation. A system using a gradient pump to determine $NO_2^-$ in the presence of high $Cl^-$ concentrations was also recommended (Gair *et al.*, 1991).

### Determination of sulfur dioxide ($SO_2$) concentration

The $SO_4^{2-}$ in diffusion tubes was calculated with the help of calibration curve. Two ranges of $SO_4^{2-}$ standards with low and high concentrations were prepared for the calibration curve. Blanks and exposed tubes were measured subsequently at optimized ion chromatograph conditions with background conductivity of 1 and 3 μS, respectively. The average value of $SO_4^{2-}$ in the tubes from two injections and after conversion into the corresponding quantities of $SO_2$ in the tube and subtraction from the field blank values at the corresponding sites was used in equation 7 to determine $SO_2$ concentration (μg/m$^3$) in ambient air. The details of calculation are shown in Appendix IV.

The results of $SO_2$ (μg/m$^3$) in ambient air calculated from four weeks exposure from Kathmandu at five different sites and those at Padova university premises were examined (Tables 5.11 and 5.12).

Table 5.11: Result of ambient $SO_2$ measurement using IC analysis exposed in Kathmandu

| Site | $SO_2$ µg/m$^3$ | |
|---|---|---|
| | IC | Test method ( Spectrophotometer) |
| 1 | 4.10 | 1.20 |
| 2 | 3.70 | 1.16 |
| 4 | 2.14 | 2.17 |

*Note-Pair t test shows No significant different at* $p \leq 0.05$.

Table 5.12: Ambient $SO_2$ measurement using IC analysis and automated fluorescent analyzer (Padova municipality) in Padova university, Italy

| NO. | Mean $SO_2$ µg/m$^3$ | |
|---|---|---|
| | One week Exposure | Two week Exposure |
| Test sampler +IC | 5.4±0.114 (n=5)<br>CV=2.1% | 11.3±0.336 (n=5)<br>CV=2.9% |
| fluorescent analyzer | 6 | 10 |

It was observed that comparison of two analysis methods for the developed passive sampler, IC analysis overestimates over spectrophotometer of about 45% while further statistical analysis using student t-test showed no significant different between the methods at $p \leq 0.05$ confidence level for the exposure analysis during rainy season from Kathmandu.

### 5.1.4.4: Comparison with automatic continuous measurement

Data for automatic sampling, measured by a chemiluminescence monitor for $NO_2$ and fluorescent analyzer for $SO_2$, were obtained from the Pollution Control Department, Padova municipality, Italy for sampling at Padova university premises.

A scatter plot diagram was drawn between the average daily measurements of $NO_2$ from the chemiluminescence monitor and the results of $NO_2$ after spectrophotometric analysis of extract from tubes exposed for one week period (Figure 5.19).

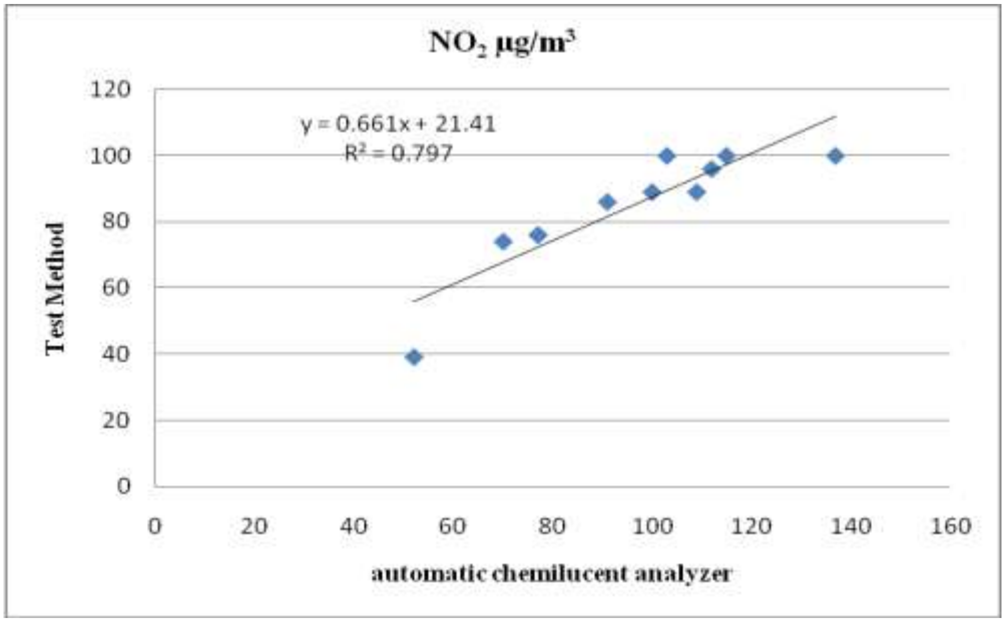


Figure 5.19: Corelation between test-method and continuous automatic chemiluminiscence monitor for $NO_2$ µg/m$^3$ measurements at Padova University, Italy (November-December, 2007).

There was an underestimation by Test method in comparision to chemiluminiscence monitor data of about 10.2% for $NO_2$. Similar to many other studies (Campbell *et al.*, 1994; Gair and Penkett, 1995; Heal and Cape, 1997; Heal *et al.*, 1999), underestimation of $NO_2$ measurements was found from diffusion tubes compared to active sampling measurements. 50% lower measurement of $NO_2$ from polyethylene tubes with TEA in comparison to chemiluminescence monitor was reported (Kasper- Giebel and Puxbaum, 1999). The study described of using two grids into the tube to correct the problems of underestimation. This underestimation of $NO_2$ measurements by diffusion tubes was related with overheating and photodegradation of $NO_2$-TEA adduct during exposure of tubes to sun in the sampling sites (Santis *et al*., 2003). The research recommended the careful extraction procedure, use of stainless steel mesh at the entrance of the tube, and use of a non-transparent plastic to reduce errors. Use of nontransparent plastic samplers were recommended in yet another study as it was found 50% lower $NO_2$ measurements in transparent plastic badge type sampler in compared to non-transparent plastic badge type sampler (Krochmal and Kalina, 1997).

No correlation was found for the results of $SO_2$ between active and passive measurement. Table 5.12 shows the $SO_2$ analysis from test passive sampler followed by IC analysis for four week exposures at Kathmandu from first exposure.

Table5.13 shows the $SO_2$ analysis from test passive sampler followed by IC analysis for one and two week exposures at Padova university premises. The test passive sampler plus IC analysis over estimated compare to Automatic fluorescent monitor about 21% while underestimation observed of about 10%.

#### 5.1.4.5: Comparison with High volume sampler measurement

Monitoring of $NO_2$ and $SO_2$ using High volume sampler was carried out in site 1 during the period of first and second exposure of test samplers showed good agreement between two methods for dry season monitoring than those from rainy season for both the pollutants monitored (Table 5.13, Appendix VII). The underestimation during post rainy season exposure analysis by test method compared to active high volume sampling method might be due to longer period of exposure of four weeks causing loss of pollutants or some unknown interferences. However, improvement in second sampling result during dry season showed the validity of the test method for the ambient monitoring of $NO_2$ and $SO_2$. However further study was required in this aspect as only three replicate readings were used.

Table 5.13: Ambient $NO_2$ and $SO_2$ measurement at site 1 by the test sampler method and the active- High volume sampler

| Parameter | Post monsoon (December) | | Dry season (March) | |
|---|---|---|---|---|
| | Test method | HVS | Test Method | HVS |
| $NO_2$ µg/m$^3$ | 1.7 | 6.6 | 22.7 | 22.7 (n=3) |
| $SO_2$ µg/m$^3$ | 0.8 | 4.5 | na | 19.9 (n=3) |

## 5.1.5: Detection limits

The detection limits are calculated for the analytical equipment and the sampling method for the tubes (Appendix VIII). The detection limit of the spectrophotometer obtained from the calibration curve with the help of equation 9 was 0.09 µg/ml of $NO_2^{\,-}$ and that was 0.05µg/ml for $SO_2$.

The detection limit for the ion chromatograph was obtained by injecting a mixed standard of 0.01µg/ml each of $NO_2^-$ and $SO_4^{2-}$. The equation 10 gave the detection limit of 0.04 µg/ml of $NO_2^-$ and 0.02 µg/ml of $SO_4^{2-}$. The minimum detectable quantity calculated from equation 11 was 0.48 µg.sec for $NO_2^-$ and 0.36 µg.sec of $SO_4^{2-}$ (Appendix X).

The standard deviation of blank values was used to calculate the detection limit for the passive sampling method. The detection limit of $NO_2$ for one week , two weeks, three weeks and four weeks exposure period were estimated to be 2.73 $\mu g/m^3$ (n=11), 1.77 $\mu g/m^3$ (n=11), 1.75 $\mu g/m^3$ (n=10) and 1.84 $\mu g/m^3$ (n=11) respectively for developed diffusive samplers (Appendix VIII).

Similarly, the detection limit of $SO_2$ for one week , two weeks, and four weeks exposure period were 5.85 $\mu g/m^3$ (n=10) ; 1.12 $\mu g/m^3$ (n=10) and 2.72 $\mu g/m^3$ (n=10) respectively for pe tubes-1 while for tubes 2 and 3 it was 2.9 $\mu g/m^3$ (n=10) for two weeks exposure period. (Appendix VIII).

The detection limits of $NO_2$ and $SO_2$ for the diffusion tubes proved suitable to be used in the Kathmandu valley as the concentrations measured were not found to be below the detection limit. The detection limit for $SO_2$ was also suitable to be analyzed by ion chromatography as it was higher than the instrument detection limit. The detection limit of the spectrophotometer may not be sufficient to measure in low concentration areas as the concentrations may be lower than the instrument detection limit. Some negative absorbance values for $NO_2$ were obtained during analysis by the spectrophotometer. Ion chromatograph under optimized conditions has to be used for the analysis of the tubes exposed in low concentrations of gases.

## Part II: Passive sampling of Ozone

### 5.2: Ambient Ozone analysis by test-method (Using spectrophotometer)

As mention earlier, only a few passive ozone monitors employing conventional chemical analysis techniques have been developed recently. This research used developing local polyethylene tube as passive ozone monitoring sampler using nitrite- coated filter (GF/A filter paper) as absorbent base. After extraction with dd water, azide modified sodium salicylate method was used for analysis of nitrate formed by the oxidation of nitrite by ozone from the air using spectrophotometer.

Calibration curve from nitrate Standards was prepared and used for analysis of blanks and exposed tubes. Same standard curve was used for the calculation of detection limit as well. Mean value of $NO_3^-$ from the exposed tubes after subtraction from that of the blanks at the corresponding exposure time and sites was used in equation 3 to determine $O_3$ in $\mu g/m^3$ concentration in ambient air. The study was carried out for only one exposure period. The exposure was carried out during March/April 2009 (Dry season); the period prevailed with higher $O_3$ for the Kathmandu as described by previous researchers (Pudasaini, 2010 and Raut, 2007).

The results of all the exposure analysis provide a reliable ambient $O_3$ sampling with good precision (Table 5.14). Precision of $O_3$ measurements were found to be in the range of 0.1 to 14%. It was hence compared adequately with the USEPA acceptance criterion (15%) for field study of passive monitoring (Ott, 2007).

Table 5.14: Ozone concentration from test- method

| S. No. | Exposure period | Ozone in ambient air ($\mu g/ m^3$) | CV(%) |
|---|---|---|---|
| 1 | 24 hrs | 85.23 ± 0.15, n=3 | 0.2 |
| 2 | 2 days | 46.56 ± 0.03, n=3 | 0.1 |
| 3 | 5 days | 19.10 ± 0.30, n=3 | 1.5 |
| 4 | 1 week | 10.11 ± 0.92, n=3 | 9.1 |
| 5 | 2 weeks | 8.82 ± 1.20, n=3 | 13.6 |

Nitrite on coated filters is slowly converted to nitrate even without exposure to ozone, and this conversion is more rapid at warmer temperature. As long as the blank samplers are kept as much as possible at the same temperature as the field samplers, adequate compensation is made by subtracting the average amount of nitrate on the blanks from each sample. Hence, diffusion tubes were prepared at the same day prior to the exposure.

The required sensitivity for outdoor sampling locations was fully considered. These include, avoidance of very local sources of nitrogen oxides (such as trucks, buses, automobiles, or other internal combustion engines); away from walls or other surfaces that will deplete the ozone concentration in the vicinity of the sampler below the ambient concentration for the general sampling area and, the sampler must be located inside a protective cover, which prevents contact with rain and also acts as a wind barrier, to stabilize the sampler collection rate.

Use of transparent polypropylene for outdoor passive monitoring of ozone demonstrated higher and variable positive interferences. Its cause was undetermined, although overheating during sun was suspected by previous study. A study conducted between the co-exposure of two sets of passive samplers, one with covered by brown paper outside wall of the tube and other without covering. There was no significance difference between the sampler collection efficiency at $p \leq 0.05$ by pair t-test, though slight higher nitrate concentrations were observed for coverless tubes (Figure 5.20). Koutrakis *et al.*, did reported similar insignificant difference in ozone monitoring (Koutrakis *et al.*, 1993).

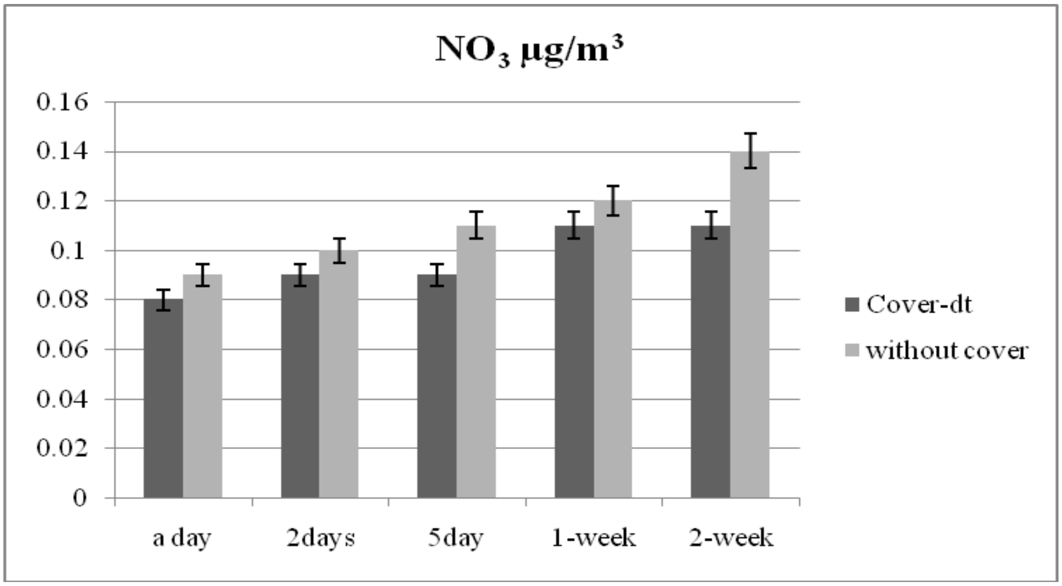


Figure 5.20: Result of ambient $O_3$ sampling with transparency of the diffusion tube.

(No significant difference at $p \leq 0.05$ by pair t-test)

Temperature and humidity are other important parameters which might affect the ambient ozone monitoring. The collection rates were reported to be unaffected by relative humidity at the ranges from 10% to 80% (Koutrakis *et al.*, 1993).

The solution used to coat the collecting filters includes sodium and potassium salts of nitrite and carbonate respectively in a solution of glycerol and water. In the presence of ozone, the nitrite ions are oxidized to nitrate ions:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_3$$

The mixed sodium/potassium crystals formed on the coated glass fiber filter collection medium are more hygroscope. Increasing the number of water molecules at the surface of the crystals enhances the oxidation reaction of nitrite by ozone. For this reason hygroscopic compound glycerol is also added to the solution. Solution components were chosen to ensure that oxidation would be ozone-specific and not be caused by other gaseous pollutants. Rate equations for aqueous nitrogen chemistry indicate that the above reaction is pH-dependent, with a rate constant that increases with pH. Thus, potassium carbonate is used to keep the collecting medium alkaline (Koutrakis *et al.*, 1993).

Other environmental pollutants might adversely affect this ozone sampling method. For example, nitric acid gas is collected simultaneously on the alkaline filters during sampling. However under typical ambient conditions this positive interference probably represents less than 5% of the nitrate formed during nitrite/ozone reaction (Koutrakis *et al.*, 1990).

Similarly expected interference from organic aerosol particles is expected to be negligible because they have diffusion coefficients order of magnitude less than gases. Interference from $SO_2$ is not expected because this gas is not a strong oxidant. Blank correction of the samples accounts for other interference effects as well notably, from oxygen (a weak oxidant), and from nitrate formed due to filter ageing.

Peroxyacetyle nitrate (PAN), as a strong oxidant, could oxidize nitrate to nitrate. Since ambient concentrations of PAN are typically 10-20 times smaller than ozone concentrations, significant interference in most locations is not expected. Ozone’s diffusion coefficient is about 1.6 times that of PAN, further minimizing the PAN’s interference. These co-pollutants interferences were beyond the scope of this study.

### 5.2.1: Suitable duration of field exposure period test

The amount of nitrate absorbed in the each diffusion tubes for the different tested period provides the efficiency of the method according to exposure duration. This will determine the most appropriate duration of exposure. The amount of nitrate concentration absorbed in a tube (n=4) was studied for different exposure period (Figure 5.21).

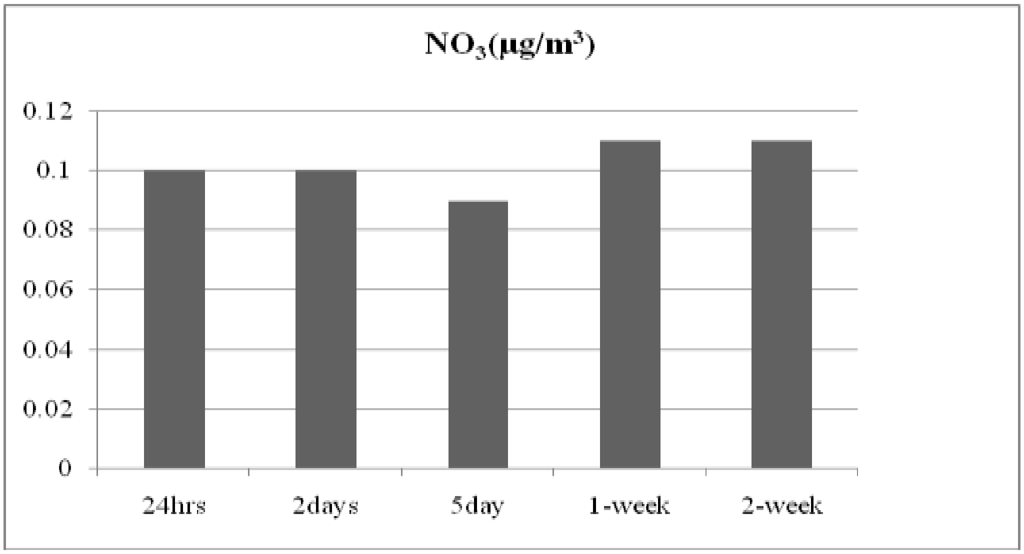


Figure 5.21: Amount of nitrate absorbed in each tube.

It was evident that the prepared diffusion tubes were suitable for 24 hour sampling in the tested environment.

### 5.2.2: Comparison with other study

The comparison of the current result with the existed previous studies was carried out (Figure 5.22). Accordingly, the 24 hrs average monitoring result of 2005 at the vicinity of the current study area, New Baneswor for the month of June using active ozone sampler was 65.8 µg/ $m^3$ (Neupane, 2006), while that using Ferm-IVL sampler carried out during 2007 was 78.5 µg/ $m^3$ for month of March-May (corrosion study project, ICIMOD).

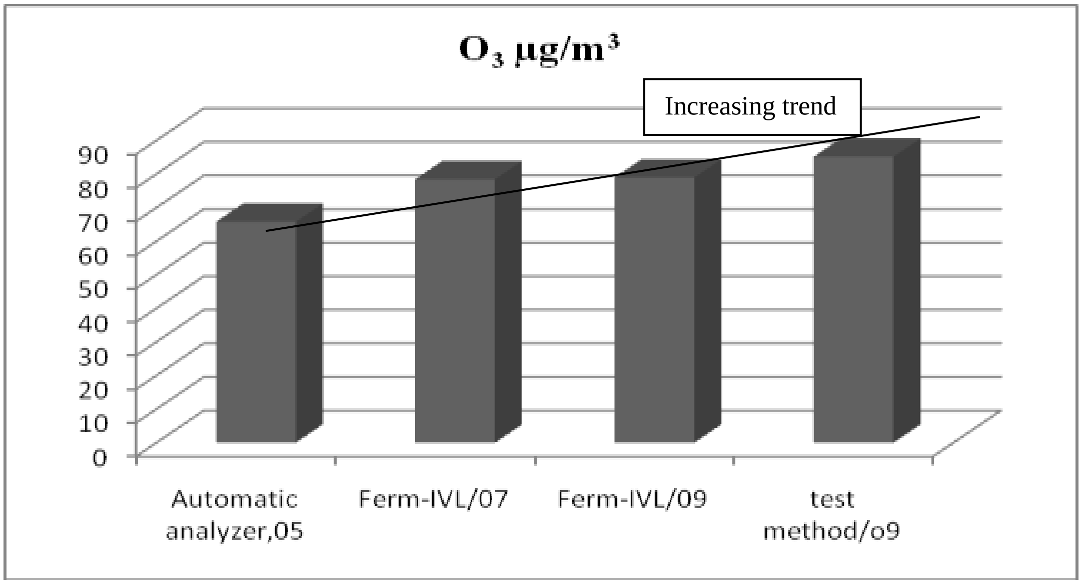


Figure 5.22: Comparison of ozone concentration analysed by different method at the viscinity of exposure site (New Baneswor) for March-May.

The current method overestimates by 22.77% and 7.9% in compared to that of automated ozone analyzer and Ferm-IVL sampler respectively. The result was acceptable according to US National Institute of Safety and Health (Seethapathy *et al*., 2008). Though, it might be unfair to compare the past studies with current method however looking at the yearly increasing trend of overall average ozone concentration in the Kathmandu, the current study could predict to be at positive direction (Figure 5.22). It was supported by the fact that ozone being a secondary pollutant and its distribution is more or less uniform in larger area. Therefore, ozone monitoring in a single station can represent an overall picture of chemical air pollutants in the area (EPA, 2003).

### 5.2.3: Detection limits

The Instrumental limit of detection from the standard curve was found to be 0.006 µg/ $m^3$ for this method. Limit of detection for developed passive sampling method was calculated from standard deviation of blank values with the help of equation 6, and is found to be 0.011 µg/ $m^3$ (Table 5.15). In other words, the method is suitable for ambient ozone monitoring in Kathmandu for the tested environmental condition.

Table 5.15: Detection limits (DL) of $O_3$ (µg/ $m^3$) for 24 hours exposure

| Number of field blanks<br>n | t-value<br>$t_{0.01, n-1}$ | Standard deviation<br>$S_B$ | Detection Limit<br>DL |
|---|---|---|---|
| 11 | 2.76 | 0.004 | 0.011 |

## Part III: Air quality assessment of Kathmandu

### 5.3: Passive monitoring and assessment of $NO_2$ and $SO_2$

The passive monitoring campaign was targeted to be done for two seasons namely rainy and dry. The campaigns were named as first monitoring sample and second monitoring sample.

In the first campaign, measurements of 52 gaseous deposition samplers ($SO_2$ - 17 and $NO_2$ - 35) were done during July-September 2007. Remaining 18 were lost due to wind and damage or wreckages.

In the second campaign, measurements of $SO_2$ were made at 21 sites (19 of those were used in the first campaign). Measurements of $NO_2$ were made at 37 sites (all of those were used in the first campaign). The measurements were made between February and April 2008.

Diffusive sampling method was used for both gases; $SO_2$ and $NO_2$ (Ferm and Rodhe, 1997; Ferm and Svanberg, 1998). The diffusive samplers used in current study were from IVL Sweden. IVL, diffusive samplers for several gases have been developed and described in the literature (Ferm and Rodhe, 1997). The IVL samplers were of badge type, 10mm long and 20 mm internal diameter. A membrane was mounted at the inlet to prevent them from wind-induced turbulent diffusion. The membrane was protected from mechanical damage by a stainless steel mesh. The samplers were normally mounted under a metal disc (rain shield) attached to an aluminum arm. The measuring range for $SO_2$ (bi-monthly sampling was about 0.1 to 50 ug/ $m^3$ and for $NO_2$ about 0.05to 50 $\mu g/m^3$. The $SO_2$ and $NO_2$ samplers had been compared to active sampling within a routine network had been described in literature (Ferm and Rodhe, 1997; Ferm and

Svanberg, 1998, Ferm *et al*, 2009). These samplers had been used for the measure of $SO_2$ and other gases in Asia, Africa and South America as well (Carmichel *et al*, 2003).

The higher concentration of both the pollutants was most apparent for second campaign compared to the first campaign. The $NO_2$ concentrations were quite similar in both campaigns (Figure 5.23). The range of $NO_2$ concentrations were found to be between 5.6 and 52.6 µg/m$^3$. The $SO_2$ concentrations were much lower in the first campaign compared to the second one (Figure 5.24). Its concentration varied between 0.6 and 23.4 µg /m$^{3.}$

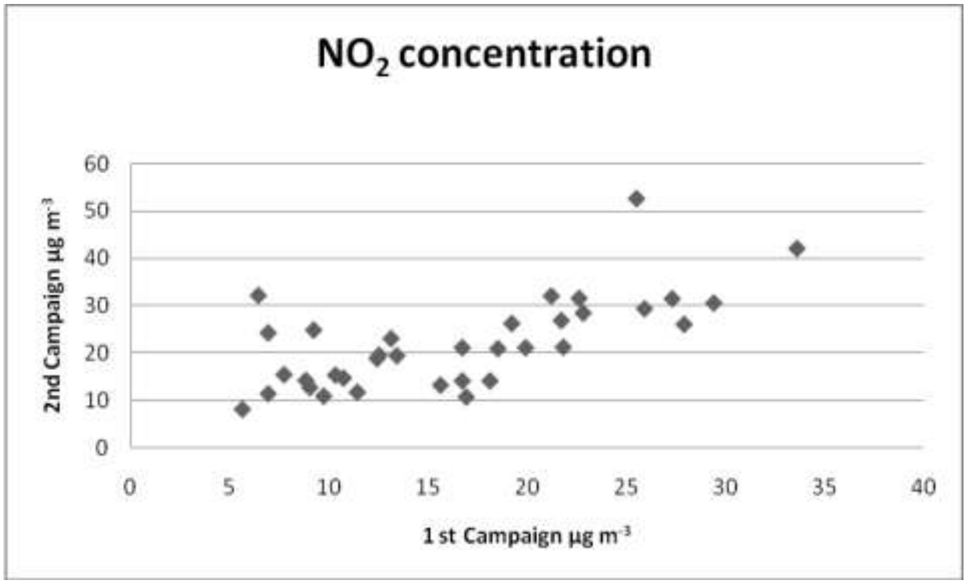


Figure 5.23: Comparison between the $NO_2$ concentration in the first and second campaigns.

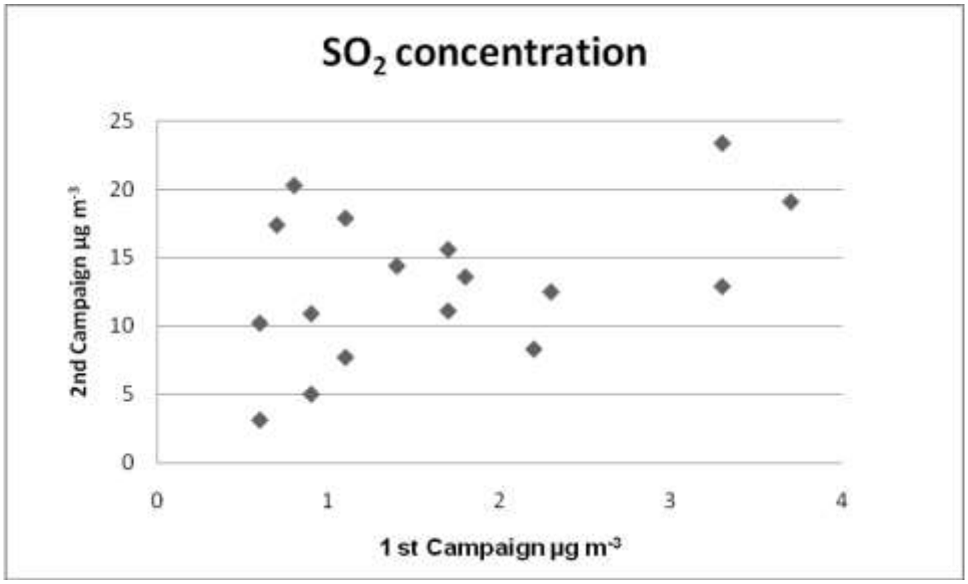


Figure 5.24: Comparison between the $SO_2$ concentration in the first and second campaigns.

The correlation between two seasons- result for $NO_2$ suggested that there might be equal amount of $NO_2$ generated during both the periods, and rain wash was responsible for the observed lower concentration during rainy season.

### 5.3.1: Mean concentration

The seasonal mean values of the $NO_2$ and $SO_2$ according to rural, urban background, intermediate road side, road side and industrial sites were monitored and analyzed (Figures 5.25 and 5.26 ).

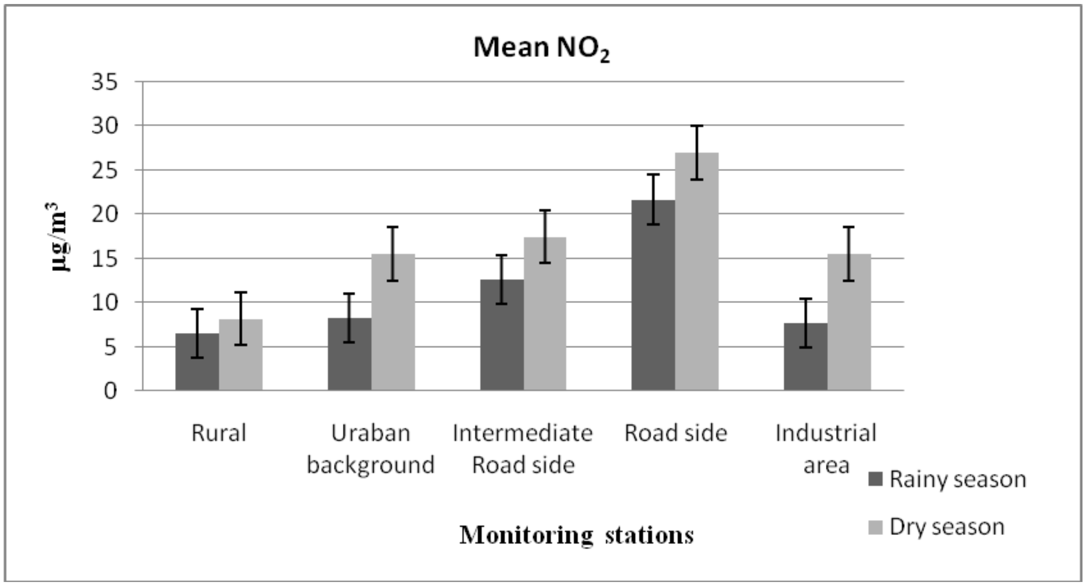


Figure 5.25: Mean seasonal concentration and standard error of ambient $NO_2$ in different areas of Kathmandu valley.

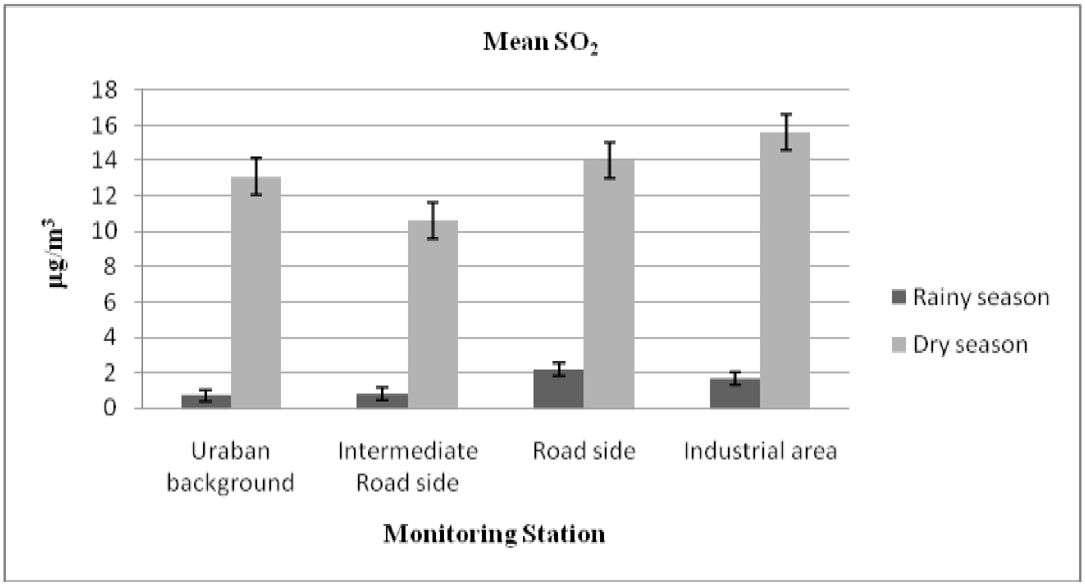


Figure 5.26: Mean seasonal concentration and standard error of ambient $SO_2$ in different areas of Kathmandu valley.

In all the cases pollutants were higher during dry season compared to rainy season. Among the different categories of areas, the mean concentration was found highest at the road side stations and it was in the order of road side> intermediate roadside> urban background> rural sites for $NO_2$ while it was in the order of industrial> roadside> urban background > intermediate sites for $SO_2$. In one of the urban background sites, Lokanthali, $NO_2$ value was highest. This site is nearby airport and planes usually take off over this site (Figure 5.27).

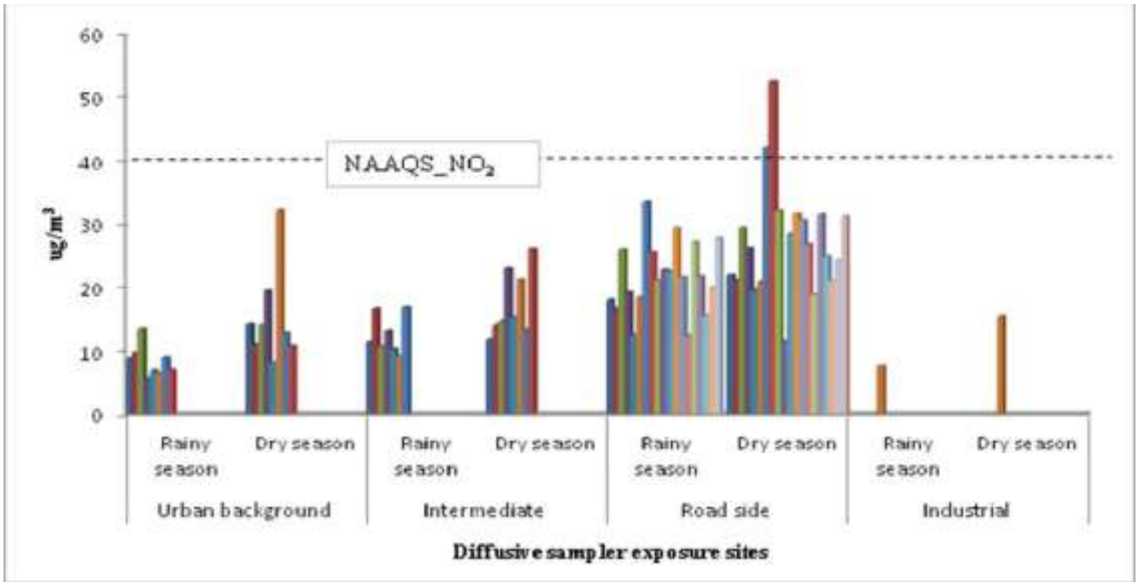


Figure 5.27: Seasonal variation of $NO_2$ concentrations in the study area.

The range of $NO_2$ concentration among the areas: 12.4-33.6μg/m$^3$ and 18.9-52.6μg/m$^3$, for road side; 9.2-16.9μg/m$^3$ and 11.8-26.1μg/m$^3$, for intermediate road side and 5.6-13.4μg/m$^3$ and 8.2-32.2μg/m$^3$, for urban background areas were reported for rainy season and dry season monitoring respectively. For the industrial area the $NO_2$ concentrations were 7.7 μg/m$^3$ and 15.5μg/m$^3$ for rainy and dry seasons. The traffic and the poor road infrastructures were responsible for the higher concentration of $NO_2$ observed at the road side stations and in fact, the major contributors of these pollutants in the Kathmandu valley. At most of the stations the concentrations were still lower than the National Ambient Air Quality Standard for $NO_2$ (40 µg/m$^3$, annual average).But, in few roadside stations measurements were higher than this NAAQS (Appendix IX).

The range of $SO_2$ were 0.9-3.7µg/m$^3$ and 5-23.4µg/m$^3$, for road side, 0.6-1.1µg/m$^3$ and 3.1µg/m$^3$ to 20.3µg/m$^3$, for intermediate road side, and 0.7 -0.7 µg/m$^3$ and 8.7-17.4 µg/m$^3$ for urban background areas for winter and dry seasons monitoring respectively. $SO_2$ concentration in the industrial site was 1.7µg/m$^3$ and 15.6µg/m$^3$ for rainy and dry seasons. The mean concentrations at all the categories of areas were higher than the overall valley average $SO_2$ concentration.

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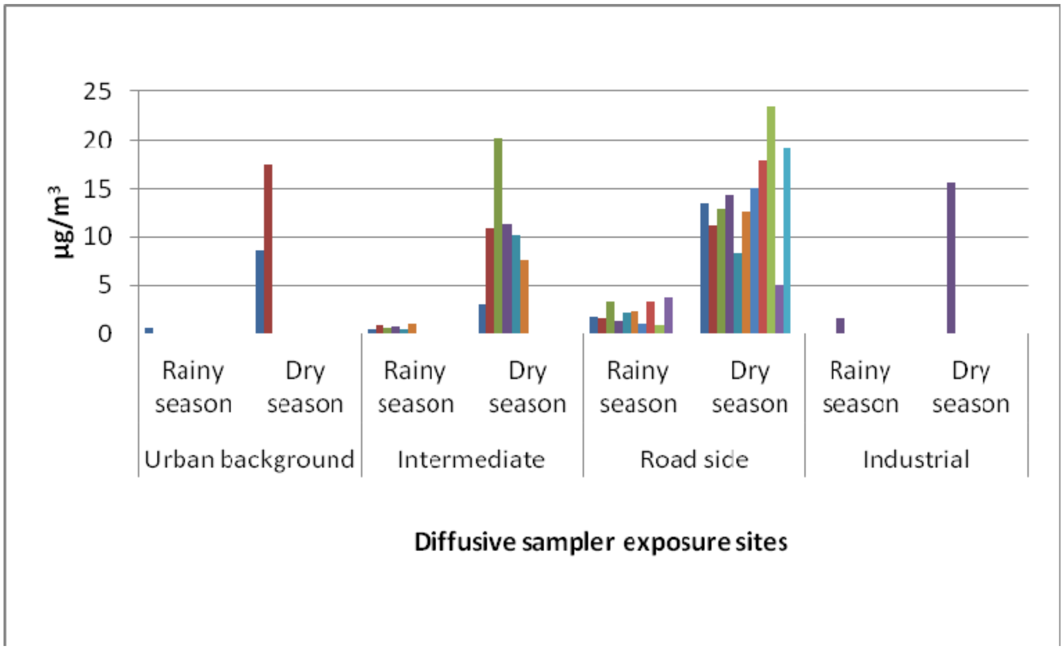
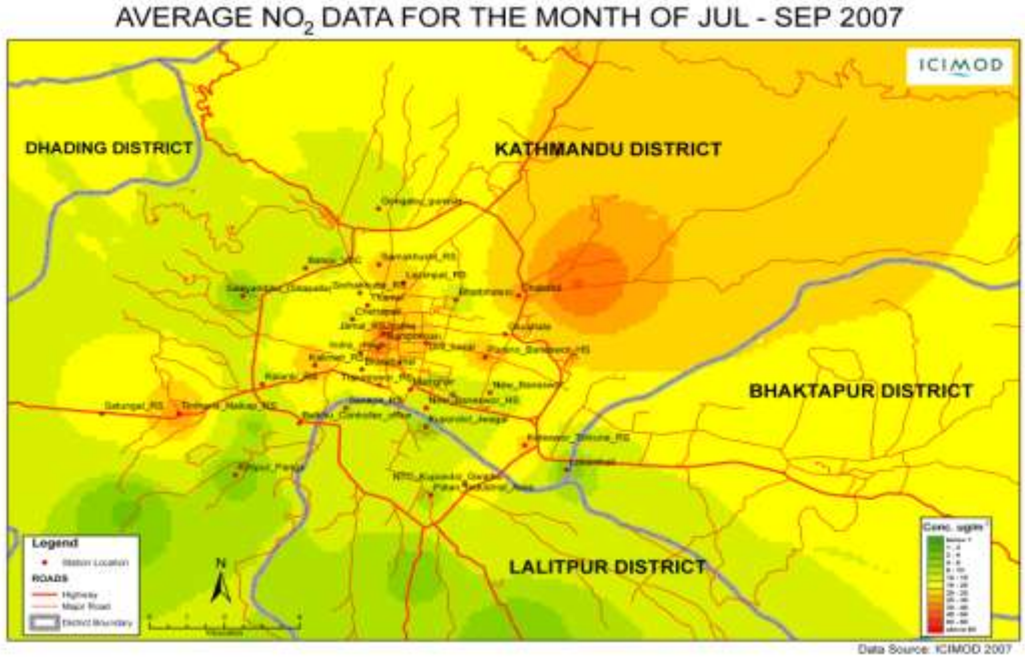


Figure 5.28: Seasonal variation of $SO_2$ concentrations in the study area.

### 5.3.2: Spatial distribution of $NO_2$ and $SO_2$ in Kathmandu valley

The spatial visual analysis of the output of the both campaigns using GIS was undertaken (Figures 5.29 and 5.30; for $NO_2$ and Figures 5.31 and 5.32 for $SO_2$). Based upon the first sampling results, the concentration of the gaseous pollutants during the rainy seasons was lower than the National Ambient Air Quality Standard. Similar results were presented in other monitoring reports too (MoEST, 2004). However, the concentrations were higher at road side stations as expected. The range of $NO_2$ and $SO_2$ measured were 5.6- 33.6 µg/m$^3$ and 0.6 – 3.7 µg/m$^3$ respectively.



Data Source: ICIMOD 2007

Figure 5.29: Passive sampling monitoring result of $NO_2$ for rainy season.

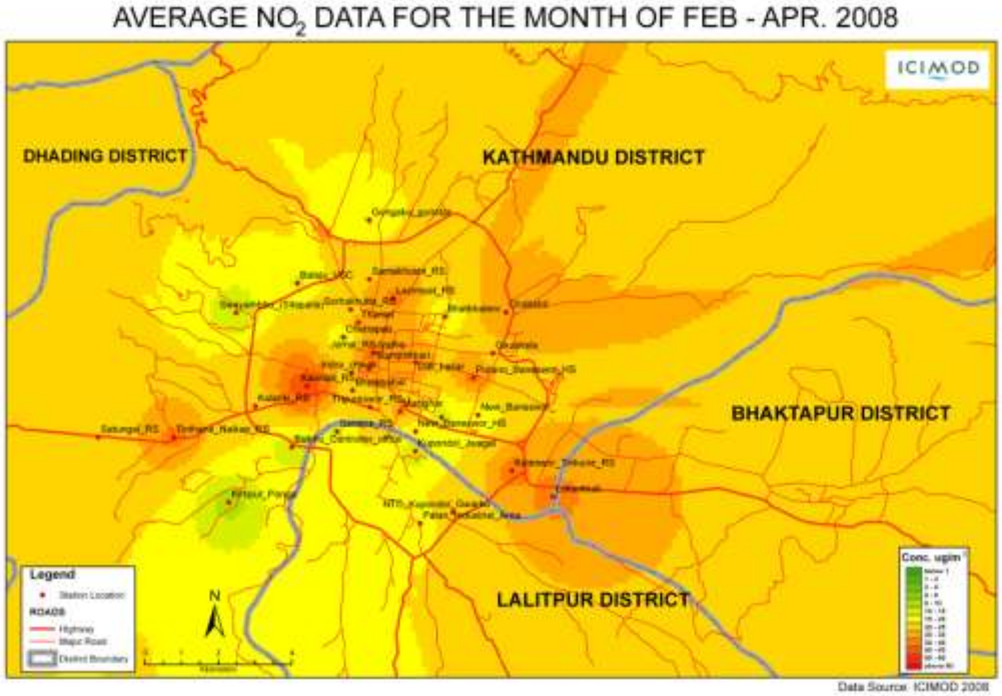


Figure 5.30: Passive sampling monitoring result of $NO_2$ for dry season.

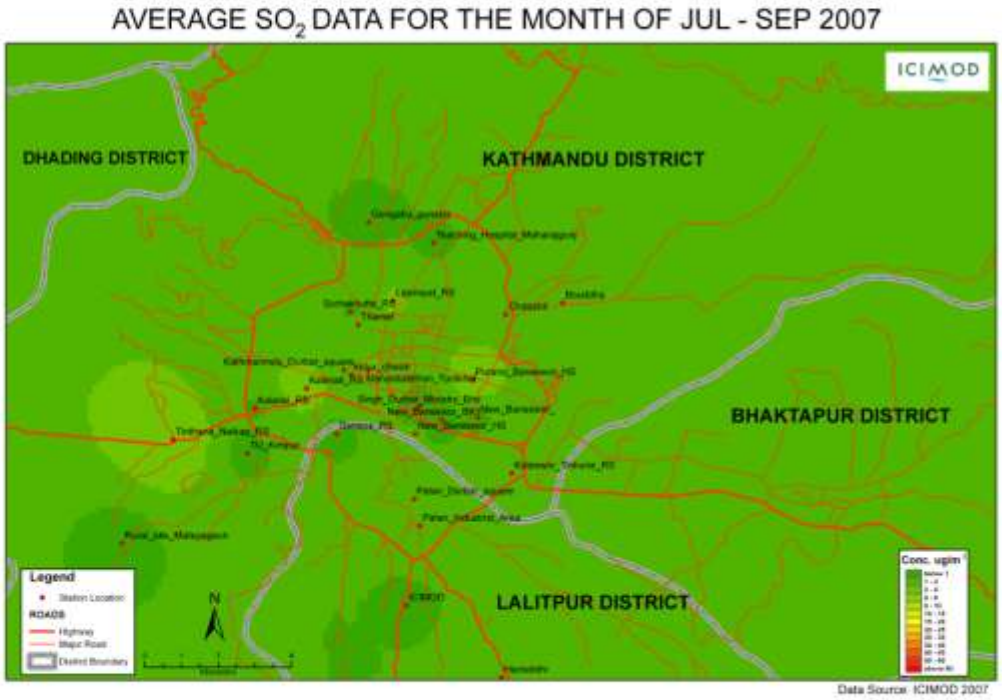


Figure 5.31: Passive sampling monitoring result of $SO_2$ for rainy season.

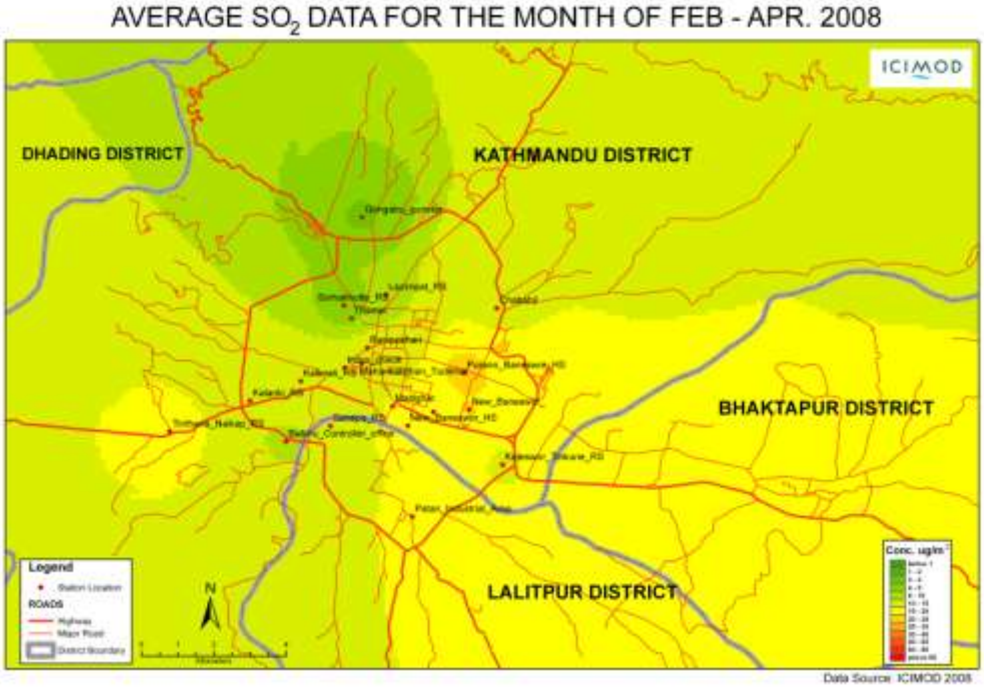


Figure 5.32: Passive sampling monitoring result of $SO_2$ for dry season.

The second monitoring campaign for dry season was carried out in the months of February- April, 2008. The higher concentration of both the pollutants for this season was observed when compared to that for the rainy season. Concentration of $NO_2$ for this season was from 10.8-52.6 µg/m$^3$ with higher concentrations at the road sides. It matched with the similar pattern in the rainy seasons- result.

The concentration of $SO_2$ for dry season was measured in the range of 3.3-23.4 µg/m$^3$ (Figure 5.32). The high concentration of $SO_2$ was at downwind part of the valley. It was of a different pattern compared to that one observed in rainy season. This high concentration was attributed, both due to wind pattern and the operation of brick kilns at this part of the valley during the dry season, which was unlikely during rainy season (Raut, 2003).

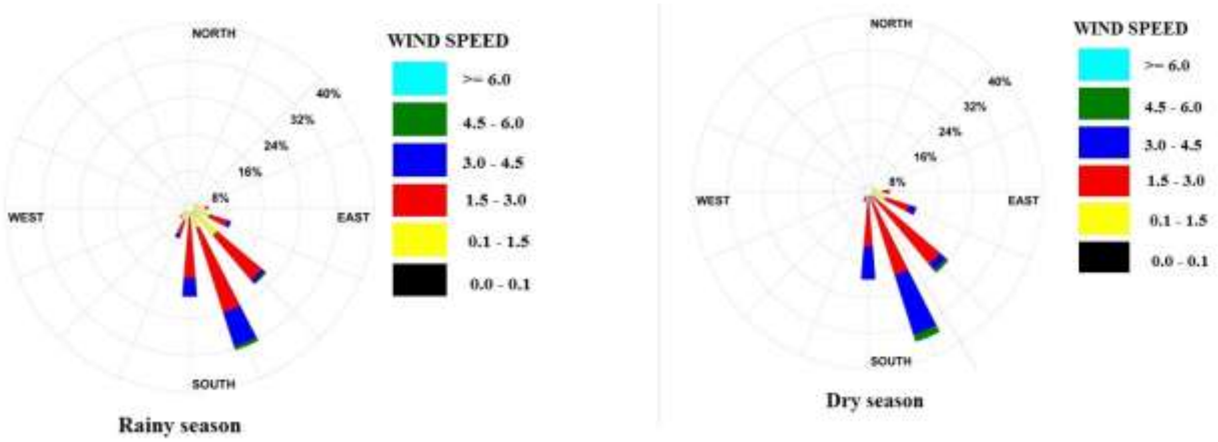
This confirms the influence of meteorological parameters and physical settings in the dispersion of pollutant concentration. Further discussion is on seasonal variation section below.

### 5.3.3: Seasonal variations

Seasonal variations are due to combined effect of meteorological factors and local environment together with other pollutants generation sources. The wind patterns are one of the significant players for pollutant transfer. The dominant winds above the valley are westerly and southwesterly during whole year (Sapkota, 2004).

There was a clear seasonal variation of pollutants concentrations in the Kathmandu valley. Higher concentrations were observed for dry season in the second campaign. Similar seasonal trends were presented in the earlier monitoring reports of the Department of Hydrology and Meteorology (DHM, 2000; Pokherel, 2002). Insight of rain, high wind speeds and unstable conditions help to clean the pollutants from lower atmosphere. Each season is characterized by its own unique meteorological parameters that influence the concentration of pollutants in ambient air.

The information/value regarding the condition of the meteorological parameters; temperatures, rainfall, humidity, wind speed and wind direction for the monitoring period was available from the DHM recorded at Kathmandu air port (Figures 5.33 and 5.34).



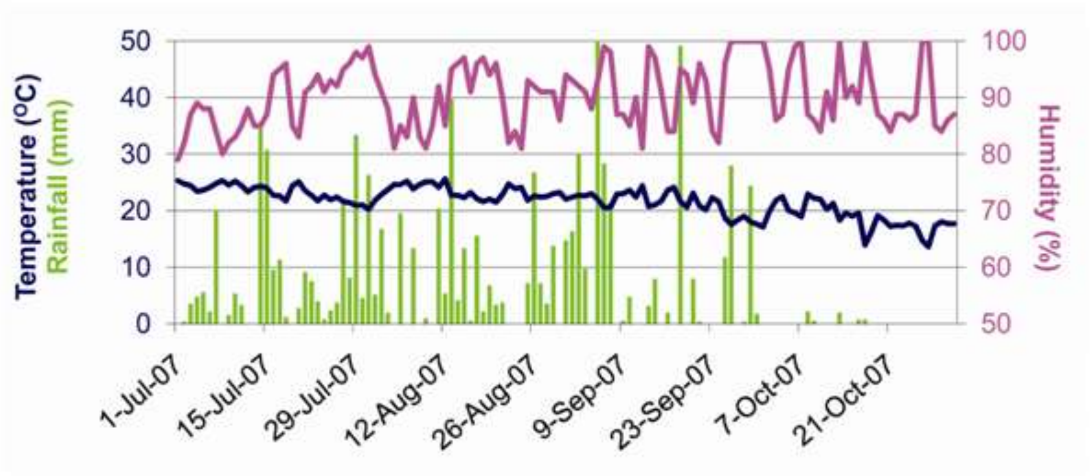
Rainy season

Dry season

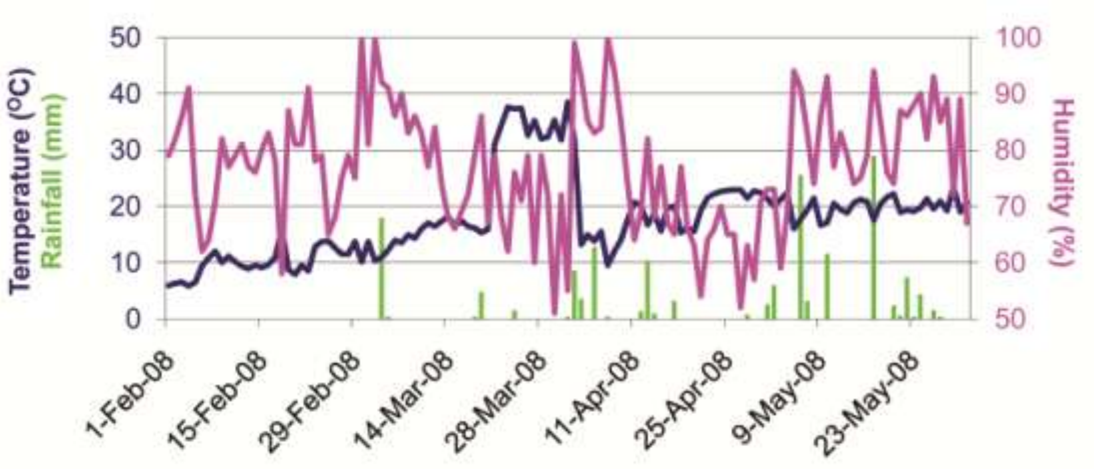
Figure 5.33: Wind rose kmph (Kilometer per hour).

The wind prevailing from South was found dominant in both seasons. During the dry season throughout the monitoring period the wind was blowing from South –East with an average wind speed of 2.5 kmph (Kilometer per hour) and maximum and minimum speed range were between 4.6-0.2 kmph. The pollutants were thus being received from South and accumulating towards south East.

The rainy season monitoring was prevailed with South wind but from the mid -September the wind direction move to South-East. The average wind speed for this monitoring period was 1.5kmph with the range of 0.1 to 3.3kmph.



Rainy season



Dry season

Figure 5.34: Meteorological parameters for two campaign monitoring period.

The effect from the wind direction and speed on seasonal pattern was apparent from the comparison between maps of $SO_2$ for two seasons/ campaigns. The pattern for $NO_x$ was not distinct as for $SO_2$, the reason could be the influence of transportation factor which is the main source of emission of $NO_x$. The major sources of $SO_2$ emission in the Kathmandu valley on the other hand were due to the result of fuel consumption in industries and domestic sectors. These industries include brick kilns and hotels. As mentioned earlier, brick kilns are mostly in operation during the dry winter months.

Similar kind of pattern for particulates and other pollutants trends were reported in several other studies (Tidblad *et al*., 2007; Gautam, 2006; Sapkota, 2004; Raut, 2003).

The wind was apparent during the whole monitoring period (Figure 5.33). In both the seasons, the wind prevailing from the South South East (SSE) was found to be dominant, with 36% for Dry season and 31% for rainy season, of the total measurable wind flowing from this direction. During the dry season, wind from the South was 20%, South East was 24%, East South East was 12% and remaining 8% were East and South South West.

Similarly for rainy season South wind was 19%, South East was 20%, East South East was 8%, South South West was 12%, South West and East were 10 %. The wind rose was further classified into different categories with wind speed of 0-0,1, 0.1-1.5, 1.5-3.0, 3.0-4.5, 4.5 – 6.0 and ≥ 6.0.The wind pattern was dominated by relatively low wind speed. Highest concentration of the pollutants occurs during low wind speed. There was no rain during February while 24.2 mm, 40.6 mm and 92.6 mm (total of 156mm) rain fall during March, April and May respectively.

The July month witnessed 254.8 mm of rain fall, while 39.6 mm, 55.4 mm and 7.6mm were observed for August, September and October 2007 respectively. Total of 357.4 mm rain fall was observed for rainy season monitoring period. Due to this monsoon rain, the pollutants get washed out from ambient atmosphere during rainy season and hence, lower concentrations of $SO_2$ observed during this monitoring period. The lower concentration of $SO_2$ was attributed due to alkaline nature of soil in this region (Kulshrestha and Kulshrestha, 2010). The lower concentration of $NO_2$ during rainy season was due to different scavenging mechanism where ozone in the atmosphere reacts with $NO_2$ to form $N_2O_5$, anhydride of nitric acid (Banerji, 1997)). Being an anhydride $N_2O_5$ reacts with water with ease to form nitric acid. Since the presence of $O_3$ in ambient air in Kathmandu valley was well established (Pudasainee *et al*.,2010), the recorded seasonal variation in $NO_2$ was justifiable.

## 5.4: Passive monitoring and assessment of $O_3$ in Kathmandu valley

Continuous monitoring of Ozone and $NO_2$ at nine sites for a year was carried out inside Kathmandu valley. In this continuous monitoring programme bi-monthly average concentration of $NO_{2,}$ $SO_2$ and $O_3$ were measured using diffusive samplers from IVL between November 2006 and November 2007. This was part of RAPIDC-corrosion project carried out by ICIMOD. The sites were therefore selected near buildings with cultural heritages.

As mentioned earlier, neither of the two intensive campaigns was run simultaneously along with the continuous monitoring at 9 stations. The samplers were analysed in the IVL-Sweden (Appendix X).

There were similar pattern of variations at the 9 sites where the concentrations were being measured continuously (Figure 5.35). The seasonal pattern for $O_3$ resembled one another with a maximum during March-May and a minimum during August-September for all the stations. The $O_3$ concentrations varied between 25 and 100 µg /m$^3$ with an average of 47 µg /m$^3$. The maximum was observed from rural site Matsygaun while minimum from Boudha.

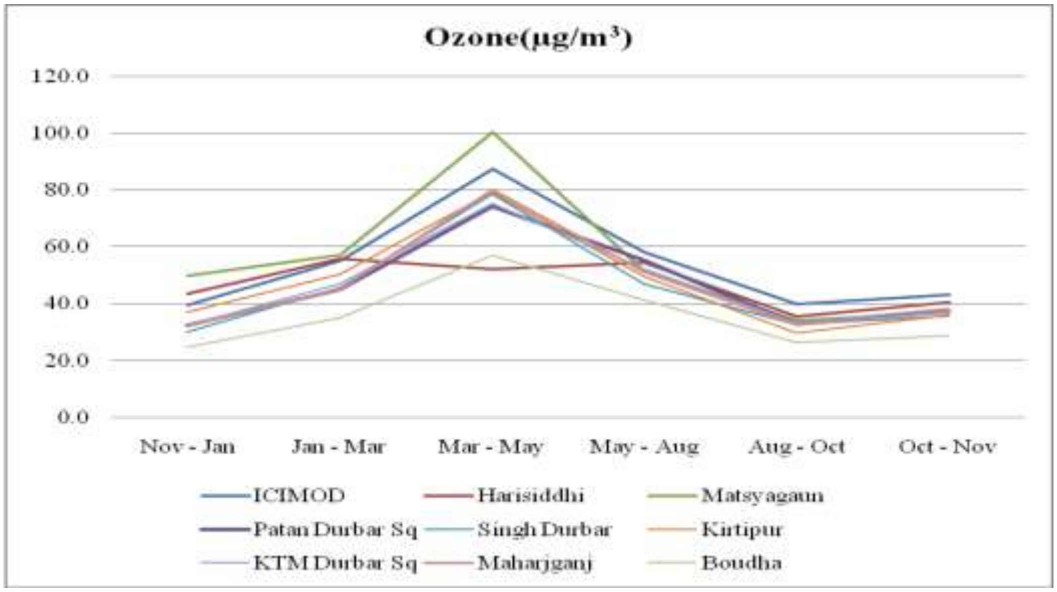


Figure 5.35: Spatial seasonal variations in concentrations of Ozone in the valley.

The pre-monsoon months of March –May, in special, was the most vulnerable time for high concentration of ozone exposure in the study area. Much higher pre-monsoon ozone concentration was due to the meteorological conditions in favour of, conducive to ozone formation through photochemical reaction. These are high temperature, high intensity and much longer period of solar radiation and low cloud cover. Lower temperature, shorter sunlight period and low intensity of solar radiation due to higher zenith angle is responsible for the lower ozone concentration in winter (Lal *et al*., 2000; Ghim *et al*., 2001).

During monsoon, though air temperature is high, enough solar radiation cannot reach the surface due to prevailing rains and more cloud cover. Consequently, non-availability of sufficient solar radiation and washout of pollutants result in low photochemical ozone formation during this period (Lal *et al*., 2000). Similar reported dramatic decrease of ozone by rain and end of ozone episodes were observed in Seoul (Ghim *et al*., 2001).

The scenario was related with number of causes including aqueous reactions in cloud consuming radicals or effects of vertical mixing, wet deposition of soluble $O_3$ precursors, decrease in solar radiation, and decrease in temperature (Ghim *et al*., 2001). Additionally the diurnal variation of ozone and stability of air also contribute to the seasonal variation. For example winter seasons are often associated with high air stability due to strong temperature inversion, hence, chemical reaction and deposition can deplete $O_3$ in surface during the night time. In monsoon season vertical mixing of air prevails and hence ozone rich night air from aloft replenish the ozone lost near the surface (Berkowitz *et al*., 2000).

Several similar seasonal ozone cycle with summer peaks were reported such as; summer high peak in Northern part of Indian subcontinent, India (Fishman *et al*., 2003); spring maximum and summer minimum tropospheric ozone in many locations of Nothern hemisphere (Chan *et al*., 1998); high summer ozone in Northern Western Mediterranean basin (Ribas and Penuelas, 2004); high ozone during pre-monsoon and low during monsoon at Poona, India (Tiwari and Shreedharan, 1973) and in Bangkok (Zang, 2002).

The concentrations of $SO_2$ varied between 0.1 and 44 $\mu g/m^3$ with an average of $5.7 \mu g/m^3$. Maximum concentrations occurred during January-February or March-April and minimum during August-September or October-November. The seasonal trend was similar for $NO_2$, but the concentrations were higher than that of $SO_2$. $NO_2$ concentrations varied between 2 and 36 $\mu g/ m^3$ with an average of 16 $\mu g/ m^3$ (Figure 5.36).

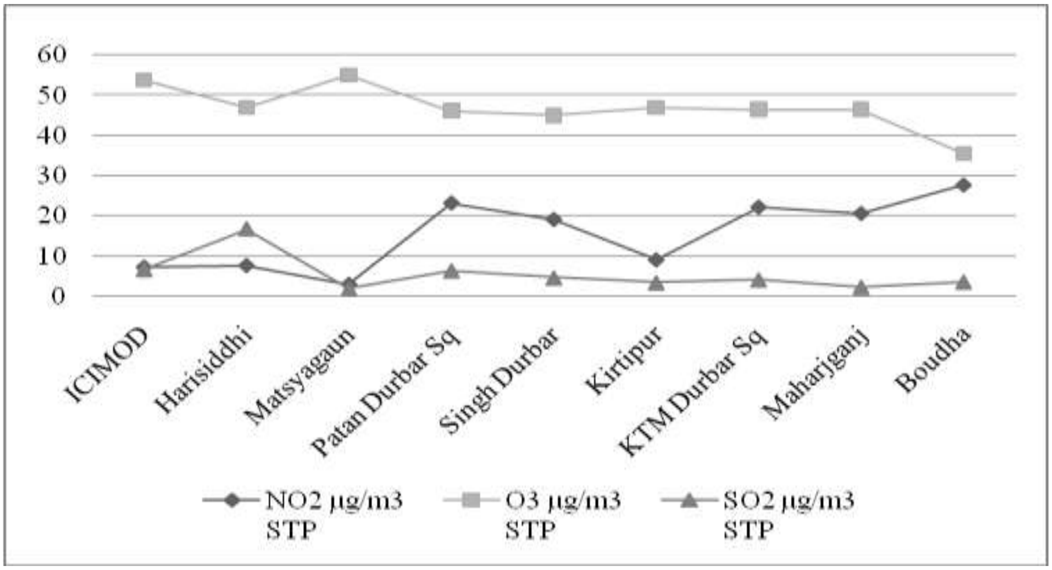


Figure 5.36: Yearly average variations in concentrations of $O_3$, $SO_2$ and $NO_2$.

The rural sites had the lowest concentrations for all the gases except ozone which had the highest concentration. It seems as emitted $NO_2$ reacts with ozone, resulting in a lower $O_3$ concentration, but a higher $NO_2$ concentration (Figure 5.36).

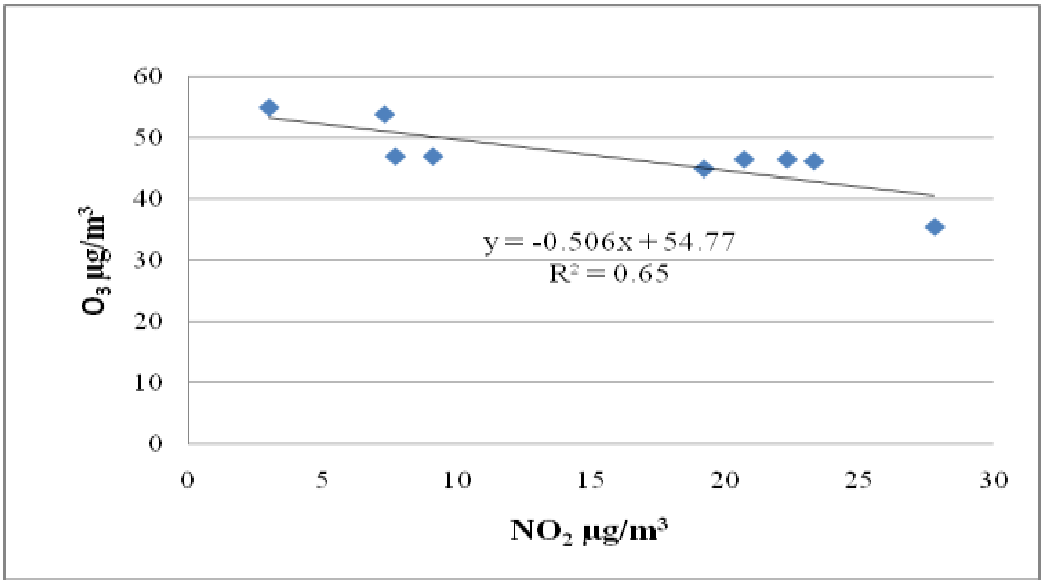


Figure 5.37: Annual average $O_3$ concentrations versus annual average $NO_2$ concentrations.

In the rural sites there were generally low/ or absence of vehicular movement and hence, lower concentration of $NO_2$ in the ambient atmosphere and high ozone concentration observed.

There was good correlation between the annual ozone and $NO_2$ concentration (Figure 5.37). Relationship of traffic influence, $NO_2$ and $O_3$ interaction was apparent from the data of the station Boudha (Figure. 5.38). Decrease in $NO_2$ was accompanied by decrease in $O_3$ as well.

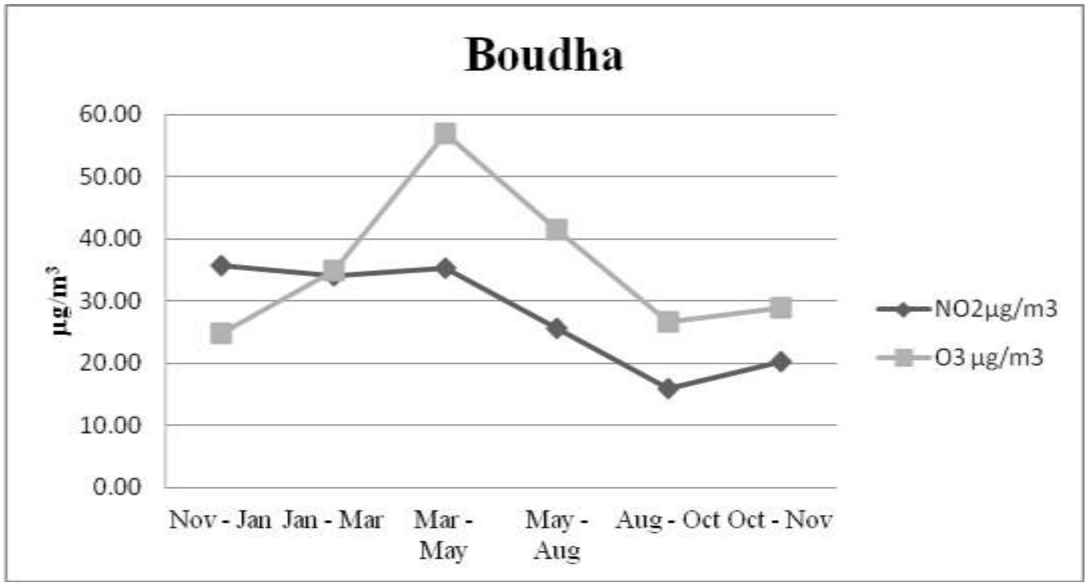


Figure 5.38: Ambient concentration of $O_3$ and $NO_2$ in Boudha which is near to high traffic area.

Based on the prvious literature, the annual average $O_3$ concentration figures of the Kathmandu valley was analyzed (Figure 5.39). There was an increase in ambient ozone concentration compared to 2003 figure while there was a slight decrease in comparison to 2004 and 2007 monitored figure. Ozone is prevalling in Kathmandu valley through out the year. Its concentration was higher during the pre-monsoon (dry period). Hence, though the annual Ozone conmcentration in Kathmandu is lower than the WHO guidelines (120 µg/ $m^3$ per 8 hour) and other standards, EPA and EU, the possible sensitivity of ozone exposure was revealed. The health risk assessment due to ozone concentration in Kathmandu reported that with the population density of around 1.8 million, 628 deaths in Kathmandu valley per year could be attributed to this present level of ozone pollution exposure (Neupane, 2006). It is therefore necessary to undertake the long term monitoring of ozone in Kathmandu. It was further supported by the increasing VOCs and traffic density in the valley (Raut, 2001; Pudasainee, 2010).

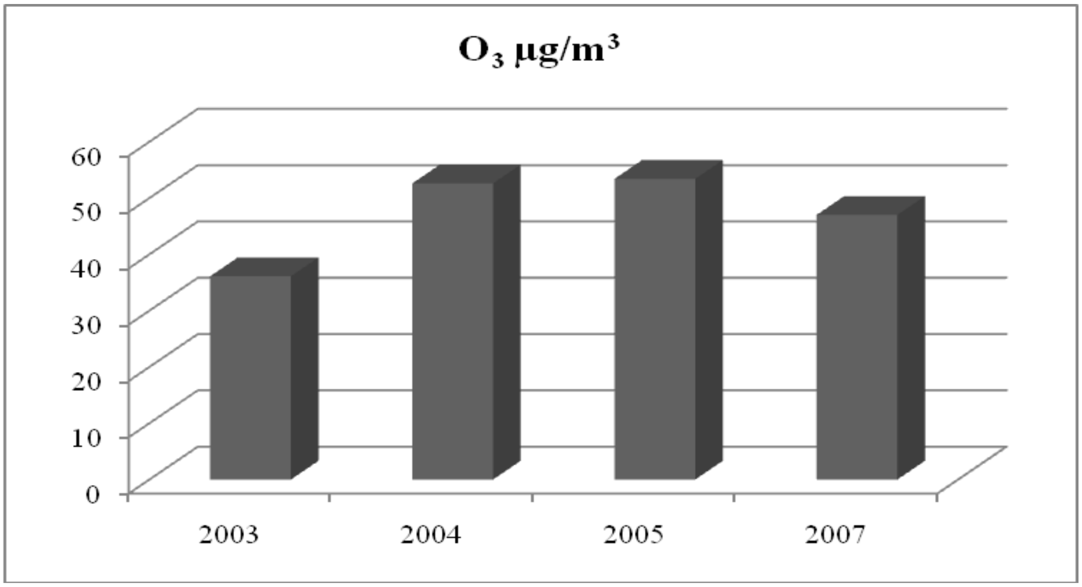


Figure 5.39: Yearly average ozone concentration in the Kathmandu Valley.

Thus ozone pollution in Kathmandu valley is already a serious problem and requires urgent attention.

## Chapter: 6 Conclusion

### 6.1: Summary

The most important achievement of this research work is the use of polyethylene tubes easily available in local market to develop as diffusive passive samplers for ambient monitoring of $NO_2$, $SO_2$ and $O_3$. These tubes were proven to be quite suitable for passive sampling. For the first time, such works are conducted in Nepal.

The research was carried out for testing of different: i) types/sizes of the locally fabricated sampler tubes as the diffusive sampler, ii) concentrations, - types of absorbent chemicals and iii) filter papers as absorbent base, so as to optimize the condition for ambient monitoring of each of the pollutants considered in the present study. The sampler performances were tested under the field and the laboratory conditions to assess suitable and required duration of exposure time, accuracy and precision of $NO_2$, $SO_2$ and $O_3$ measurement in comparison to those measurements made parallel with other filter base passive samplers (IVL Badge Ferm-samplers) and active methods – automated and -high volume sampler. Based on the finding of the present research, it can be concluded that the fabricated passive diffusive samplers are appropriate for ambient monitoring of $NO_2$, $SO_2$ and $O_3$ in Kathmandu valley.

In case of $NO_2$, $SO_2$ it was observed that during high pollution state-dry season exposure period of one week for $NO_2$ and two to four weeks for $SO_2$ is suitable for the ambient sampling and monitoring in Kathmandu with the tested / developed experimental condition. The diffusive sampler tube type one (Tube-1) - made of polyethylene tubes (length 5cm and diameter 1cm) together with GF/A filter paper with 20 µl of 30% v/v TEA/ water as absorbent are proven to be most suitable for the sampling.

The comparison of the performances of the fabricated diffusive sampler tubes with that of the active sampler showed a good correlation ($r^2 = 0.91$, $p \leq 0.001$) in case of $NO_2$ monitoring for Tube-1. But no such correlation was observed in case of $SO_2$ monitoring. The diffusion tubes gave underestimation of $NO_2$ measurements and over estimation of $SO_2$ concentrations compared to active sampling measurements. The results were consistent with other studies such as Campbell *et al*., 1994; Gair and Penkett, 1995; Heal and Cape, 1997; Heal *et al*., 1999.

There was a good correlation between the results of the measurements of $NO_2$ and $SO_2$ with the fabricated diffusion tubes and that made with Ferm-IVL passive samplers developed by IVL-Sweden. There was no significant difference between two methods at $p \leq 0.05$. Fabricated passive samplers however underestimated the ambient $NO_2$ than the estimation made by Ferm-IVL samplers. Regression analysis revealed the valid comparison of the parameters: - slope, - intercept and - Pearson correlation coefficient (*r)*; such that they are within the tolerance limit set by US EPA's acceptance criterion for environment monitoring (Ott, 2007; EPA, 2010).

Precision of the passive sampling method for measurement expressed as coefficient of variation (CV) was13.3% with an overall range of 2.3-20.8% for $NO_2$. It was 14.5% with an overall range of 3.4-20.2% for $SO_2$. The results for the estimation of precision were consistent with other previous studies (Atkins *et al.,* 1986; Gerboles and Amantini, 1993; Bush *et al*., 2000).

From this comparison, it can be concluded that Tube-1 type tubes were better suited for sampling than two other types of tubes tested. The Tube-2 and Tube -3 were more transparent than the tube-1 which might be the possible reason for the lower estimations with these tubes. Transparency of the tube lowers the sampling efficiency possibly due to photo- degradation, as has been shown in other studies (Krochmal and Kalina, 1997; Santis *et al*., 2003).

A comparison of three absorbents concentrations; 20%; 30% and 50% v/v TEA- $H_2O$ for trapping of $NO_2$ showed no significant differences at the tested environment using ANOVA at $p \leq 0.05$ confidence levels for the first exposure set (rainy season). A significant difference among the values for the three different concentrations was however, observed for the dry season samples exposure, a condition of higher ambient concentration of the pollutants. Fifty percent (50%) v/v TEA-$H_2O$ was found to be not suitable for use. The reason might be because, the high concentration results the incomplete complexation between nitrite ions and TEA due to lack of hydroxyl ions in the solution as described in other previous studies (Kirby *et al*., 2000; Palmes and Johnson, 1987). Similar exposure analysis for $SO_2$ also showed the insignificant differences among the concentration and volume of the aliquot of TEA taken as absorbent at 20%, 30% and 50% v/v TEA-$H_2O$ at $p \leq 0.05$ confidence levels. The drop out of absorbing medium was highest for 20% v/v TEA-$H_2O$. The results are consistent with other previous studies (Shakya, 2004).

The instrumental detection limit and detection limits of the diffusion tubes for the passive sampling of $NO_2$ and $SO_2$ were found suitable for the study area. The instrumental detection limits obtained from calibration curve were 0.09 µg/ml and 0.05µg/ml for $NO_2^-$ and $SO_4^{2-}$, respectively.

The standard deviation of blank values was used to calculate the detection limit for the passive sampling method (IUPAC, 2000). The detection limit of $NO_2$ for one week , two weeks, three weeks and four weeks exposure period were estimated to be 2.73μg/m$^3$ (n=11), 1.77μg/m$^3$ (n=11), 1.75μg/m$^3$ (n=10) and 1.84μg/m$^3$ (n=11) respectively for developed diffusive samplers. Similarly, the detection limit of $SO_2$ for one week , two weeks, and four weeks exposure period were estimated of 5.85μg/m$^3$ (n=10) ; 1.12μg/m$^3$ (n=10) and 2.72μg/m$^3$ (n=10) respectively for polyethylene tubes-1.

Polyethylene tube (T-1) with nitrite –coated filter paper (GF/A) was used for ground $O_3$ measurement (Koutrakis *et al*.. 1990, Braueer and Brook, 1995; Tang and Lau, 2000) and is found to be useful for ozone monitoring in Kathmandu Valley. The results of all the exposure analysis provided a reliable ambient $O_3$ sampling with good precision. Precision of $O_3$ measurements were found to be in the range of 0.1 to 14%. It, hence, stood adequately within the USEPA acceptance criterion (15%) for field study of ambient passive monitoring (Ott, 2007). Thus, it is evident that the fabricated diffusion tubes are suitable for 24 hour sampling in the tested environment. The test method although made an overestimation by 22.77% and 7.9% in comparison to those of automated ozone analyzer and Ferm-IVL samplers respectively. The result is within acceptable range according to US National Institute of Safety and Health (Seethapathy *et al*., 2007). The detection limit for developed passive sampling method was 0.011 μg/ m$^3$, which is suitable to measure $O_3$ in study area.

The passive monitoring and assessment revealed the quality of air prevailing in the urban Kathmandu. Accordingly, all the three pollutants- monitored -$NO_2$, - $SO_2$ -$O_3$ concentrations in winter dry season were higher than that in the rainy season. Gaseous pollutants ($NO_2$ and $SO_2$) were below national ambient air quality standard for both the monitoring period however $NO_2$ at several points exceeded the National Ambient Air

Quality Standard (NAAQS). Higher concentrations of $NO_2$ were observed at the high traffic density areas showing that transportation, rather than the industry was responsible for the $NO_2$ pollution in the city. The $SO_2$ pollution in the city, on other hand, was related with the industrial emission especially due to brick kilns and hotels. The concentration of $SO_2$ was higher around the city centers and the South-East side – Bhaktapur -of the valley, especially during dry season.

In case of $O_3$ the concentrations is found to vary between 25 and 100 µg /m$^3$ with an average of 47 µg /m$^3$. The maximum concentration was observed from samples of rural site Matsygaun while minimum was observed from that of Boudha. The pre-monsoon months specially March –May was the most vulnerable time for high concentration ozone exposure in the study areas.

Though the concentrations of $NO_2$ and $SO_2$ for rainy seasons in most cases were found to be lower than the national ambient air quality standard value, higher concentrations were observed in certain cases. Mostly road sides and urban parts showed an increased level of pollutants.

Information on meteorological conditions has very important role, as it provided greater insight into the daily variations in air quality and the effects of past air quality management decisions. It helps in making more effective decisions towards improving the future air quality. Meteorological parameters such as: rainfall, specific humidity, temperature, wind speed and wind direction, monitored continuously in the study area are found to be highly correlated with the pollutant concentration.

In comparison to the cities of other developing countries, air pollution in the Kathmandu has increased significantly (CIA-Asia, 2011). It is expected that the outcome as well as the methodologies developed in this study will be useful not only for the future air pollution monitoring in other urban areas, but also for the improvement of monitoring and evaluation systems, building air quality management strategies, and preparation of clean air plans.

## 6.2: Future study

It is felt that there is a need for maintaining and expanding the existing monitoring stations both for monitoring additional air pollutants and current monitored pollutants in Kathmandu valley and such an expansion requires large investments with additional operational expenses. An urgent action for adopting inexpensive, simple and reliable methods for simultaneous and wide-spread air quality monitoring, at multiple points over large areas is deemed needed for Nepal. It is to be stressed over here that the passive sampling methodology developed and demonstrated in Kathmandu valley presented in this study has potentiality to be one such methodology to fulfill this need.

Future studies should be targeted towards developing such passive sampling techniques capable of overcoming the systematic bias observed in the field exposure results due to seasonal and other possible reasons as well.

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# Appendix I

## List and summary of some of the documents related to air pollution in Nepal.

The literatures have been compiled on chronological basis.

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# Appendix II

Table: Detail information on two campaign passive monitoring sites

| SN | Monitoring site | Category | Latitude ($^0$N) | Longitude ($^0$E) | Altitude (m) |
|---|---|---|---|---|---|
| 1 | Balaju-VSC | Uraban background | 27.7249 | 85.2964 | 1314 |
| 2 | Balkhu-Controller office | Uraban background | 27.6846 | 89.2950 | 1303 |
| 3 | Batbhateni-gahanapokhari | Uraban background | 27.7167 | 85.3325 | 1321 |
| 4 | Bhimsenthan | Road side | 27.7022 | 85.3041 | 1310 |
| 5 | Bhotebahal | Road side | 27.6986 | 85.3099 | 1305 |
| 6 | Chabahil | Road side | 27.7178 | 85.3475 | 1326 |
| 7 | Chetrapati | Intermediate Road side | 27.7116 | 85.3077 | 1313 |
| 8 | Dillibazar | Road side | 27.7055 | 85.3254 | 1305 |
| 9 | Gausala | Intermediate Road side | 27.7077 | 85.3443 | 1326 |
| 10 | Gongabu | Intermediate Road side | 27.7403 | 85.3140 | 1310 |
| 11 | Gyaneswor-Mali gaun | Uraban background | 27.7055 | 85.3254 | 1303 |
| 12 | Gwarko | Road side | 27.6687 | 85.3346 | 1300 |
| 13 | Indrachwok | Road side | 27.7029 | 85.3096 | 1303 |
| 14 | Jamal | Road side | 27.7078 | 85.3150 | 1304 |
| 15 | Jyatha | Uraban background | 27.7078 | 85.3150 | 1304 |
| 16 | Kalanki-RS | Intermediate Road side | 27.6947 | 85.2861 | 1328 |
| 17 | Kalimati | Road side | 27.6996 | 85.2987 | 1443 |
| 18 | Kathmandu Darbarsquar | Intermediate Road side | 27.7042 | 85.3039 | 1314 |
| 19 | Kirtipur-Panga | Uraban background | 27.6711 | 85.2796 | 1365 |
| 20 | Koteswor | Road side | 27.6788 | 85.3489 | 1306 |
| 21 | Kupoundol-Neela | Uraban background | 27.6836 | 85.3253 | 1296 |
| 22 | Kupoundol-NTC | Road side | 27.6686 | 85.3345 | 1300 |
| 23 | Lazimpat-RS | Road side | 27.7211 | 85.3199 | 1817 |
| 24 | Loknthali | Uraban background | 27.6725 | 85.3590 | 1317 |
| 25 | Mahankalsthan | Road side | 27.7040 | 85.3199 | 1309 |
| 26 | Maitighar | Road side | 27.6934 | 85.3216 | 1304 |
| 27 | New Baneswor1-BK | Uraban background | 27.6920 | 85.3317 | 1310 |
| 28 | New Baneswor2. -HS | Uraban background | 27.6885 | 85.3253 | 1311 |
| 29 | New Baneswor3-RS | Uraban background | 27.6925 | 85.3407 | 1316 |
| 30 | Patan Industry area |  | 27.6659 | 85.3265 | 1326 |
| 31 | Purano Baneswor2-HS | Road side | 27.7017 | 85.3395 | 1321 |
| 32 | Ranipokhari | Intermediate Road side | 27.7079 | 85.3153 | 1307 |
| 33 | Samakhusi | Road side | 27.7258 | 85.3140 | 1308 |
| 34 | Sanepa | Intermediate Road side | 27.6884 | 85.3061 | 1297 |
| 35 | Satungal | Road side | 27.6871 | 85.2477 | 1369 |
| 36 | Sorhakhutte | Road side | 27.7184 | 85.3095 | 1319 |
| 37 | Swoyambhu-Sitapaila | Uraban background | 27.7176 | 85.2814 | 1362 |
| 38 | Thamel, MOEST | Intermediate Road side | 27.7152 | 85.3113 | 1321 |
| 39 | Tinthana-Naikap | Road side | 27.6871 | 85.2661 |  |
| 40 | Tripureswor | Road side | 27.6945 | 85.3142 |  |
|  |  |  |  |  |  |

# Appendix III

Table: Continuous monitoring sites

| | station | **Latitude (ºN)** | **Longitude (ºE)** | **Altitude (m)** |
|---|---|---|---|---|
| 1 | ICIMOD | 27.6465 | 85.3232 | 1327 |
| 2 | Harisiddhi | 27.6288 | 85.3464 | 1364 |
| 3 | Rural site, Matsyagaun | 27.6616 | 85.2535 | 1493 |
| 4 | Patan Durbar Square | 27.6725 | 85.3251 | 1326 |
| 5 | Singa Durbar, Ministry of Env. | 27.6950 | 85.3262 | *1302* |
| 6 | TU, Kirtipur | 27.6837 | 85.2842 | 1336 |
| 7 | Kathmandu Durbar Square | 27.7042 | 85.3079 | 1314 |
| 8 | Maharajgunj ,Teaching Hospital | 27.7353 | 85.3298 | 1339 |
| 9 | Bouddha | 27.7206 | 85.3614 | 1327 |

# Appendix IV

The concentration of $SO_2$ (µg/m$^3$) in ambient air for 4 weeks exposure of Developed diffusion tube is calculated as follows:

SO4$^{2-}$ amount in tube = 0.33 µg of $SO_4^{\ 2-}$
Corresponding quantity = (64/96) * 0.33 * 2 µg of $SO_2$ in the tube
= 0.44 µg of $SO_2$

(The $SO_4^{\ 2-}$ amount was multiplied by 64/96 to convert $SO_4^{\ 2-}$ to $SO_2$ and was multiplied by 2 as 2 ml was the volume used to extract the sample).

Length of tube, l = 0.05 m
Diffusion coefficient, D = 1.27 * $10^{-5}$ m$^2$ s$^{-1}$
Radius of tube, r = 0.006 m
Time of exposure, t = 28*24*60*60 s
= 2419200 s
Recalling the equation 7 from chapter 1,

$$C_1 = \frac{Ql}{1.27x10^{-5}(\pi r^2)t} \quad \dots\dots\dots\dots\dots\dots\dots.(7)$$

$$= \frac{0.44*0.05}{1.27x10^{-5}(3.14*0.006*0.006)2419200}$$

= 6.334 of $SO_2$ (µg/m$^3$)
The concentration of $NO_2$ (µg/m$^3$) in ambient air is calculated in the same way using the equation 6 from chapter 1.

# Appendix Va

**Two way ANOVA**

Table1: Weekly variation of passive sampling of ambient $NO_2$ for dry season

| | Sum of Squares | df | Mean Square | F | Sig.(5%) |
|---|---|---|---|---|---|
| Between Groups (Sites) | 0.1352 | 1 | 0.1352 | 33.8 | >7.71 |
| Between solutions/Within Groups (Weeks) | 0.006 | 3 | 0.002 | 0.5 | >6.59 |
| Residual | 0.0016 | 4 | 0.004 | | |

Table2: Weekly variation of passive sampling of ambient $SO_2$ for dry season

| | Sum of Squares | df | Mean Square | F | Sig.(5%) |
|---|---|---|---|---|---|
| Between Groups (Sites) | 0.1446 | 2 | 0.723 | 29.83 | >5.14 |
| Between solutions/Within Groups (Weeks) | 0.00083 | 3 | 0.000277 | 0.011 | >4.76 |
| Residual | 0.14543 | 6 | 0.02424 | | |

Table3: ANOVA test to compare between Tea conc. on ambient $NO_2$ sampling for dry season

| | Sum of Squares | df | Mean Square | F | Sig.(5%) | Sig.(1%) |
|---|---|---|---|---|---|---|
| Between Groups (Sites) | 0.1429 | 2 | 0.071467 | 5.56 | >3.89 | >6.93 |
| Between solutions/Within Groups (Weeks) | 0.50144 | 6 | 0.08357 | 6.5 | >3 | >4.82 |
| Residual | 0.1543 | 12 | 0.012854 | | | |

Table4. ANOVA test to compare between Tea conc. on ambient $SO_2$ sampling for dry season

| | Sum of Squares | df | Mean Square | F | Sig.(5%) | Sig.(1%) |
|---|---|---|---|---|---|---|
| Between Groups (Sites) | 0.01637 | 2 | 0.008185 | 5.052 | >4.46 | >8.65 |
| Between solutions/Within Groups (Weeks) | 0.0437 | 4 | 0.010925 | 6.743 | >3.84 | >7.01 |
| Residual | 0.01296 | 8 | 0.0162 | | | |

# Appendix Vb

Table: Comparison of absorbent bases (different filter papers) for ambient $NO_2$ –Pair t-test

| Two absorbents compared | No. of samplers | Mean $NO_2$ | Significance two-sample t-test difference P-value |
|---|---|---|---|
| GF-filter<br>What-4 | 9<br>9 | 6.7<br>5.3 | 18.313 |
| GF-filter<br>Q-5 | 9<br>9 | 6.7<br>5.0 | 10.272 |
| Q-5<br>What-4 | 9<br>9 | 5.0<br>5.3 | - 4.28 |

Table: Comparison of absorbent bases (different filter papers) for ambient $SO_2$ –Pair t-test

|  | No. of samplers | Mean $SO_2$ | Significance two-sample t-test difference P-value |
|---|---|---|---|
| GF-filter<br>What-4 | 3<br>3 | 7.1<br>2.98 | 9.05 |
| GF-filter<br>Q-5 | 3<br>3 | 7.1<br>2.91 | 7.36 |
| Q-5<br>What-4 | 4<br>4 | 2.92<br>2.89 | 0.19 |

# Appendix VI

## List of Materials

### Chemicals

1. Methanol ($CH_3OH$), Carlo Erba, Italy
2. Acetone ($CH_3COCH_3$), 99.5%, E.Merck, Germany
3. Triethanolamine ($C_6H_5NO_3$), 99%, BDH Chemicals Ltd., England
4. Sodium hydroxide (NaOH), 99%, Merck, Germany
5. Sulfanilamide ($C_6H_8N_2O_2S$), >98%, purum, Fluka, Switzerland
6. N-1 Naphthyl ethylendiamine dihydrochloride ($C_{12}H_{14}N_2.2HCl$), purum, Fluka, Switzerland
7. Phosphoric acid ($H_3PO_4$), 86.4%, AR grade, J.T. Baker, USA
8. Sodium nitrite ($NaNO_2$), >98%, purum, Fluka, Switzerland
9. Sulfate ($SO_4$) stock standard (1000 µg/ml), Merck, Germany
10. Hydrogen peroxide ($H_2O_2$), 30%, Carlo Erba, Italy
11. Sodium carbonate ($Na_2CO_3$), 99.7%, Carlo Erba, Italy
12. Sodium bicarbonate ($NaHCO_3$), 99.5%, Merck, Germany
13. Sodium iodide (NaI), 99%, Carlo Erba, Italy
14. Deionised water, milli-Q water

### Equipments

1. Spectrophotometer, Perkins Elmer Lambda 25
2. Dionex Ion Chromatograph DX-300, Dionex Corp., USA
3. Injection valve with a 25 µl sample loop, Rheodyne
4. Anion guard column, IonPac AG4A (4X50 mm)
5. Anion separation column, IonPac AS4A (4X250 mm)
6. Anion self-regenerating suppressor – I (4 mm)
7. Conductivity detector
8. BDS, Barspec Data System, Barspec System Inc., Israel
9. Vacuum pump, Water Associates, USA
10. Ultrasonic bath, model 8891, Cole-Parmer Instrument Co., USA
11. Filter unit, Millipore, USA
13. Diffusion tubes (Polyethylene), local chemical shop
14. Diffusion tubes, Ferm badge –IVL sweden
15. GF filter paper, Whatman no. 40 filter paper
16. Protective shields (polyethylene box)
17. Wires, adhesive tapes, Plastic forceps, parafilm
18. Syringe pre-filters, 0.45-$\mu$m pore size, Millipore Corp., Bedford, MA.
19. Membrane filter, 0.45 µm cellulose acetate, Sartorius, Germany
20. Disposable syringe (1 ml), Nipro Tuberculin, Nipro (Thailand) Corp. Ltd.
21. Micropipette, pipettes, beakers, volumetric flasks, and measuring cylinders etc.

# Appendix VII a

## Ambient Air Quality Monitoring

(A) Sampling in December, 2007

Sampling Area: Bijulibazar, Kathmandu
Sampling Station: Top of the CEMAT Building
Sampling Date: December 5, 2007 to December 6, 2007
Sampling Time: 5:05pm of Dec, 5 to 5:05 pm of Dec,6 (for 24 hours)
Sampler used: Respirable Dust Sampler (Envirotech Model APM 460 NL)

Table: Reading for $NO_2$ Sampling (5th December 2007)

| Volume of standard Solution (mL) | Concentration (µg/mL) | Absorbance (at 550 nm) |
|---|---|---|
| Blank | | 0.000 |
| Reagent blank | | 0.020 |
| 1.0 | 0.05 | 0.046 |
| 2.0 | 0.10 | 0.092 |
| 3.0 | 0.15 | 0.122 |
| 4.0 | 0.20 | 0.154 |
| 5.0 | 0.25 | 0.193 |
| Sample | | 0.113 |

Rotameter reading:
Initial reading: 0.58 lit. Per minutes.
Final reading: 0.40 lit. Per minutes.

Table4: Reading for $SO_2$ Sampling (5th December 2007)

| Volume of standard Solution (mL) | Concentration (µg/mL) | Absorbance (at 560 nm) |
|---|---|---|
| Blank | | 0.000 |
| 0.5 | 0.15 | 0.306 |
| 1.0 | 0.30 | 0.593 |
| 1.5 | 0.45 | 0.839 |
| 2.0 | 0.60 | 0.995 |
| Sample I | | 0.148 |
| SampleII | | 0.139 |

Rotameter reading:
Initial reading: 0.58 lit. Per minutes.
Final reading: 0.40 lit. Per minutes.

# Appendix VII b

(B) Sampling in Mach, 2008

Sampling Area: Bijulibazar, Kathmandu
Sampling Station: Top of the CEMAT Building
Sampling Date: March 30, 2008 to March 30, 2008
Sampling Time: 9:55am of Mar,30 to 2:00 pm of Mar, 30 (for 4 hours)
Sampler used: Respirable Dust Sampler (Envirotech Model APM 460 NL)

Table: Reading for $NO_2$ Sampling (30th March 2008)

| Volume of Standard Solution (mL) | Concentration (µg/mL) | Absorbance(at 550nm) |
|---|---|---|
| Blank | | 0.000 |
| 0.2 | 0.06 | 0.001 |
| 0.4 | 0.12 | 0.026 |
| 0.5 | 0.15 | 0.044 |
| 1 | 0.30 | 0.092 |
| 1.5 | 0.45 | 0.144 |
| 2 | 0.60 | 0.185 |
| Sample | | 0.020 |
| | (**0.57for 24hrs Sampling**)<br>22.66 ug/m3 calculated | 0.179 &0.18 |

<u>Rotameter reading:</u>
Initial reading: 0.58 lit. Per minutes.
Final reading: 0.40 lit. Per minutes

Table 6: Reading for $SO_2$ Sampling (30th March 2008)

| Volume of Standard Solution (mL) | Concentration (µg/mL) | Absorbance(at 550nm) |
|---|---|---|
| Blank | | 0.000 |
| 0.5 | 0.0025 | 0.042 |
| 1 | 0.050 | 0.094 |
| 1.5 | 0.075 | 0.142 |
| 2 | 0.100 | 0.182 |
| 3 | 0.150 | 0.279 |
| 4 | 0.200 | 0.369 |
| 5 | 0.250 | 0.468 |
| Sample I | | 0.140 |
| Sample II | | 0.135 |
| | 0.11 (19.98 ug/m3) | 0.178(24hr sampling) |

<u>Rotameter reading:</u>
Initial reading: 0.58 lit. Per minutes.
Final reading: 0.40 lit. Per minutes.

# Appendix VIII

Table: Detection limit for passive sampling method (DL of $NO_2$ and $SO_2$ in µg/m$^3$ for field exposure)

| Number of field blanks n | t-value $t_{0.01, n-1}$ | Standard deviation SB | Detection limit DL |
|---|---|---|---|
| $NO_2$ for one week exposure of tubes (Tube-1) | | | |
| 11 | 2.76 | 0.99 | 2.73 |
| $NO_2$ for two weeks exposure of tubes (Tube-1) | | | |
| 11 | 2.76 | 0.64 | 1.77 |
| $NO_2$ for three weeks exposure of tubes (Tube-1) | | | |
| 10 | 2.82 | 0.62 | 1.75 |
| $NO_2$ for four weeks exposure of tubes (Tube-1) | | | |
| 11 | 2.76 | 0.67 | 1.84 |
| $SO_2$ for one week exposure of tubes (Tube-1) | | | |
| 10 | 2.82 | 2.07 | 5.85 |
| $SO_2$ for two weeks exposure of tubes (Tube-1) | | | |
| 10 | 2.82 | 0.49 | 1.15 |
| $SO_2$ for three weeks exposure of tubes (Tube-1) | | | |
| 10 | 2.82 | 0.96 | 2.72 |
| $SO_2$ for two weeks exposure of tubes (Tube-2 and Tube-3) | | | |
| 10 | 2.82 | 1.04 | 2.9 |

# Appendix IX

Table: National Ambient Air Quality Standards (NAAQS) 2003 and WHO AQG

| **Parameters** | **Time weighted average** | **Concentration in Ambient Air (µg/m$^3$)** | **WHO AQG (µg/m$^3$)** |
|---|---|---|---|
| TSP | Annual | - | - |
| | 24-hours* | 230 | |
| PM$_{10}$ | Annual | - | 20 |
| | 24-hours* | 120 | 50 |
| Sulfur dioxide | Annual | 50 | - |
| | 24-hours** | 70 | 20 |
| Nitrogen dioxide | Annual | 40 | 40 |
| | 24-hours** | 80 | - |
| Carbon monoxide | 8-hours* | 10,000 | 10,000 |
| | 15 minutes | 100,000 | |
| Lead | Annual*** | 0.5 | 0.5 |
| | 24-hours* | - | - |
| Benzene | Annual | 20**** | |
| | 24-hours* | - | - |

*Notes:*

**24 hourly values shall be met 95% of the time in a year. 18 days per calendar year the standard may be exceeded but not on two consecutive days.*

***24 hourly standards for NO2 and SO2 and 8 hours standard for CO are not to be controlled before appropriate test methodologies have been implemented.*

****If representativeness can be proven, yearly averages can be calculated from PM10 samples from selected weekdays from each month of the year.*

*****To be re-evaluated*

# Appendix X

## Calculation of detection limit for ion chromatograph:

The DL for the ion chromatograph was calculated from the signal twice the standard deviation of the noise level with the help of equation 10 (Kanokkarn, 2003). For this, 25 µl volume of mixed standard solution each 0.01 µg/ml of $NO_2^{\ -}$ and $SO_4^{\ 2-}$ was injected into the ion chromatograph at the output range 1 µS. The minimum detectable quantity (MDQ) was calculated by a peak signal with two times the noise level (equation11).

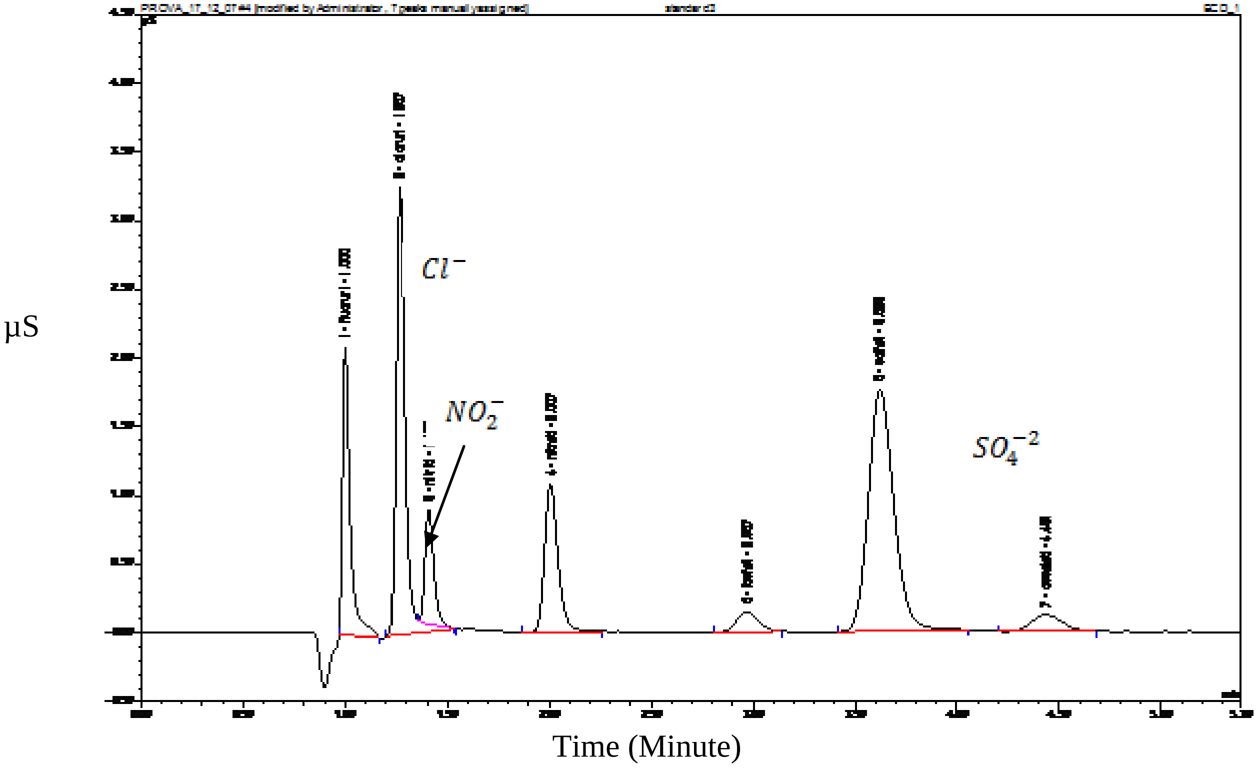

Figure:X-1 Chromatogram obtained from 0.01µS of $NO_2^-$ and $SO_4^{2-}$ mixed standard solution at output range 1 µS presenting Standard sample run.

Table: X-1Results of detection limits (DL) and minimum detectable quantities (MDQ) of $NO_2^-$ and $SO_4^{2-}$

| Anion | Concentration $m_x$ (µg/ml) | Noise signal n | Peak area (arbitrary unit) R | Width at half-height $W_{1/2}$ (sec) | DL µg/ml | MDQ µg. sec |
|---|---|---|---|---|---|---|
| $NO_2^-$ | 0.01 | 1467 | 17080 | 12 | 0.04 | 0.48 |
| $SO_4^{2-}$ | 0.01 | 1467 | 39118 | 18 | 0.02 | 0.36 |

# Appendix XIa

CEMAT
WATER LAB P. LTD.
(Water Analysis, Treatment Consultancy & Environment Research)

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Fax : 977-1-4780182
P. O. Box : 3953
E-mail : cemat@ccsl.com.np
Bijuli Bazar, New Baneshwor
Kathmandu, Nepal

## To whom it may Concern

It is to inform you that this organization is happy to provide Ms.Rejina (Maskey) Byanju, Doctorate fellow of Central Department of Chemistry, Institute of Science and Technology, TU, the all kinds of laboratory facilities available in this consultancy according to her requirement to complete her research on "Development of low cost passive sampling diffusion tubes for spatial monitoring of $NO_2$, $SO_2$ and $O_3$ for Kathmandu valley".

We wish her all the success in her research work.

9 April, 07

Sunil Palak
(Director)

Our Services : * Physical, Chemical, Bio-chemical and Biological Analysis of (i) Water and Waste Water (ii) Soil, Food stuffs, Drinks, Alcohol, Chemical Material, Air etc. (iii) Pathological Analysis (Blood, Urine, Stool etc.)* Environmental Monitoring * Establishment, Operation, Maintenance & Supervision of Analytical Laboratory * Training on Water Quality and Treatment * Quality Monitoring * Consultancy on Treatment of Water and Waste Water * ELA & other Environmental Research.

# Appendix XIb

ICIMOD

FOR MOUNTAINS AND PEOPLE

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Web www.icimod.org

**To Whom It May Concern**

I have the pleasure of recommending Ms. Rejina Maskey Byanju. She has been associated with ICIMOD as an Environment Officer from June 2006 to October 2008. During her tenure, she was involved in gathering air pollution related data and information, assisting in data analyses in order to carry out Rapid Urban Assessment for the Kathmandu Valley. This project was one of the component under the Programme Male' Declaration on Control and Prevention of Transboundary Air Pollution and its Likely Effect – the first ministerial level environment agreement in South Asia and supported by United Nations Environment Programme (UNEP). During the course of her assignment, she assisted in conducting top-down emission inventory of the Kathmandu Valley and supported GIS based analysis and modeling on air quality. During her 2 year period she also networked with relevant research and academic institutions and individuals and supported the preparations of the Kathmandu Valley Environment Outlook and Biodiversity Year Book report, which were supported by UNEP.

I find her a sincere and hardworking researcher with great potential to excel in the field related to environment. She has a pleasant, easy-going disposition, is fun to be with at both professional and social gatherings, and is cheerful, positive, and friendly. Her professionalism is a well-balanced blend of competence, experience, and cordiality.

I wish all the success in her future endeavors.

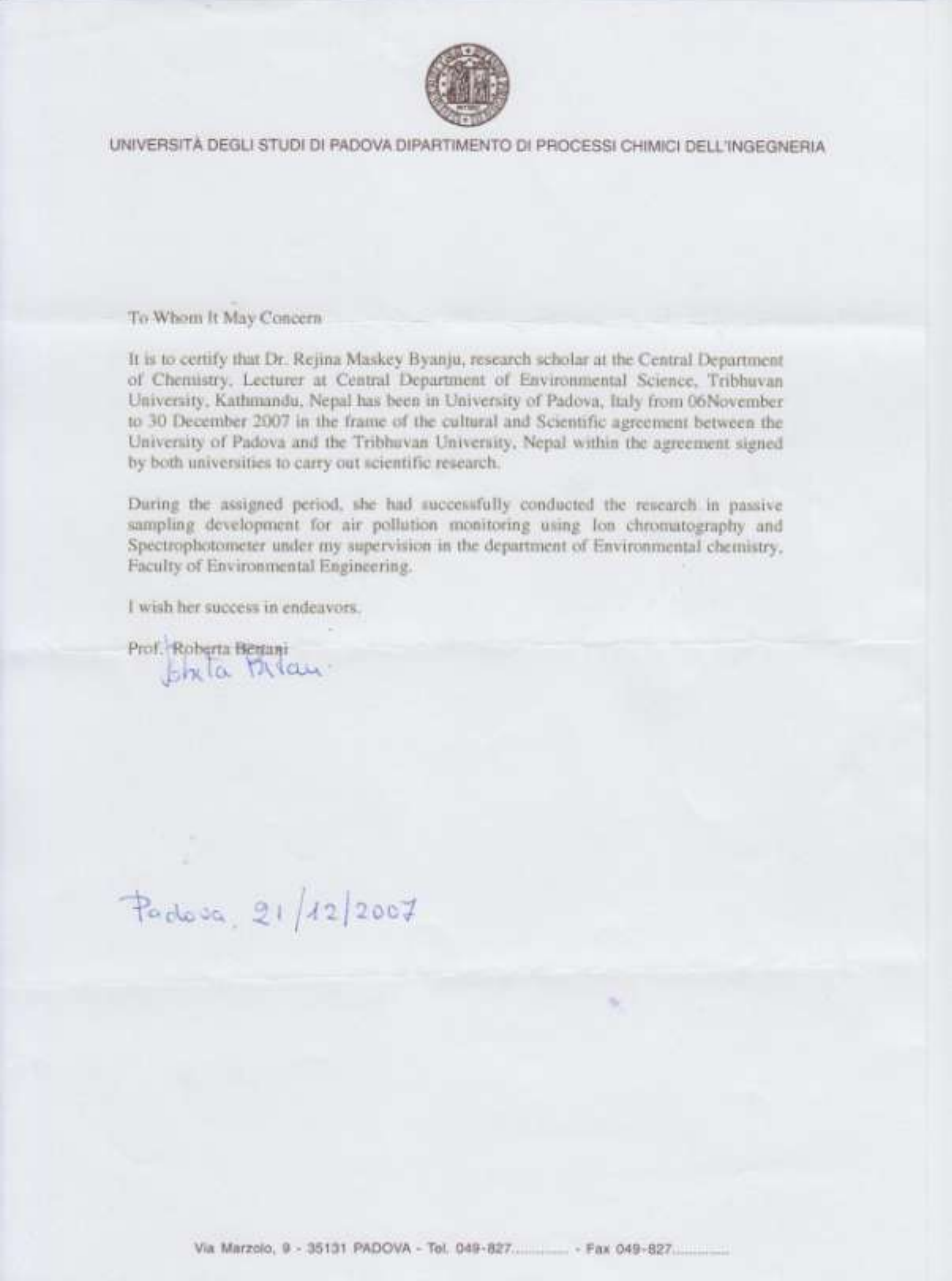
Basanta Shrestha
Division Head MENRIS
ICIMOD

1 Feb 2012

International Centre for Integrated Mountain Development

Direct Lines
Directorate: 5003316, Integrated Water and Hazard Management: 5003177
Environmental Change and Ecosystem Services: 5003013
Sustainable Livelihoods and Poverty Reduction: 5003040/5003141
Knowledge Management Support and Development and IT & Communication: 5003246
Mountain Environmental Natural Resources Information Systems: 5003242

# Appendix XIc



UNIVERSITÀ DEGLI STUDI DI PADOVA DIPARTIMENTO DI PROCESSI CHIMICI DELL'INGEGNERIA

To Whom It May Concern

It is to certify that Dr. Rejina Maskey Byanju, research scholar at the Central Department of Chemistry, Lecturer at Central Department of Environmental Science, Tribhuvan University, Kathmandu, Nepal has been in University of Padova, Italy from 06November to 30 December 2007 in the frame of the cultural and Scientific agreement between the University of Padova and the Tribhuvan University, Nepal within the agreement signed by both universities to carry out scientific research.

During the assigned period, she had successfully conducted the research in passive sampling development for air pollution monitoring using Ion chromatography and Spectrophotometer under my supervision in the department of Environmental chemistry, Faculty of Environmental Engineering.

I wish her success in endeavors.

Prof. Roberta Bertani

Padova, 21/12/2007

Via Marzolo, 9 - 35131 PADOVA - Tel. 049-827.............. - Fax 049-827..............

# Appendix XII

## Research paper:

1. **Byanju, R.M**, Gewali, M.B and Manandhar, K. (2012). **"**Passive sampling of ambient nitrogen dioxide using local tubes ", *Journal of Environmenta Journal of Environmental Protection***,** 3, 135-239**.** ISSN Print: 2152-2197, Published Online February 2012 in, Scientific Research Publishing, USA, www.sciRP.org/Journal/jep/
2. **Byanju, R.M**, Gewali, M.B, Manandhar, K., Pradhan, B.B, Dangol, P. and Ferm, M. "Urban air quality assessment of Kathmandu by passive sampling technique", *Journal of Environmental Science and Engineering A,1(4),467-483.*, ISSN 2162-5298 (Print) ISSN 2162- 5301(Online), David Publishing, USA.
3. Byanju, R.M, Gewali, M.B and Manandhar, K. (2011). "Low cost Passive Monitoring of Nitrogen dioxide and Sulphur dioxide in ambient air" *journal of Nepal Chemical Society*, 27 (1): 34-45.
4. Byanju, R.M, Gewali, M.B and Manandhar, K. (2010). **"**Low Cost Passive Samplers for Measurement of Ambient Ozone" *Proceeding: The First National Youth Conference on Environment (NYCE-I):* 190-198**.** June 3-4, 2010, Kathmandu, Nepal. www.himcca.org

5. **Byanju, R.M**, Gewali, M.B and Manandhar, K. "Development of low cost passive sampler for ambient nitrogen dioxide - an effort from developing world" *Asian Journal of Water, Environment and Pollution,* No. AJWEP/837/180111, IOS Press.nl (On Review)

**Paper presented:**

**Byanju, R.M,** Gewali, M.B and Manandhar, K. 2008. "Low cost Passive samplers for Determination of Nitrogen dioxide and Sulfur dioxide in ambient air", *Abstract CHEM11 FIFTH NATIONAL CONFERENCE ON SCIENCE AND TECHNOLOGY*, Nov. 10-12 , Kathmandu Nepal. Abstract CHEM11

**Poster:** Measuring Air Pollutants by Diffusive Sampling and Other Low Cost Monitoring Techniques" in Kraków, Poland, 15 – 17 September 2009. http://www.rsc-aamg.org/Pages/Presentations/Krakow2009.htm

**Byanju, R.M**, Gewali, M.B and Manandhar, K. 2010. "Low Cost Passive Samplers for Measurement of Ambient Ozone" *The First National Youth Conference on Environment (NYCE-I):* 190-198**.** June 3-4, 2010, Kathmandu, Nepal. Abstract www.himcca.org

**Byanju, R.M**, Gewali, M.B, Manandhar, K., Pradhan, B.B, Dangol, P., Pradhan, S., Shrestha, B., Ferm, M, Liljeberg,M., and Sjoberg, K. 2010. "Rapid Urban Air Quality Assessment of Kathmandu Valley" *2010-A-133-IUAPPA , 15th IUAPPA World Clean Air Congress,* Vancouver, British Columbia, Canada on September 12-16, 2010. www.iuappa2010.com

Bidya Banmali Pradhan, Pradeep Dangol, **Rejina Byanju**, Suyesh Pradhan, 2010. "Rapid Urban Assessment of Air Quality for Kathmandu-Patan", *International symposium on Benefiting from Earth Observation: Bridging the data gap for Adaptation to Climate Change in the Hindu Kush Himalaya,* 4-10 October,2010 Kathmandu Nepal. Abstract Volume ThemVII pp 104.