Measurements and Prediction of Particulate Number Concentrations and their Chemical Composition over Yanbu Industrial City, Saudi Arabia

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

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Abstract

The University of Manchester
Jaafar Nashed Hameed AL-Mahmoudi; Degree Title: PhD
Measurements and Prediction of Particulate Number Concentration and their chemical composition over Yanbu Industrial City, Saudi Arabia Date: July 21, 2011

Abstract: Many recent studies have highlighted the substantial health-related impacts of particle number (PMno) rather than particle mass. The aim of this study is to determine the correlation of trace gases with PMno, to identify the chemical composition of particle different sizes and to predict the NOx and PMno over Yanbu Industrial City (YIC).

Trace gases (NOx, SO2, H2S, O3, CO), PMno with diameter (7nm-10μm), traffic and meteorological parameters were measured at three sampling sites in YIC. The maximum PMno (333,971 cm⁻³) at downwind site#1 was about 2.5 times higher than that (123,842 cm⁻³) at upwind site#2 and about 1.2 times higher than that (263,572 cm⁻³) at downwind site#3. The average PMno distribution at downwind sites consisted of one distinguishable mode (nucleation mode<20nm) whereas the upwind site had two modes (the nucleation and the accumulation modes). The correlation of PMno with NO/NOx (r>0.7) are generally stronger than with NO2 at sites#1 and 2, whereas for site #3 the correlation between PMno with NO2/NOx are better than with NO. PMno has generally either weak or poor correlation with SO2 and CO, respectively. Particle samples of different sizes (7nm-10μm) were chemically analysed using an ion chromatograph (IC) for inorganic ions and inductively coupled plasma mass spectrometry (ICP-MS) for trace metals at site#3. The ionic analysis revealed that sulfate and ammonium was mainly present in particle of size < 0.38μm while nitrate and chloride was mainly present in particles of size > 0.38μm. Non-sea salt sulfate was dominant in all particle sizes compared to the marine sulfate which is minor. The total sulfate and nitrate contributed 50.3% and 24.4% of the total ionic mass respectively followed by chloride (13.3%) and ammonium (10.6%). The trace-metals analysis results indicated that Na represented more than 94% of the total mass and the contributions of the remaining metals (Al, Sr, Zn, V, Cr, Fe, etc) were about 6%.

A further part of this study consisted of the coupling of the WRF/CALMET system with the CALPUFF model, which was applied to predict NOx and PMno concentrations. The WRF model was employed to generate the meteorological input data for CALMET. WRF predictions were evaluated with surface data and upper air profiles using RASS/SODAR and radiosondes. WRF tends to underestimate the surface temperature on average with biases of up to -3.4°C and also underestimates temperature profiles with average biases ranging between -2.7 and -5.2°C when compared to the RASS profiler, but with a lower bias (< -2.4°C) when compared to radiosonde profiles. The mean wind speed bias for the majority of the cases was close to the benchmark of ±0.5m/s, but the mean wind direction bias for half of the cases exceeded the benchmark of 10°. It was concluded that WRF predictions can be used for air dispersion modeling to produce reasonable outputs. NOx predictions by CALPUFF showed that the contribution of the traffic to the highest concentrations during the nighttime was up to 80%, but after sunrise the contribution from industries became higher (up to 70%). The highest predicted NOx concentration (~313μg/m³) was much lower than the national ambient standard (660μg/m3) and the community area is affected much by industries during mid-morning hours when the wind shifting from land breeze to sea breeze. The fractional bias (FB) ranged between -0.1 and 1.06 indicating that the model tends to under-predict the NOx observations. PMno predictions of two sizes (7-40nm and 7nm-10μm) were derived based on the NOx predictions. All FB values were ranged between -0.1 and 0.5. It was concluded that PMno predictions were generally better than those of the NOx due mainly to adding the background term (intercept) for the PMno predictions.
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Chapter 1: Introduction & Literature Review

1.1 Introduction

Particulate matter air pollution becomes an important issue especially in urban areas due to their impact on human health and environment. Particulate matter are a mixture of various sizes emitted from different sources with different chemical compositions (Wilson and Shu, 1997). These particles are often divided into coarse particles (diameter larger than 2.5μm) and fine particle (diameter smaller than 2.5μm) (Kittelson, 1998). The latter size (Fine particles) can further be divided into two size ranges; ultrafine or nuclei mode (0.01μm to 0.1μm) and accumulation mode (0.1 to 1μm). Ultrafine or nuclei mode particles are emitted directly by combustion sources or form by nucleation during dilution and rapid cooling of the exhaust (Kumaret al., 2010). The main characteristic of ultrafine particles is their high number per unit air volume with a negligible fraction of the total mass concentration. The other size (accumulation mode) is formed by coagulating of ultrafine particles and condensation of gases and vapors onto pre-existing particles. The lower range of the accumulation mode usually accounts for most of the surface area but the upper range accounts for most of particle mass. The atmospheric lifetime of accumulation mode is in the order of a few days and even longer because these particles are generally too small to be removed by gravity and too large to coagulate into larger particles.

Fine and ultrafine particles are composed largely of soot, organic compounds and elemental carbon, and secondary reaction products of sulfur dioxide, nitrogen oxides, and hydrocarbons (Kleeman and Cass, 1998; Pun and Seigneur, 2001). The half-life of fine particles defined as “days to weeks” (Wilson and Shu, 1997). On the other hand, coarse particles (2.5μm to 10.0μm) are generated primarily from suspended soil/street dust, sea salt, and other crustal materials (Boon et al., 1998). The coarse particles have an approximate half-life of “minutes to hours” (Wilson and Shu, 1997).

Many epidemiological studies have shown a strong link between increased concentration of PM$_{10}$ and increased mortality, morbidity and respiratory symptoms (Dockery and
Pope., 1994; Pope et al., 1995a). However, a large number of fine and ultrafine particles have been proposed as a major contributor to such health effects (Seaton et al., 1995; Delfino et al., 2005; Oberdorster et al., 2005). Oberdorster et al. (1994) showed that a high number concentration of ultrafine particles (<0.1um in diameter) may cause serious health effects in rats even with low mass concentration. Other studies have found a link between ultrafine and fine particles and respiratory health in asthmatic adults and children (Peters et al., 1997; Pekkanen et al., 1997). Peters et al. (1997) noted that number concentration of ultrafine particles were more closely associated with variations in lung function than PM$_{10}$ particles because ultrafine particles have a relatively higher deposition rate and penetration through lung tissue than larger particles. However, Pekkanen et al. (1997) demonstrated equally strong effects for both both sizes (ultrafine and PM$_{10}$).

In this literature review, the following aspects will be discussed: impacts of particulate matter on human health and environment; sources and chemical composition of particulate matter; particulate measurements in urban, semi-urban and rural areas; parameters affecting particulate matter levels; dispersion modeling of particulate matter and gases and finally particulate matter ambient standards. The reason for choosing this area of study is because: (1) there is an increasing concern on the particulate number measurements because of its impact on human health and environment; (2) Little work has been done to simultaneously measure both the number distribution and chemical composition of atmospheric ultrafine particles in urban areas; (3) little work has been done on prediction of particulate number of different sizes; (4) there are increasing sources of particulate number as shown by several studies (such as Bagley et al., 1996 and Hunter and Gray, 1997, Kumar et al, 2010) which show that emissions of particle mass concentrations from new vehicles decreased dramatically but at the expense of an increase in the fine and ultrafine particle number.
1.2 Impact of particulate matter on human health and environment

Particulate matter was one of the main air pollutants demonstrated to have serious impact on human health, climate change, and variety of chemical processes in the atmosphere (Kumar et al., 2010). Scientific studies prove that particulates (especially particles of diameter less than 1µm) play a role in climate change (Dingenen et al., 2004). Both observations and predictions suggest that the increase in the atmospheric particulate matter load may delay the global warming expected due to greenhouse gases (GHGs). The increase in GHGs since pre-industrial times causes an overall warming of 2.4Wm−2, whereas the increase in aerosols is producing a cooling of up to 2.5Wm−2 (IPCC, 2001). As a result, GHGs are warming and aerosols are cooling which means more or less cancel each other. Atmospheric aerosols can affect global climate change directly by scattering and absorbing, in case of black carbon, sunlight (Schwartz, 1996) and indirectly through changing the radiative properties and lifetime of clouds (Twomey, 1991) and negative effect on visibility (Seinfeld and Pandis, 1998).

As scientific evidence has linked increased health risk to exposure to particulates especially to fine and ultra-fine particulates (Dockery et al., 1993), many studies have been directed towards the health effects of particulate matter (e.g. Dockery and Pope, 1994; Samet et al., 2000 and Pope et al., 2002). The health effects of particle matter have been studied extensively and a strong correlation between human mortality and particulate matter concentration has been found (Dockery et al., 1993; Jarrett 2005). There are studies (Wilson and Spengler, 1996) to suggest that an increase in ambient aerosols levels are associated with short-term changes in mortality, hospital admissions, lung function and symptoms while other studies (Pope et al., 2002; 1995a) to suggest the association with long-term prevalence of symptoms and mortality from respiratory diseases. Berico et al., (1997) show that particulate matter less than 10µm in size (PM_{10}) have significant association with decline in lung function, respiratory and cardiovascular disease death and PM_{2.5} is shown to be very high correlated with deaths from cardiopulmonary disease and lung cancer. Studies by Wyzga (2002) and Andersen et al (2008) indicate that PM_{10} is associated with respiratory responses and PM_{2.5} with
cardiovascular and cardiorespiratory diseases. Bown, (1994) claimed that 10,000 people per annum are dying prematurely because of PM$_{10}$ emissions, mainly from car exhausts.

In an epidemiology-based study by Kunzli et al., (2000) to quantify the effects of air pollution particulate matter from data collected in several urban areas (Austria, France and Switzerland), it was noted that an increase of 10µg/m$^3$ in PM$_{10}$ caused 6% of total mortality per year. Of this, about 50% of all mortality cases caused by air pollution were attributed to traffic sources. Vedal (1995) reported that an increase of 10µg/m$^3$ (an exposure increment) above ambient level of 20µg/m$^3$ of inhalable particulate (PM$_{10}$) may result in a linear increase in human health impacts. Another epidemiological study by Wilson and Spengler,(1996) showed that a 10µg/m$^3$ increase in PM$_{10}$ mass concentration with short term/episodic exposure may cause an increase of 0.5-1.5% in premature total mortality while long term exposure may cause an increase up to 5% in premature total mortality.

It is also found by Pope et al., (2002; 1995a) that associations between day-to-day air pollution exposure (fine particulate, sulfur oxide) and all cause, lung cancer, and cardiopulmonary mortality. Further, it is found that an increase of 10µg/m$^3$ in ambient long-term PM$_{2.5}$ was associated with increased risk of all-cause, cardiopulmonary (4%), lung cancer mortality (6%), and increased lung cancer mortality (8%), although the magnitude of the effect, and hence the risk, somewhat depended upon the time scale of pollution monitoring. On the other hand, measurements of large particles (coarse and total suspended particles) were not consistently associated with mortality (Pope et al., 2002). Schwartz et al, (1996) noted that each 10µg/m$^3$ increase in PM$_{2.5}$ concentration was associated with an increase of 1.5% in the total daily mortality. Burnett et al (1999) and Linares and Diaz (2010) reported a link between a 10µg/m3 increase in PM$_{2.5}$ concentration and up to 3.3% rise in cardiorespiratory-cause admissions among elderly people. However, in contrast a study conducted by Chen et al (2005) in greater Vancouver area on people aged over 65 years showed no significant association between increases in PM$_{2.5}$ and increase in the number of respiratory-cause admission among the elderly but the larger particle size (PM$_{10-2.5}$) has higher effect on respiratory admissions.
than PM$_{2.5}$; which tends to underscore the disparity in the results reported in the literature review regarding the effects of PM$_{2.5}$ on hospital admissions seen from a quantitative point of view. This study indicates the importance of chemical composition of particles which may give clearer picture on the effect of particulate matter on human health.

Whilst numerous studies have linked the particle matter exposure to adverse effects on human health, several toxicological studies (Oberdorster, 1992, 2001, 2000; Brown et al., 2000; Ferin et al., 1990; Donaldson et al., 1998) have concluded that at the same mass concentration and chemical composition, ultrafine particles (diameter <100nm) are more toxic and harmful than larger particles. Particle shape and size play a major role in controlling where the inhaled particles deposit inside the human respiratory system (Hinds, 1999; Lipkea et al., 1979). Small particles (<1µm in diameter) have a high probability of deposition deeper in the human respiratory system and are likely to worsen respiratory diseases. Further, these particles have higher burdens of toxins because when they are absorbed inside the human body, they can result in health consequences other than respiratory health effects.

Dockery et al., (1993) and Pope et al., (1995a) have shown that the correlation between particle concentration and health effect increases with decreasing particle size. Another study by Yeh et al., (1997) has reported that the total deposition fraction of ultrafine particles in the deep lung increases with decreasing particle diameter with the most affecting size between 5 and 100 nm. A toxicological study by Lingard et al (2005) supported these findings indicating that ultrafine particles are more harmful on human health than larger particles per unit mass, and toxicity per unit mass increase as particle diameter decreases.

Many studies (Penttinen et al., 2001; Moshammer and Neuberger, 2003; Ghio and Devlin, 2001) have shown that besides the mass of fine particles, the number concentration, the particle surface area and the elemental composition of particles were related to respiratory health effects (especially respiratory problems).
Currently, there are several hypotheses used to explain the association between ambient particle matter exposure and observed adverse health effect. One hypothesis suggests that particle surface contaminants, such as transition metals (e.g. lead, cadmium, vanadium and iron), contribute to the burden of ill health (Gilmour et al., 1996), wherein the ultrafine particles are thought to act as transporter to those contaminants, initiating local lung damage when the particles deposit on the surfaces of epithelial tissues. Another hypothesis argues that the physical characteristics (e.g. number, size, shape properties) are important in producing adverse health effects (Berube et al., 1999).

There have been several studies (e.g. Ober dorster, 2001) that do not focus on the inhaled mass but rather on the number or the total surface of particles inhaled because the larger particles, containing most of the mass, are deposited in the human upper respiratory tract and are more easily removed. On the other hand, particles (smaller than about 2.5µm) can get down to the lungs and subsequently be deposited in the lower lung area (alveolar region). It has been shown by Seaton et al., (1995) that in the alveolus, the presence of a number of particles is more important to the adverse effect than total mass. Donaldson et al., (1998) suggested that ultrafine particles could penetrate deep into pulmonary interstitial spaces in the lungs and thus provoke inflammation.

There are strong indications that the particle number concentration has more impacts on human health than the particle mass (Donaldson et al., 1998). Peters et al., (1997) has linked respiratory problems with the ultra-fine particle number concentration of ultra-fine particles rather than to larger particle. Number concentrations of ultrafine particles were shown by Peters et al., (1997) to be more closely associated with variations in lung function than with other larger particles (PM$_{10}$ or fine particles). Some studies (Weichen et al., 2007 and Sioutas et al., 2005) suggest that human health effects appear to better correlate with submicrometer particle number concentration rather than particle mass concentration. However, Pekkanen et al., (1997) demonstrated equally strong health effects for both ultrafine and PM$_{10}$ particles.
Research by Zimmer (2002) indicated that toxicological response associated with the exposure to ultrafine particle may be more appropriately represented by particle number or particle surface area rather than particle mass. Moshammer et al., (2003) suggested that particle mass concentrations, mainly emitted from mechanical processes, may not be associated with adverse health effects. Therefore, Penttinen et al., (2001b) recommend that air quality monitoring should include measurements of particle number, which mainly reflect ultrafine particles.

1.3 Physical Characteristics of particulate matter

Particle size is probably the most important parameter for characterizing the behavior of aerosols. All other properties of aerosols depend on particle size, some (such as surface area) very strongly. Further, most aerosols cover a wide range of sizes. A hundred fold ranges between the smallest size and the largest particle size of an aerosol is common.

Pitts Barbara et al. (1999) and Kittelson, (1998) suggested that the particles can be divided into two groups. Particles with diameters greater than 2.5µm which are defined as coarse particles and those with diameter less than 2.5 µm are called fine particles as shown in figure 1.1. The fine particle mode can be further broken down into particles with diameters between 0.1 and 1 µm, known as the accumulation range, and those with diameters between 0.01 and 0.1 µm, known as the transient or Aitken nuclei range (Raes et al., 2000) and particle of <20nm as nucleation mode (Emily et al., 2007).
The residence time of particles in the atmosphere depends mainly on the particle size. For example, particles in accumulation range (0.1-10µm diameter) can stay in the atmosphere up to typically about one week (Kittelson, 1998). Whereas, larger particles (i.e., > 10µm diameter) are easily removed very quickly by gravitational settling and smaller ones (i.e. <0.1µm diameter) by mainly diffusion and coagulation. A typical residence time for 10 nm particles is only about 15 min (Harrison, 1996). The main mechanism for removal of such tiny particles in the atmosphere is coagulation with other particles in the accumulation mode. Wilson and Suh, (1997) suggested that the average atmospheric half-life of fine particles is in the range of “days to weeks” whereas the half-life of coarse particles is in the range of “minutes to hours”.

Particulate matter can be solid or liquid. Liquid particles are nearly always spherical, but solid particles usually have complex shapes. Kumar et al (2010) suggest that nanoparticles have a variety of shapes (e.g. tabular, irregular, aggregated or agglomerates) rather than an ideal sphere. In the development of the theory of aerosol properties, it is
usually assumed that the particles are spherical. These theories (correction factors and the use of equivalent diameters) can be applied to non-spherical particles.

The other physical property is particle density, which is referring to the mass per unit volume of the particle itself. The particle density may vary from 1000kg/m³ (Kumar et al., 2010) to more than 2000kg/m³ (Godoy et al., 2009) depending mainly on the chemical composition and water content (Gidhagen et al., 2005). Also another common measure of concentration is number concentration, the number of particles per unit volume of aerosol, commonly expressed as number/cm³. Particles of different sizes have different chemical composition and different sources.

1.4 Sources and chemical composition of particulate matter

There are two types of particles: primary particles (released directly from a source in the particulate phase) and secondary ones (formed from gaseous precursors). Primary particles are emitted by a number of combustion and non-combustion sources into the atmosphere. The non-combustion sources including natural ones (such as dust storms, sea salt, tyre and brake wear etc.) usually emit primary particulate in sizes larger than 2.5µm, but the combustion sources (automobiles, industries) emit primary as well as gaseous precursors of secondary particulate which are lower than 2.5µm. On the other hand, secondary particulate can be emitted by both types of sources and formed in the atmosphere during the oxidation of gaseous precursors (such as SO₂, NOₓ, etc.).

In urban areas the sources of atmospheric particles can be divided into two major groups: one group that contributes mostly to the number concentration, while the other is related to the mass concentration (Ruuuskane et al., 2001). The anthropogenic sources (especially traffic) are the main contributor to the number concentration of particles (especially ultrafine particles) while non-combustion sources are the major source of mass concentration and they are emitting much higher amount of PM than that from anthropogenic sources. A study by Pey et al. (2009) for the urban atmosphere of
Barcelona in Spain revealed that 65% of the total particle number concentrations (in the range 13-800nm) associated with vehicles emissions while other sources (industrial emissions or mineral dust, sea spray) account for 1-2% of the number concentration but contribute between 20 and 30% of the PM mass. On a global scale, it was estimated by Colls J. (1998) that the total particles mass production on average is \(5.5 \times 10^9\) ton/year, 90% is of biogenic origin and 10% due to anthropogenic sources. Also, IPCC (1996) indicated that PM emissions reach \(3.4 \times 10^9\) ton/year. Anthropogenic sources account for small fraction (10%) of the total PM emissions, whereas the natural sources may contributes up to 85% \((2.9 \times 10^9)\) ton/year. However, these figures may change dramatically depending on time and place. For example, on a local scale such as highly industrial or urban areas, anthropogenic sources play more important role than biogenic sources. Jacobson (2002) estimated that in the United States in 1997, about \(37 \times 10^6\) ton of PM\(_{10}\) were emitted. Of these emissions, about 67% to 71% were anthropogenic in origin. He also suggested that on a global scale, more than 50% of all particle emissions are anthropogenic in origin. However, these studies have not shown any specific number on how much the emissions of fine or ultrafine particle from biogenic and anthropogenic sources.

Fugitive dusts from both paved and unpaved roads are considered as another source of particles in urban areas. For example, according to the Washington State Department of Ecology (WSDOE, 1993) and based upon the 1993 emissions inventory for Sparkane, WA, paved and unpaved roads dust contributed over 74% of the area's PM\(_{10}\) (neglecting wind-blown dust from natural sources). Particulate emissions from paved road surface are a complex mixture of components generated from various sources. The particles originating from the roadway are either emitted directly from vehicle exhaust (Pierson and Brachazek, 1983) or produced through vehicle brakes, tires, and general vehicle wear processes (Rogge et al., 1993). In addition, particles which settle onto the road from other sources (nearby and distance sources) become part of the mixture and can be subsequently suspended by vehicle movements or wind.
Abu-Allaban et al. (2003) performed measurements at two roadside locations to determine emissions factors for tailpipe, brake and tire-wear and re-entrained road dusts. The results indicate that tailpipe emissions and road resuspended particles are the dominant sources that contribute mostly to the total PM emissions factors. The results also show that PM$_{2.5}$ is mainly emitted from tailpipe, with some secondary particulate from background sources and a small contribution from geological sources. Some nearby activities (such as cooking and vegetative “burning”) were also observed as minor source for this particle size. The main sources for PM$_{10}$ mode include mostly tailpipe emissions, resuspended road dust, and background particulate. The brake-wear source was noted mainly in the PM$_{10}$ mode. This study by Abu-Allaban et al. (2003) also revealed that the contribution of resuspended road dust depends on several factors, namely vehicle speed, road conditions (i.e., degree of silt loading), and the percent of heavy duty vehicle. The contribution of break-wear to the PM$_{10}$ mode were highest near the freeway exit sites with less significant for other sites. PM$_{10}$ emission rates from road dust varied from 40 to 780mg/km and 230 to 7800mg/km for light-duty and heavy-duty vehicles, respectively depending slightly on the degree of silt loading. Emission rate for the case of PM$_{2.5}$ varied from 10 to 50mg/km and 60 to 480mg/km for light-duty and heavy-duty vehicles, respectively.

1.4.1 Sources of Different sizes of PM:

Studies showed that different sizes of particulates have different origin. Analysis of contribution of different sources sectors for 2001 from NAEI showed that road transport is responsible for only 18% of the total PM$_{10}$ emissions, 35% of PM$_{1.0}$ emissions but more than 50% of PM$_{0.1}$ emissions. Amato et al., (2009b) carried out source apportionment in the urban atmosphere of Barcelona (Spain) and found that the traffic emission account for 18-21, 25-32 and 30-36% of the PM$_{10}$, PM$_{2.5}$ and PM$_{1}$ mass concentration, respectively. Dongarra et al (2010) studied the particle matter of different sizes with chemical composition at three sampling sites in the city of Palermo (Sicily, Italy) and indicated that approximately 50% of particulate matter is from road traffic and
also noted that PM$_{2.5}$ and PM$_{10}$ loads in urban area with high traffic density may be up to 140% higher than in suburban sites.

Janhall et al. (2004) studied the particle emissions from the vehicles. The results show that different sizes of particles attributed to various origins. The finest particles (10-50nm) had high correlation with traffic density, while the larger particle size (50-170nm) were long distance transported, and related to low traffic intensity and aged nitrogen oxides. High loadings of 170-368nm particles were accompanied with high concentration of sulfur dioxide due to likely emission from a local combustion source.

Holton et al. (2002) defined an idealized atmospheric particle size distribution with the different characteristic modes. Aitken or nuclei mode particles often contain ‘primary’ particles and are mostly emitted directly by combustion sources. Accumulation mode particles have most of the submicron mass and contain typically ‘secondary’ particles in origin which are formed by chemical transformation in the atmosphere (such as sulfate, nitrate, and organics). Coarse-mode particles tend to be produced by mechanical processes such as soil dust.

Harrison and Maricq (2001) also indicated that particles with different sizes come from different sources. Nucleation mode particles (<0.02μm diameter) are either directly emitted from gasoline engines or result from gas-to-particle conversion of different chemical compounds such as sulphuric acid and ammonia. Aitken mode particles (0.02-0.1μm) are directly emitted from combustion sources (i.e. traffic, mainly diesel engines) but also result from condensational growth of nucleation mode particles. Accumulation mode particles emitted mainly from industrial combustion sources and resuspension from road surface. Some particles (especially in accumulation mode) in the atmosphere also originate from natural sources such as sea spray and wind blown dust. One-micron particle may be produced by natural sources, resuspension and combustion processes. Particles of 1 and 10μm diameter are mainly generated by mechanical processes; dust, resuspension of soil, industrial processes and sea-salt (Laakso et al., 2003).
Holton et al., (2003) indicated that fine particles below roughly 1µm are mainly secondary particles or emitted directly by combustion sources whereas coarse particles (with diameters>1µm) are mainly primary particles and result from the surface of the earth (sea, land, vegetation).

By considering the road transport sector, tyre and break wear emissions in 2001 accounted for approximately 23% of the total road transport emissions (AQEG, 2004). This study also suggests that the contribution of resuspended road dust to the total PM\textsubscript{10} can be as large as those from the exhaust emissions and in some cases much large. (AQEG, 2004) The total UK emissions of coarse particles in 2001 showed that the industrial processes sector contributed most (34%) followed by domestic combustion (19%). However, for smaller particles (<2.5µm diameter), the road traffic sector is the most important (39%), followed by industrial processes (21%). In fact, the road traffic sector is even more important at the ultrafine particle size (<PM\textsubscript{0.1}) compared to other sources, where it accounts for 54% of the total emissions.

Road traffic and stationary combustion sources generates a significant number of nanoparticles of diameter <10nm (Shi J. et al., 2000). In this study, it was shown that nanoparticles account for more than 36-44% of the total particulate number concentration near the roadside (4m from kerb) and at about 25m downwind from kerb. Although both a diesel and a petrol-fuelled vehicle generated nanoparticles, the fraction of nanoparticulate from a stationary combustion source was even greater in a plume 350m downwind.

Breed et al. (2002) analysed samples from three episodic events (24-hr PM\textsubscript{10}>50µg/m\textsuperscript{3}) and three non-episodic events (24-hr PM\textsubscript{10}≤50µg/m\textsuperscript{3}) to determine the possible sources and chemical composition. The results showed that combustion sources contributed more to particle size of <2.5µm while geologic material is responsible for particle with size between 3 and 4µm. The output of this study also showed that as the ambient PM\textsubscript{10} level decrease, the proportion of PM\textsubscript{2.5} tend to increase suggesting that more frequent non-
episodic PM\textsubscript{10} level are dominated by fraction $<2.5 \mu m$. Also, the author suggested that in Prince George (Canada), episodic events were influenced mainly by geological sources while the non-episodic events are impacted mostly by anthropogenic sources (industrial, combustion) and to less extent by geological material. These authors confirmed that the fine and ultrafine particles generally represent anthropogenic sources (mainly traffic) while the coarse particles represent geological sources. Although, geologic material sources contribute to some extent to the fine fraction of ambient PM\textsubscript{10} level, its major contribution to the coarse size range is noted for its presence in ambient PM\textsubscript{10}.

1.4.2 Source contribution to PM\textsubscript{10}:

Inventory in apportioning airborne PM\textsubscript{10} to its sources for the UK was indicated in the quality of Urban Air Review Group (QUARG, 1996). In this report, it was shown that the major sources of PM\textsubscript{10} in the UK as a whole in 1993 were as follows: road traffic sources, 24%; non-combustion processes, 24%; public power, etc. 15%; commercial institutional and residential combustion facilities, 16%; industrial combustion plants and combustion processes, 17%. In contrast, the statistical data for Greater London indicates a road traffic account for 86%, the remainder arising from traffic 6%, commercial and institutional 4%, industrial 2% and construction sources 2%. Harrison (1996) achieved similar results which showed that about 90% of the PM10 particles emitted in greater London in 1990 were associated with road traffic.

Harrison et al., (1997) show that there are three main sources of PM\textsubscript{10} in the UK urban atmosphere as follows: (1) Primary fine particles from combustion and industrial sources, in practice predominantly road traffic. (2) Coarse size particles generated from road surface dust and resuspension of soil particles by combined effect of wind flow and traffic-induced turbulence. (3) Secondary aerosol, mostly sulfate and ammonium nitrate derived by oxidation of sulphur and nitrogen oxides respectively.
A study conducted by Countess (1996) revealed that major sources of PM$_{10}$ aerosols were motor vehicles, resuspended road dust, and marine aerosols. The contribution of motor vehicle was higher than the marine contribution at urban sites but much lower at marine background sites. Road dusts accounted for up to 29% of PM$_{10}$ at urban sites. Fresh marine aerosols were characterized by reduced levels of sulfate, nitrate, and motor vehicle emissions. In term of particle number, a recent study by Kumar et al., 2010 indicated that particle number concentrations in marine and forest environment are typically lower by 2-3 orders of magnitude than those in urban areas.

Hosiokangas et al. (1999) used a receptor modeling method to identify the main sources and their contribution to the measured concentrations of PM$_{10}$ particles in Kuopio, Finland during January to April, 1994. The daily mean concentration of PM$_{10}$, SO$_2$, CO and BS and elemental concentrations of PM$_{10}$ samples for 38 days were measured and analysed. The results revealed that source contributions to the average PM$_{10}$ concentration of 27.2μm/m$^3$ were: Soil and dust represents 46-48%, traffic exhaust 13-14%, heavy fuel oil 12-18% and wood burning ca. 11% and unidentified sources is 15-23%. This study also showed that the main source during dust episode is soil and street dust, but burning processes and road traffic emission dominate during winter months. However, this study may be misleading because of the impact of a dust episode and the limited number of samples.

Chow et al. (1992) used a Chemical Mass Balance technique to carry out a PM$_{10}$ source apportionment study at six sites within California’s San Joaquin Valely. It was noted at the site with the highest annual average concentration of PM$_{10}$ that 54% of PM$_{10}$ was generated from primary geological material, 15% from secondary ammonium nitrate, 10% from primary vehicle emission, 8% from primary local construction activities and 4% from other miscellaneous sources.
1.4.3 Source contribution to PM$_{2.5}$

In recent years, emissions from certain anthropogenic sources (mainly stationary sources) has been reduced in most of the developed countries due to less consumption in high sulphur content fuel. On the other hand, emissions, especially for fine and ultra-fine particles, from other anthropogenic sources (traffics) are increasing. It has been estimated in highly industrialized countries that traffic-related aerosol air pollution accounted for more than 50% of the total particulate air pollution (Harrison, 1996).

Emissions from vehicles, especially diesel, are the main contributors of fine particles to the atmosphere in urban areas. It was estimated by Schauer et al. (1996) that 51-69% of the fine particles in Los Angeles downtown during 1982 were related to road traffic emissions. Approximately one-quarter of these fine particles were not directly emitted from vehicles but produced by fugitive dust sources. There were not many studies discussing nanoparticles sources, but measurements made near roadways suggest that vehicles can be considered as dominant source for this particle size. Harrison (1996) states that ultrafine particle number concentrations are much more elevated near traffic roads than are PM$_{10}$ mass concentrations. Another study conducted by Booker (1997) in urban and rural Oxfordshire indicated that particle number concentration was highly correlated with vehicle traffic but PM$_{10}$ concentration was uncorrelated with traffic.

Many studies emphasize the major impact of traffic emissions on PM level. Wrobel et al. (2000) examine the influence of traffic on particulate air pollution in an urban area. The authors analysed the measurements of two size fractions: >1.9µm (coarse fraction) and <1.9µm (fine fraction). The traffic contribution to PM was determined based on 13 elements (Mg, Al, Si, S, Ca, Ti, Fe, Zn, Pb and others). The results show that the traffic contribution in the coarse mode was about 80% up to 150m from the road, about 40% at 200-270m and 20% at 1500m. The traffic contribution to the fine particle condense concentrations of individual elements was between 50 and 70% at 5m from the road; then this percentage decreased, followed by an increase distance from the road.
1.4.4 Emissions from Petrol and Diesel vehicles

In order to estimate the vehicle contribution to PM, NOx as well as CO were considered as makers since many studies (QUARG, 1993b) show that vehicles are the main responsible for these pollutants. Deacon et al. (1997) found close correlations between PM$_{10}$ and NO$_X$ and CO for much of the time at all 16 sites. This study confirms the importance of vehicle-emitted PM$_{10}$ as a contributor to atmospheric concentration and confirms the ratio of PM$_{10}$ to carbon monoxide from road traffic. Secondary sulfate and nitrates show less scale spatial variability if compared with the primary sources of PM$_{10}$. Secondary particles do not appear to be a major contributor to urban concentration in winter episodes, but it can be important during summer photochemical episodes. This study indicate three main sources contributing substantially at UK sites: Vehicle exhaust, secondary sulphate and nitrates, and resuspended surface dust and soils.

Several studies confirmed the importance of the traffic particles emissions especially for fine and ultra-fine sizes. Wahlin et al. (2001) studied the particle distribution at different sizes ranging from 0.01 to 0.7um using different mobility analyzer. This study showed high correlation between the CO, NOx and ultrafine particles at street level, which indicates the fact that the road traffic is the major source of ultrafine particles in urban environment.

Motor vehicles emissions contribute significantly to atmospheric particle concentrations in urban areas (APEG, 1999). They are thought to be the major source of ultrafine particles emissions (especially nano-particles) in urban areas without major industrial activities. Murawska et al. (1998) and Ristovski et al. (1998) indicate that the majority of particles from vehicle exhaust are in the size range 20-130nm for diesel engine and 20-60nm for gasoline engines. Charron and Harrison (2003) made measurements of particulate number size distribution in the range 11-452nm on the side of the busy Marylebone Road in the central London and they found that the accumulation mode particles are more correlated with emissions from heavy-duty traffic (mainly diesel
vehicle) whilst ultrafine mode particles show a stronger correlation with light-duty traffic.

Northern Front Range Air Quality Study (NFRAQS) performed in the Denver area (USA) highlighted the importance of the road traffic contribution to ambient PM$_{2.5}$ concentration (Fujita et al., 1998). It was noted that 38% of the observed wintertime PM$_{2.5}$ was attributed to mobile sources. Gasoline vehicle contributed (28%) of the observed PM$_{2.5}$, while diesel vehicles were account for (10%) of PM$_{2.5}$. This means that the gasoline-fuelled vehicle PM$_{2.5}$ contribution exceeded the contribution from diesel vehicles by approximately a factor of 3. This contrasts with an earlier study conducted by (Schauer et al., 1996) for the downtown Los Angeles site which show that 64% of the mobile source contribution was from diesel vehicles and 36% was from gasoline vehicle emissions.

A comparison study was conducted by Gertler, (2005) to evaluate the relative contribution of diesel and gasoline powered vehicles to ambient PM in the US. This study show that the 2000 USEPA inventory attributes (62%) of mobile source contribution to diesel engines and (38%) to gasoline engines, while on contrary the California inventory predicts (33%) of the emissions are from diesel engines and 68% are from gasoline engines. Another study by Colvile et al., 2001 found that PM$_{10}$ emissions from diesel-engine vehicles were much larger (67% of total) than from petrol engines (11%).

Colls J. (1998) indicated that petrol (spark-ignition) engines have been shown to emit as many nanoparticles, around $10^{14}$km$^{-1}$, as diesel engines under high speed cruising conditions. This understanding may change the common perception that it is diesel engines that are mainly responsible for particle pollution from vehicles.

In studies conducted by Morawska et al. (1998) and Ristovski et al., (1998) on diesel and gasoline vehicles, it was noted that the average emissions of ultrafine particles from gasoline engines were up to a few orders of magnitude lower than that from diesel
engines. Therefore, the contribution of diesel engines to the total emission inventory in an airshed could be significant or even dominant in areas of increased density (bus or truck routes within the city). A recent study by Roth et al (2008) found that typical signature size distribution for diesel and gasoline engine exhaust clearly into two modes with strong nucleation mode (7-29nm) and accumulation mode peaking at 60nm.

Other studies focus primarily on particles emitted by diesel engines, because particulate mass emissions from diesel engines typically are up to 100 times higher than those from petrol engines (Kittelsohn, 1998). However, if very tiny particles or number emissions need to be considered, spark ignition may also be a concern. By considering the emissions for engines, it is stated by Kittelson (1998) that most of the mass particle emitted by engines is in the accumulation mode, 50nm < Dp <1000nm, range, while most of particle number is in the nanoparticle range, Dp< 50nm. The author also stated that nanoparticles typically consist of hydrocarbons or sulfate and form by nucleation during exhaust dilution and cooling process, while accumulation mode particles consist of mainly carbonaceous soot agglomerates formed directly by combustion.

Motor vehicles (especially heavy-duty diesel) emit fine particles directly and precursor gases that react in the atmosphere to form secondary particulate matter. Cass and Gray (1995) estimated that in the 1980’s, on-road diesel contributes 15% of fine particulate carbon and 44% of black carbon emissions in the Los Anglos air basin. Several studies by Solomon et al., 1980; Chow et al., 1992, 1994 and 1995; Watson et al., 1994a and Philip et al (2007) showed that secondary ammonium nitrate, chemically formed from direct emissions of NOx comprises a significant fraction of fine particulate mass during the fall and winter months.

Kirchstetter et al., (1999) made an assessment for fine particulate and nitrogen oxide emissions from light- and heavy-duty vehicles in two tunnel bores: first bore carried both light-duty vehicles and heavy-duty diesel trucks, and the second bore was restricted to only light-duty vehicles. Their results showed that heavy-duty diesel trucks emitted 24, 37, and 21 times more fine particles (PM2.5), black carbon (BC), and sulfate (SO4^2-) mass
per unit mass of fuel burned than light-duty vehicles. In addition to having higher emissions of fine particle mass, heavy-duty diesel trucks emit approximately 15-20 times the number of accumulation mode particles than that of light-duty vehicles per unit mass of fuel burned. Also, the study indicated that PM$_{2.5}$ emissions from both types of vehicles were composed mostly of carbon; diesel-derived particles contained more BC (51±11% of PM$_{2.5}$ mass) than did light-duty fine particle emissions (33±4%). Sulfate comprised about 2% of total PM$_{2.5}$ mass emissions from both heavy and light-duty vehicles. This study suggested that heavy-duty vehicles in California are contributing more than three-quarters of exhaust fine particles emissions and nearly half of oxides of nitrogen emissions from on-road motor vehicles.

Many studies have shown that vehicles are major contributors for the level of fine particulate matter. Harrison et al. (1997) studied the hourly concentration of PM$_{10}$ and PM$_{2.5}$ in Birmingham (U.K.). This study show that based on the correlation between NO$_x$ and particulate matter it was estimated that vehicle exhaust emissions contributes an average of 32% of PM$_{10}$, and 41% of PM$_{2.5}$ during a six month study period, with more in episodes, whilst making only a negligible contribution to coarse mode particles. Statistical analysis for the data also showed a good correlation between PM$_{10}$ and PM$_{2.5}$ in the winter season, with PM$_{2.5}$ particle contributing 80% of PM$_{10}$. In summer months, coarse particles (PM$_{10}$- PM$_{2.5}$) account for almost half of PM$_{10}$ mass concentration and the influence of resuspended surface/soil dusts and of secondary particulate is evident. The chemical analysis showed three main sources dominating PM$_{10}$ composition: vehicle exhaust emissions, secondary ammonium salts and resuspended surface dusts.

Giugliano et al., 2005 measured PM$_{10}$, PM$_{2.5}$ and PM$_1$ at 4 different characterized urban sites to assess the contribution of traffic to the observed concentration levels of fine particulate. It is proven the contribution of PM$_{2.5}$ and PM$_1$ to PM$_{10}$ concentration which was the lowest during summer holiday when traffic is significantly reduced, while this contribution was at their highest during winter when there is heavy traffic. The analysis of PM$_1$ contribution to PM$_{2.5}$ estimated to be 90% regardless of the site and the period of the year. Further, this study pointed out that the secondary particulates (Sulfate, nitrate
and ammonia) account for 30% of the PM$_{2.5}$ mass in summer and 50% in winter, but these components account only for 10% of PM$_{2.5}$ mass at the Tunnel site in the city center. The elemental carbon contribution was ranging between 1% and 10% and was no significant difference between winter and summer months. On the other hand, the organic carbon was in the wider range (6.7-36%) and the seasonal average contribution is statistically different, with a higher during winter (26.6%) compared to 19.3% in summer. This value of organic carbon is in agreement with the results by Philip et al (2007).

Evaluation and quantification the contribution of ultrafine particles emissions from traffic close to a road with respect to the size distribution was conducted by Molnar et al. (2002). The result confirmed a good correlation between PM$_{2.5}$ and accumulation mode particles (100-368nm). In contrast, there was no obvious correlation between number concentrations of ultrafine particles (10-100nm) and PM$_{2.5}$ or the accumulation mode particles. These results agreed with a previous study by Ruuskanen et al. (2001), but disagree with other study by Ruellan and Cachier (2001) which found a high correlation between hourly average number concentration of ultrafine particles and PM$_{2.5}$ at a road site in Paris during summertime.

Beauchamp et al. (2004) classified his observations into two groups: one with normal traffic conditions and one with far fewer heavy duty vehicles (HDV). They found that the levels of PM$_{10}$ and NOx increased during periods of high HDV numbers, whereas the levels decrease significantly when HDV are completely banned. In contrast, the variations of aromatic compounds and CO were minor between these two periods. Furthermore, on workdays NOx concentrations reached a maximum that corresponded to a peak in HDV numbers, whereas the aromatic hydrocarbons peaked later when LDV number reached their maximum. This study concludes that increased levels of NOx and PM$_{10}$ can be predominantly attributed to high HDV number.
1.4.5 Chemical composition of PM

Particulate matters have a very diverse chemical composition which varies in time and space. Further, the chemical composition of aerosol particle varies with particle size. The chemical composition of particulate matter includes mainly sulphate, nitrates, ammonium, sodium chloride, elemental and organic carbon and a range of minerals although contributions of some components are higher than others in certain size (Putaud et al, 2010). These components are either primary component (emitted directly into the atmosphere) or secondary ones, which are formed in the atmosphere by chemical reactions.

Colls J. (1998) suggested that the nuclei mode (<50nm) consists mainly of the volatile organic and sulphur compounds that form during exhaust dilution and cooling, together with solid carbon and metallic compounds from the combustion sources. This mode dominates the number distribution, but contributes only a few percent to the mass. The accumulation mode, between 50nm and 1µm, contains carbonaceous agglomerates and their adsorbed materials and make up most of the mass. The coarse mode contains around 10% of the mass, made up of a small number of large particles which have been re-entrained from deposits on the walls of the exhaust system. Kittelson, (2002) also reported that ‘nuclei mode particles’ (particle size<30nm) primarily consist of volatile material (mainly heavy hydrocarbons) generated from lubricating oil with some of sulphuric acid, carbon or metallic ash. On the other hand, ‘accumulation mode particles’ (particulate in the range of 30-500nm) consist of soot and condensed hydrocarbons and primarily non-volatile, but a wide range of overlap exists between the two modes.

Dodd et al. (1991) measured the composition of various elements in particles collected in a rural area in Maryland as a function of size and observed in individual samples as many as four distinct modes between 0.09 and 1µm. For example, in one particle sample, there were multiple peaks at ~ 1µm containing Na, Fe, Ti, Mn, and Al, at 0.5-0.6 µm containing As, Sb, Se, V, La, and Ce, and at 0.28µm containing S and a single peak at
~0.1µm containing Na, Ga, Ti, Al, La, Ce, and Fe. Dodd and co-workers suggest the smallest particles represent primary emissions from high-temperature combustion sources, whereas the larger ones result from both secondary reactions (e.g., forming sulfate) and direct contribution from multiple sources.

Chemical composition of ultrafine particle (UFP, particle diameter<0.1µm) were determined at an urban and at a rural site in the Helsinki area by Pakkanen et al. (2001a). The results of this study showed that the average chemical composition of UFP was similar at both sites. The highest contribution to UFP at both sites was the non-analysed fraction assumed to contain primarily carbonaceous material and some water. It was estimated that amount of water was about 10% (50ng/m³) and that of carbonaceous material about 70% (350ng/m³). These results are similar to, or perhaps slightly higher than that observed by others which have indicated that about 50-70% of UFP mass consists of carbonaceous material (Berner et al., 1996 and Hughes et al., 1998). Of the measured components, the study show that sulfate, nitrate, and ammonium made up a significant fraction of UFP mass. The contribution of sulfate was 6-7% (32-40ng/m3) of UFP which is dominated over ultrafine nitrate 1-2% of UFP mass (4-11ng/m3). The contribution of ammonium to UFP in Helsinki was about 5% (22-25ng/m³). The most important metals at both sites were Ca, Na, Fe, K, and Zn with average UFP concentrations ranged between 0.7 and 0.6ng/m3. Of the heavy metals, Ni, V, Cu, and Pb were important with average concentration ranged between 0.1 and 0.2ng/m³.

Dongarra et al (2010) studied the inorganic and organic concentrations in different particle sizes at three sampling sites in the city of Palermo (Sicily, Italy) and pointed out that 31–47% (in weight) of PM₁₀ and 29% of PM₂.₅ is made up of water-soluble ions and ammonium sulphate and nitrate particles accounted for 14–29 wt% and crustal and marine components, combined, account for 41-49% in of particulate matter mass concentrations.

Little work has been done to simultaneously measure both the particle number distribution of different sizes with chemical compositions in urban areas. Hughes et al.
(1998) examine the number concentration, size distribution, and chemical composition of atmospheric ultrafine particles under wintertime condition in Pasadena, CA, near Los Angeles. The results of this study show that the fine particle mass concentration is dominated by particles larger than 0.1 µm diameter. Further, it was noted that water soluble inorganic Ionic species (mainly nitrate and sulfates) are commonly found in particles larger than 0.2-0.3 µm diameter, with the highest concentrations present in particles larger than 0.5µm diameter. By contrast, particles with size range of 0.1< dp < 0.3um are mostly carbonaceous, particles with size of dp < 0.1 µm are found to consist of 46-62% elemental carbon and organic compounds.

Borkely-Kiss et al. (1999) collected aerosol samples from urban and rural areas in an eastern Hungary for several years. The results revealed that in the coarse fraction, seasonal average concentration of elements of predominantly natural origin (Al, Si, Ca, Ti, Fe with enrichment factors less than 6) are obviously lower in the winter period due to effects of frozen soil and snow sources, while these natural elements increased in summer months due to increased erosion of the ground. In the fine mode, elements of anthropogenic origin (S, Cl, K, V, Mn, Zn, Br, Pb with high enrichment factors) are present more abundantly during the winter months.

The EPEFE Auto-Oil Program (EPEFE, 1995) characterized the particulates emitted from diesel vehicle running with different fuel formulations, but all with similar sulphur content of around 400 ppm, about 10 times higher than current levels. It was found that the particle mass concentration consisted of around 70-80% as elemental carbon, around 13-23% as heavy hydrocarbons from the fuel and lube oil and 7% as sulfates. The primary contribution to sulfate is however minor compared with secondary sulphate formation.

Marcazzan et al. (2001) analysed 24-hour simultaneous samplings of PM$_{10}$ and PM$_{2.5}$ during Dec. 1997- Sep. 1998 in the central urban area of Milan to investigate the relationship between the two fractions and compare their elemental composition and their possible sources. The results revealed that PM$_{2.5}$ is a great part of PM$_{10}$ and that a good
correlation exists between these fractions of particulate matter which supported recently by Putaud et al (2010) who also suggested that there is no a single ratio between both sizes valid for all sites but this ratio may range from 0.5 to 0.9. The elemental composition results showed that in the PM$_{2.5}$ concentrations of crustal elements are very low while many anthropogenic elements (such as S, Pb and heavy metals) have high concentration. In PM$_{10}$, S, Ca, Mn and Zn, show quite constant values while K, Fe, Br, Pb have lower levels in summer than in winter and Al, Si concentration increases in summertime. On the other hand, in PM$_{2.5}$ S, Mn, Cu, have similar values in winter and summer, while K, Zn, Br and Pb decrease and Al, Si, Ti, Ca, Fe increase in summertime.

Pakkanen, Korhonen et al. (2001) used the Aitken modes to estimate local sources for ultrafine particles. The results showed that in the Helsinki area there are two groups of elements. First group represented by Ba, Ca, Mg, and Sr had some common source for UFP, possibly the emission from motor vehicle. Fe, Co, Mo and Ni represented the second group of elements in the UFP, the likely main source for these elements is oil combustion.

Chemical profiles of four different sizes (PM$_{1.0}$, PM$_{2.5}$, PM$_{10}$ and PM$_{30}$) were compared by Chow et al. (1994). The results showed that paved road dust profiles of PM$_{1.0}$ and TSP are most dissimilar, while the PM$_{2.5}$ and PM$_{10}$ profiles tend to look alike. The organic carbon abundances range from 10±2% in TSP to 26±4% in PM$_{1.0}$. The OC/TC ratios are similar, between 0.86 and 0.91, among the four different sizes. Abundances of crustal species such as Al, Si, K, Ca, Ti, and Fe differ by no more than a few percent among these different sizes.

A study conducted by Querol X. (2002) to identify the detailed physical and chemical characterization and emissions sources of total suspended particles (TSP) in the city of Hueva in Spain. The results showed that PM$_{10}$ accounting for only 40% of TSP mass (37 µg/m$^3$ for PM$_{10}$ and 91 µg/m$^3$ for TSP). The main sources and chemical composition identified in this study are: The crustal sources (Al, Mn, Ca, Fe, Mg, K) accounted for a mean of a 40% of the TSP mass; the anthropogenic species such as NH$_4$, NO$_3$ account
for 24% of the bulk TSP; and marine components (such as Cl and Na) reached 5% of the TSP mass; other trace components accounts for less than 1% of the TSP mass.

Seinfeld et al. (1998), Gray et al. (1986) indicated that between 10% and 65% of PM$_{2.5}$, in the USA consists of carbonaceous material, either directly emitted as primary particulate or produced from gas-particle conversion processes (secondary particles).

Misaelides P. (1993) analyzed toxic elements in airborne particulate matter at two sampling points located in the urban and the rural areas of Thessaloniki, Greece. This study showed that some elements (As, Br, Sb and Zn) were significantly higher in urban area (the city center) than in rural area. With respect to their origin, As, Sb, Br, Zn and partially Cs seem to originate from anthropogenic sources, whereas Cr and Ca are soil-derived.

Emission measurements and chemical composition of PM$_{10-2.5}$ (coarse) and PM$_{2.5}$ (fine) in Beirut, Lebanon were analysed by Shaka and Saliba (2004). Their results revealed the presence of common inorganic ions like SO$_4^{2-}$, NO$_3^-$, SiO$_4^{2-}$, CO$_3^{2-}$, and NH$_4^+$, and organic compounds such as aliphatic carbons, alcohols, carbonyls, and organic nitrate. Comparison of PM$_{2.5}$ and PM$_{10-2.5}$ chemical compositions showed that PM$_{2.5}$ contains higher concentrations of both inorganic ions and organic compounds. Carbonate species are present as carbonated ion form in PM$_{2.5}$ and as carbonate in PM$_{10-2.5}$, higher concentration of organic species, i.e. alcoholic and carboxylic acid long chains are mostly present in PM$_{2.5}$ while in PM$_{10-2.5}$ higher water concentration were detected.

More than 700 aerosols samples were collected and analysed by Orlic et al. (1999) during a two year period, 1996-1997, in Singapore. The objectives of this study were to determine the average elemental concentrations in fine and coarse aerosol fraction as well as to identify major pollution sources at two different sampling locations; industrial area and residential area. The results showed that sulfur, with mean concentration of about 2000ng/m$^3$, is the most dominant element in the fine particulate at both sites and its major source are oil refineries and oil-powered plants. Sulfur is followed by
potassium with an average concentration of 300ng/m3 and its main source is biomass burning processes.

On the other hand, on the coarse fraction dominant elements are Al, Si, Fe, Ti and Na, Cl and all these elements come from natural sources (soil erosion and sea-spray). Sulfur and potassium are also present in the coarse fraction. The value of total elemental concentrations (TEC) (about 3521ng/m3) represents only about 10-15% of the total mass of PM2.5 concentration, but fine soot, mainly carbon with addition of H, O and N account for 90% of the total PM2.5 mass. The TEC of coarse fraction is almost double (6801ng/m3) the amount of the fine fraction. With regard to apportionment of sources, the results showed two major components: natural and anthropogenic. Within the natural components the following were major contributors: soil (Al, Fe, Ti, etc.) and sea-spray (Na, Mg and Cl). Within the anthropogenic component, the following dominant elements/groups are present: sulfurs (S), metals (Mn, Ni, Cu, Zn), smoke (K), construction site/surface road dust (Ca, K, Ti, Fe) and vehicular emission (Pb, Br). Some of these elements (such as K, Ca, Ti and Fe) are often associated to more than one source (industrial and soil). This study concluded that all anthropogenic elements (S, K, Pb, Br) were mainly present in the fine size fraction (< 0.5µm diameter) while all natural components (Si, Ca, Ti, Fe) peaked at the coarse size fraction (about 5µm). Also, anthropogenic components (S, K, metals) make up to 70% of TEC in the fine fraction while the remaining 30% associated with the natural components (soil and sea-spray). The coarse fraction composition was in the opposite of the above.

The chemical composition of marine aerosols in Eastern Mediterranean, Haifa and Tel Aviv were studied by Ganor et al. (1998). The results showed that during the sea breeze calcium sulfate, sodium sulfate and sulfuric acids were the main constituents of aerosols; on the other hand, during the land breeze, other particle compositions (sulfate, nitrates, phosphate, and trace elements, etc) stemming from industries, increased in concentration.

Jacobson (2002) suggest some generalisations about composition such as: (1) newly nucleated particles usually contain sulfate and water, although they may also contain ammonium; (2) metals that evaporate during industrial emissions recondense, primarily
onto accumulation mode soot particles and coarse mode fly-ash particle; (3) the metal emitted in the greatest abundance is usually iron. Sea spray and soil particles are primarily in the coarse mode.

Road traffic emissions are among the major contributors to fine and ultrafine particle concentration in the urban atmosphere (Kleeman, et al., 1998). A study by Kleeman, (2000) to analyse size and composition distribution of fine particles from motor vehicles show that chemical composition analysis showed that particulate emissions from the gasoline engines are largely composed of organic compounds while particulate emissions from diesel engines consisted mainly of elemental carbon and organic compounds.

Chemical composition of fine and coarse particles at the urban, semi-urban and rural sites was studied by Pakkanen et al. 2001. The results revealed that the chemical composition of the urban and rural fine particles were almost similar and contained mainly of sulfate 21% and 25%, nitrate 12% and 11%, crustal matter 12% and 13%, ammonia 9% and 10% and others (mainly carbonaceous material and water) 43% and 37% respectively. The chemical composition of coarse particle at urban site and semi-urban site were nearly identical and they were dominated by crustal materials (59%) and non-analysed components (such as carbonaceous material and water) 28%, while the other components were much lower: sea-salt 7%, nitrate 4% and sulfate 2%. However, at the rural site, the chemical composition of coarse particle was lower for crustal matter (37%) and sea-salt (3%) but higher for non-analysed components (51%).

Several studies conducted by Pakkanen et al. 1999 and Ojanen et al., 1998 on the composition of the aerosols in Finland. In urban conditions, Vallila, PM$_{2.5}$ consist mainly of SO$_4$ (20%), OC (19%), BC (19%), NO$_3$ (14%), NH$_4$ (9%), soil (8%) and sea-salt (3%). But in background area, Luukki, PM$_{2.5}$ consist of SO$_4$ (25%), OC (18%), BC (9%), NO$_3$ (11%), NH$_4$ (9%) and sea-salt (3%). The coarse particles composition is quite different having about 50% of soil-based materials.
A typical approximate breakdown of particulate matter composition in the UK (QUARG, 1993) may be expressed as follows: ammonium ~ 5%, sulfate, nitrate and chloride ~ 30%, carbonaceous material ~ 40%, metals ~ 5% and insoluble material (minerals) ~ 20%. Alfarra M.R. (2004) studied the chemical composition of PM in urban as well as in rural areas. The results from this study showed that a significant accumulation mode with a peak around 400-500nm was observed at all sites (Edinburgh, Manchester, Vancouver, Langley) and was principally composed of sulfate, nitrate, ammonium and organic material. He and his co-workers found that at the urban sites the small organic mode was found to be highly correlated with NOx in Manchester and with CO, 1,3-butadiene, benzene and toluene in Vancouver with Pearson’s r values of 0.86, 0.76, 0.71, 0.79 and 0.69, respectively. These correlation results suggest that combustion sources (dominated by road traffic) are the main source of the organic species at the mentioned sites.

1.5 Particulate measurements in urban, semi-urban and rural areas

Total particle number concentrations vary from place to place depending on how much the impact of anthropogenic sources on those places. For example it is found that the particle number is less than 10 cm⁻³ over Antarctic Plateau in winter, and infrequently at mid-latitudes in polar outbreaks, to around 10⁵ cm⁻³ in large cities (aerosols/climatology of Tropospheric Aerosols, 2003). Over clean ocean regions, particle concentrations are typically several hundred cm⁻³, varying seasonally, with a maximum level in summer months. It is suggested that in truly clean continental areas (e.g. across Australia), particle concentrations are more typically around 700 cm⁻³ in the boundary layer and decreased to about 200 cm⁻³ above the boundary layer.

The difference between numbers of particles below 100nm is larger between the roadside site and the urban background than between the urban background and the rural site (AQEG, 2004) because freshly emitted particles below 100 nm have a short lifetime in the atmosphere due to coagulation and other processes. Their number rapidly drops with distance from the road (Zhu et al, 2009). On the contrary, for particles above 300 nm the difference between the roadside site and the urban background is smaller than the
difference between the urban background and the rural site. Earlier measurements in London using electron microscopy by Waller, (1967) found 10,000 particles cm$^{-3}$ at background locations, 30,000-50,000 particles cm$^{-3}$ in street and 160,000 particles cm$^{-3}$ in road tunnels and during foggy conditions. It was found that the particle concentration over clean maritime environment is around 200 particles cm$^{-3}$ (Harrison, 1997).

Jaenicke (1993) suggests the total number concentration (nucleation, Aitken and accumulation) for remote continental areas is about 6,000 cm$^{-3}$ and for urban environment (e.g. street canyon) more than $10^5$ cm$^{-3}$ whereas Laakso et al. (2003) showed 2,000 and 17,000 cm$^{-3}$, respectively. Putaud et al. (2010) observed the total particle number concentration as low as 2000 cm$^{-3}$ in 3 sectors of Europe (Northwestern, Southern and Central) and can exceed 40,000 cm$^{-3}$ at urban and kerbside sites. Further, Laakso et al., (2003) indicated that in urban conditions nucleation mode dominates total number concentration, in rural conditions Aitken mode.

Hussein et al. (2004) indicated in his study that in rural areas typical particle number concentrations are between 1,000 and 10,000 cm$^{-3}$ varying seasonally whereas in urban environments air quality, which is strongly influenced by road traffic sources, the particle number concentration usually exceeds 10,000 cm$^{-3}$. Harrison et al., (1999) found that particle number concentration near a busy road in Bristol, Rd Birmingham was 7.5 times higher than the background level. Another study by Ruuskanen et al., (2001) showed that the median of the hourly mean total number concentration at an urban site in Helsinki was about 20,500 cm$^{-3}$ (mostly ultrafine particles), with a maximum value of 145,000 cm$^{-3}$. They also found that the particle number concentrations were similar in both Alkmaar in Netherlands and Erfurt in Germany.

Wehner et al., (2002) made measurements of particle number size distribution from 3 to 800 nm at two sites in Leipzig of Germany: one site is a street canyon representing the urban traffic and the other site is the building of the Institute for Tropospheric Research (IfT) as the urban air background. At both sites, the maximum concentrations occurred during rush hour. However, the concentration of 10nm particle in the street canyon was
10 times higher than that at the IfT, whereas for the concentration of 100nm particle in the street canyon was about 3 times higher than at the IfT. The main difference between the two sites occurred at diameters below 50nm. The maximum concentration measured at the IfT building was at 24nm diameter, whereas that at the street canyon was 13nm diameter. The measurements in the street canyon show that the maximum particle number concentration occurred on weekdays at diameter for 10 to 20 nm in the morning hours (06:00-12:00). The number concentration increased dramatically during the early morning hours from 25,000 cm\(^{-3}\) at 03:00 to 150,000 cm\(^{-3}\) at 07:00 and then decreased during afternoon and evening hours due to probably less traffic emissions and more wind dilution, reaching to about 20% of the maximum at midnight.

### 1.5.1 Correlation between NO\(_x\), CO and Particle number

There are many studies (Morawska et al., 1998b; Thomas and Morawska, 2002; Marconi et al., 2007; Emily et al., 2007; Roth et al., 2008; Wang et al., 2010) which show strong correlation between the concentrations of submicrometer particles and the concentration of NO\(_x\) and CO. Morawska et al., (2002) found in the vicinity of a major road (about 100m) with traffic volume of 10\(^5\) vehicles per day that 50% increase in traffic flow rate results in similar increases of both CO and NO\(_x\) concentrations and a higher increase of about 70% in particle number concentration. The authors also noted during 5-year observations that the mean particle number concentration on weekdays was about 8.8\(\times\)10\(^3\) cm\(^{-3}\) and on weekends about 5.9\(\times\)10\(^3\) cm\(^{-3}\) which is 47% difference. In highly polluted urban environment that are significantly influenced by motor vehicle emissions, particle number concentration may exceed 10\(^5\) cm\(^{-3}\).

Ketzel et al. (2003) found that the particle number concentration highly correlated (R>0.83) with NOx through a wide range of particle sizes and this result is in agreement with Wang et al., 2010 who conducted measurements of pollutants gases and particle number concentrations at two sites, one near a major highway and another near a busy urban street in Copenhagen, Denmark. The results suggested the Pearson correlation
 coeficient between NOx and particle number is higher than 0.85 for particle diameter between 30 and 100nm and slightly lower for diameter less than 30nm.

Wehner et al., (2002) noticed that the NO concentration correlated well with total particle number concentrations (weekdays: R= 0.89; Sunday: R=0.93). This correlation was poor during afternoon hours where NO was increasing whereas the particle concentration was decreasing slowing due to two reasons. First reason related to truck density which decreased in the afternoon and particle number is highly correlated with truck density. The other reason is related to ambient temperature which is lower during morning hours and this affect the dynamics of the formation of secondary aerosols whereas in the afternoon the temperature is higher. Further, this study show that with increasing distance from road, the total particle number concentration decreased but the maximum of the size distribution increased. However, in the urban area the number concentration of accumulation mode was relatively independent of the measurement location and therefore this can be assumed representative of the urban-air background.

Emily et al (2007) conducted measurements of particulate number concentrations in the range of 5-1000nm and gases (NOx, CO and 1,3-butadiene) at two sampling locations (roadside and elevated (8.5m) site) on Narborough Road in Leicester, UK. The results of this study concluded strong linear relationship between these gases and nucleation (2-20nm) and Aitken mode (20-100nm) concentrations at both sites. The correlations between the gases pollutants and Aitken modes are stronger than that for nucleation mode. The correlation coefficient (r²) between nucleation mode particulate concentration and gases (NOx and CO) are in the range of 0.51 to 0.55 at the elevated site and in the range of 0.43 and 0.63 at roadside and this correlation increase to the average range of 0.76 for the NOx and to the average range of 0.73 for CO for the Aitken mode. The correlation between particle number and NOx is slightly better than that of CO. These values are in agreement with the earlier study by Longley et al (2005) who also found lower correlation for sub 10nm particle compare to larger size particles. The possible reason for stronger correlation between Aitken mode and gases than nucleation mode is because Aitken mode particles are primary particulate which has similar source profile to
primary gases pollutants emission of NO\textsubscript{x} and CO whereas the nucleation mode particulate are possibly secondary particles formed through condensation and also the nucleation particles may coagulate directly after emission from the source to larger size.

Roth et al., 2008 conducted simultaneous measurements for NO\textsubscript{x} and SO\textsubscript{2} and particle number in the range of 0.007-10\textmu{}m during spring and autumn 2003 in the center of Strasbourg. The authors tested the correlation between number of particles on each ELPI plate and gas concentrations (SO\textsubscript{2} and NO\textsubscript{x}) and the results indicates that the particle number with diameter size between 0.10 and 0.62\textmu{}m are highly related to the NO\textsubscript{x} with correlation coefficients of higher than 0.5 whereas the correlation between SO\textsubscript{2} and particles number is less clearly correlated. Based on these results, it can be inferred that the particles (especially ultra-fine) are emitted together with a high level of produced NO\textsubscript{x} from same source (mainly traffic) and much of the emitted gases induces gas-particle conversion.

Having found a strong correlation between especially NO\textsubscript{x} and particulate number concentration, monitoring traffic emissions in urban areas has become increasingly important in recent years. Further, all these findings that high correlation between NO\textsubscript{x} and ultrafine particles (especially lower than 200nm) support strongly the hypothesis that NO\textsubscript{x} can be used as tracer to estimate the particle number emissions from anthropogenic sources (especially traffic).

1.5.2 Particulate Number emissions from traffic

In recent years, fundamental improvements in traffic engine design and the introduction of catalytic converters and unleaded fuels, technological advances have led to a considerable reduction in both gaseous (mainly NO\textsubscript{x}) and particle mass emissions. However, although these advances have lead to reduce the large particle emissions, they have not resulted in a decrease in the emission rates of ultrafine particles which are main component of number concentration. Quite to the contrary, the changes in the combustion process have in fact resulted in increased emissions of fine and ultrafine particle number (Hall et al., 1998; Kittelson, 1998). In response to this, studies changed
from using mass-based to number based methods to emphasis the importance and presence of ultrafine particles especially from traffic although some studies (Keywood et al., 1999; Tuch et al., 1997) have shown well association between particle numbers (mainly ultrafine particles) and particle mass (dominated by accumulation mode).

Many studies (Hitchins et al., 2000; Morawska et al., 1999; Marconi et al 2007; Zhu et al., 2009) have focused on the emission of particle from traffic and have correlated the increase in particle number (especially particle with <100nm size) with the increase in traffic density. Pey et al., 2009 conclude that the contribution of road vehicles can be up to 86% of the total particle number concentrations in the 13-800nm size range whereas the contribution from other sources (photochemically induced nucleation, industrial sources, mineral dust) are minor. Marconi et al 2007 collected long-term particle number measurements at two sites in Rome, Italy in a traffic oriented site and at urban background site and they noted particle number concentrations at both sites are very close correlated with the traffic volume with highest mean values during rush hours. The particles emitted by diesel vehicles usually have larger size and lower concentration number than those emitted by petrol vehicles (Charron et al., 2003). However, Kittelson et al (2004) had different opinion he concluded that the emissions in terms of mass and number concentrations from diesel vehicles is about 10-100 times more compared with petrol vehicles but the latter source may emit a higher proportion of small-sized particles (i.e. nanoparticles), by number, under high speed and load conditions.

Jones and Harrison (1994) studied the correlation between traffic activity and both PM\textsubscript{10} and particle number concentrations in Birmingham, England. It was noted that the particle number concentrations is correlated closely with the traffic count and responding rapidly to local traffic conditions. On the other hand, the PM\textsubscript{10} levels, considered as reflective of particle emissions across the whole upwind urban area, showed a greater response to traffic volumes through-out the city rather than to changes in localized sources. This study also suggests that the coagulation of ultrafine particle was a major influence on particle number concentrations, and the concentrations of very fine particle
are likely much greater closer to the sources such as motor traffic, than at more distant locations.

Li et al. (1993) characterized outdoor submicrometer aerosols by continuous DMPS measurements for 24h. The lowest particle number concentration \(10^4\) particles cm\(^{-3}\) was noted in the absence of traffic activity and the highest number concentration levels \(4.35 \times 10^4\) particles cm\(^{-3}\) were occurred whenever an automobile or motor cycle passed the sampling site, the higher values coinciding mostly with rush hour traffic. Some studies (Gouriou et al., 2004, Roth et al, 2008) indicated that during rush hours in high traffic roads, particle number concentration may reach as high as \(10^6\) particles cm\(^{-3}\) in immediate road vicinity and decrease rapidly with increasing distance from the road.

Hussein et al. (2004) studied the aerosol number size distribution within the particle diameter size range 8-400nm in the Helsinki urban area in Finland during a long-term period (1997-2003). The results of temporal variation show that there is close correlation between traffic density and particle number concentration. Among the workdays, the highest particle number concentration was noted on Fridays while among the weekends the lowest particle number concentrations were noted on Sundays. Seasonally, the lowest total number concentrations were observed during summer holiday months (June-July) due to lower traffic density and the highest total number concentration observed during March-April. It was also found that more than 80% of the number size distributions in the Helsinki urban area had three modes: nucleation mode \(D_p<30\text{nm})\), Aitken mode \(20-100\text{nm})\) and accumulation mode \(D_p>90\text{nm})\). Two different sampling sites in Helsinki were used for measurements (Siltavuori and Kumpula); in the first site (Siltavuori), the arithmetic means of the particle number concentrations were \(7000\) cm\(^{-3}\), \(6500\) cm\(^{-3}\), and \(1000\) cm\(^{-3}\) respectively for nucleation, Aitken, and accumulation modes. In the second sampling site (Kumpula) the concentrations were \(5500\) cm\(^{-3}\), \(4000\) cm\(^{-3}\), and \(1000\) cm\(^{-3}\) respectively. The difference between the two sites was due to building construction where at Kumpula the building construction produce big particles which cause a large coagulation sink and reduce the ultrafine particle and a large condensation sink to prevent new particle formation. The total particle number concentrations for both
nucleation and Aitken modes were usually significantly higher on workdays than that on weekends, but there was no significant difference in accumulation mode.

Simultaneous measurements of the total number, number concentrations of ultrafine (0.01-0.1μm) and accumulation (0.1-0.5μm) particles, as well as mass concentration of PM$_{2.5}$ particles were conducted in three European cities (Helsinki, Erfurt and Alkmaar) by Ruuskanen et al. (2001). The measurements were taken from sites close to the major streets (less than 100m away) and conducted during the winter period. The results show the concentration of ultrafine particles differed significantly between weekdays and weekends in all cities, whereas no difference was observed in the concentration of accumulation and PM$_{2.5}$ particles. The daily PM$_{2.5}$ levels were found to be poorly correlated (0.23-0.61) with the daily total and ultrafine number concentration but better correlated with the number concentration of accumulation particles. This study also showed that the hourly averages of particle numbers were reached up to 188,000 cm$^{-3}$ and the highest concentrations were noted on weekends. The differences between daily and hourly averages were minor but the hourly peak values were between 2.5 and 4 times higher than the daily maximum.

The relationship between the traffic emissions and particle numbers and sizes were also examined by Charron et al. (2003). Particle number and sizes in the range 11-452nm have been measured semi-continuously at Marylebone Road, London over a period from April 1998 to August 2001. This study show that particles in the range 11-100nm represent about 71% to 95% of the particle number between 11 and 450nm. They also noticed that there is decrease in particle numbers from the morning rush hour and this decrease is associated with a shift of the mode size distribution from about 23nm (beginning of rush hours) to about 31nm (afternoon rush hour). This study also indicates accumulation mode particles are associated with emissions from heavy-duty traffic (mainly diesel vehicles) while ultrafine particles (30-60nm diameter) show a strong correlation with light duty vehicles. On the other hand, particle in the range 11-30nm behave differently showing no clear relationships to traffic volume and they are not directly emitted from vehicles exhausts but formed in the atmosphere after emissions due
to cooling and the dilution of semi-volatile gases. Traffic-generated particles of less than 20nm diameter are typically formed during mixing of the exhaust plume with ambient air by nucleation and condensation processes and this has a major influence on particle size distribution at roadside and urban sites (AQEG, 2004).

1.5.3 Particle number measurements near street

As discussed earlier that the traffic can be considered as the main source emission of particles in urban areas and therefore the maximum particle number concentration is expected be near roads and streets.

Zhu et al. (2002) made comparison study for measurements made on Interstate 710 freeway and 405 freeway in Los Anglos. The reason for choosing these freeways is because they are considered as one of the busiest freeways in the USA. The main difference between the two freeways is that diesel vehicles on the 710 freeway represent about 30% of vehicles while they represent <5% on the 405 freeway. The results show that the total particle number concentration close to the 405 freeway is higher than that near the 710 freeway, but the number concentration drops faster with downwind distance. It is also noted that the number concentration dropped to about half of its original value at 30 m somewhere between 90 and 150m which is in agreement with the findings by Hitchins et al (2000), who also noted that particle number concentrations drop by 50% at 100-150m. However, for both freeways in general number concentrations for smaller particles (d_p<50nm) dropped sharply with increasing distances from the highway, but number concentration decrease slightly for relatively larger particles (d_p>100nm). This suggests that coagulation is more important than atmospheric dilution for the smallest ultrafine particles (d_p<50nm) and vice versa for larger particles. The maximum observed number concentration next to the freeway was about 30 times higher than that for the background location. Total nuclei mode particle number (size of 6 to 25nm) accounted for about 70% of the total ultrafine particle number and the concentration dropped sharply, by about 80% at 100m downwind of the freeway, and leveled off after 150m. Further, Ultrafine particle concentrations at 300m downwind of the freeway were comparable to the background value at location of 300 m upwind of the freeway.
Generally, particulate number concentration decayed exponentially with downwind distance away from the freeway. This study also showed that mass concentration decreased by a few percent as the distance increased from the traffic road, while CO, BC, and particulate number concentration dropped by about 60% in the first 100 m and then leveled off somewhat after 150 m.

This study by Zhu et al. (2002) also show that the average concentration of CO, BC, particulate number, and mass concentration on 405 freeway at 30 m were in the range of 1.7-2.2ppm, 3.4-10.0ug/m³, 1.3-2.0 ×10⁵/cm³, and 30.2-64.6ug/m³, respectively. CO, BC, and particle number concentration tracked each other extremely well as distance from the freeway increased. On the other hand, the range of average concentration of CO, BC and total particle number concentration on 710 freeway at 17m were of 1.9-2.6ppm, 20.3-24.8µg/m³, and 1.8-3.5×10⁵/cm³ respectively. Further, Zhu et al., (2009) also studied particle number concentrations at three types of roadways in Austin, Texas and concluded that particle number increased dramatically when one moves from the upwind to downwind of the roadways and decayed exponentially with increasing distance from the roadway. The authors also noted the smaller particles (6-25nm) decayed faster than larger particles (100-300nm) due to mainly coagulation process.

Wahlin et al. (2001) made measurements of particle number concentration and size distribution in a Copenhagen street canyon during January-March 1999 and year 2000. The results revealed that the particle number in the ultrafine size range below 100nm (especially below 30nm) decreased significantly probably due to the reduction of the sulphur content in diesel fuel from approximately 0.05% to less than 0.005% implemented all parts of Denmark in July 1999. This reduction was consistent with a 56% fall in the average particle emissions from the diesel vehicles in the street and there was no change in the particle emission from petrol cars.
1.5.4 **Vertical and horizontal profiles of particle matter**

It is important to study the changes in the vertical and horizontal concentration of particles in urban cities. In this regard, studies are not consistent, especially when it comes to emissions near the street level. Some studies suggest that total suspended particulate matter, PM$_{10}$ and/or PM$_{2.5}$ show a moderate decrease (<30%) with increasing height or distance from major traffic roads (Rubino et al., 1998; Morawska et al., 1999). On the other hand, some other studies show up to about five-fold vertical and/or horizontal variations for particulate mass or number concentration (Vankeva et al., 1999; Bauman et al., 1982).

Pakkanen et al. (2003) made simultaneous measurements at 3.5 and 20m heights in Vallila, Helsinki, about 2km northeast from the city center. The results show that average submicron particle mass concentrations were practically identical at both heights (11ug/m$^3$) but super-micron mass was substantially higher at street level. The average mass size distributions suggested that traffic exhaust increased particles mass concentration in the size range of 0.15-0.4μm, especially at the street level, while regional or LRT particles and/or local high-level sources were important in the size ranges of 0.07-0.15μm and 0.4-1.3μm respectively.

Roorda-Knape et al. (1998) made outdoor measurements of PM$_{10}$, PM$_{2.5}$, black smoke and benzene at four different horizontal distances (at 50, 100, 150 and 300m) from the roadside. This study concluded that both NO$_2$ and black smoke concentrations decrease with increase distance from a road, whereas there is no major decrease in PM$_{10}$, PM$_{2.5}$ and benzene concentrations. The mean street/background ratio was about 2.6 for black smoke, whereas a much smaller ratio of 1.3 was found for PM$_{10}$ and PM$_{2.5}$. Nitta et al. (1993) conducted daily averaged measurements of suspended particulate matter (SPM) at different distances from a busy road in Tokyo, Japan for seven days. A minor decrease was noted: mean SPM concentration declined from 77μg/m$^3$ at 0.0m distance to 69μg/m$^3$ at 20m and 64μg/m$^3$ at 150m.
Morawska et al. (1999) conducted measurements of the horizontal variation and vertical profile of submicrometer particulates (16-626nm) near a major arterial route in the urban area of Brisbane, Australia. The results show that the horizontal ground-level concentrations did not show statistically significant differences in fine particle number concentration from 15m up to 200 m distance away from the road. The vertical profile measurements except for building close to the road (about 15m) also revealed no high correlation between height and particle number concentration.

Shi et al. (1999) studied particle size distributions at three adjusted sites in Birmingham. One site (A) located at a busy roadside (2 m a way from kerbside); another site (B) at 30 m away from site A and the other site (C) is approximately 100m away from site A. The fourth site (D) was in the center of the university and it is considered as an urban background. This study showed that the average number concentration at roadside measured on four separate days (across 3 years) was in the range of 1.6-1.9×10^5 cm^-3, with more than half of measured particles smaller than 30nm. A 24-h average of 2.68×10^5 cm^-3 ±1.29×10^5 cm^-3 was measured in urban background air which is in agreement with what reported by Hughes et al. (1998). The total particle number concentration at the site B and D was only approximately 28% and 11% of that at site A respectively. The total particle number concentration decrease by 11% from site A to Site B due to coagulation alone compared to 72% decrease in measured data. Further, Shi et al. (1999) observed a faster decline of particle number concentration than mass concentration.

Hitchins et al. (2000) studied measurements of particle size distribution and concentration in the size range of 0.015-20μm, at increasing distances from a road (from 15 m up to 375 m) and the particle trend for different wind conditions in relationship to the road. This study showed that there is a clear decrease in particle number concentration of fine and ultrafine sizes (in the range 0.015-0.697μm) as distance from the road increases. Further, the results showed that the concentrations at distance of 50-100m decays to about half that of the maximum value occurring at 15 m from the road when the wind is blowing directly from the road. However, there is no obvious change
on total particle number concentration at a distance larger than 15 m from the road when
the wind is blowing towards the road and away from the sampling points. Total larger
particle number were not much higher than the average urban environmental values, and
decrease with distance from the road, reaching up to 60% at 150 m from the road for
wind from the road. At a distance of 375m from the road, PM$_{2.5}$ decreased to about 75%
for wind from the road and up to 65% for wind parallel to the road.

Shi et al. (2001) made measurements in Birmingham at distances of 4 m and 25 m from
the kerbside downwind from the traffic during October 1998 and February 1999. The
results showed that road traffic and stationary combustion sources generate a significant
number of nanoparticles (<10nm diameter). This study indicated that nanoparticles
measured at the roadside (4m from the kerb) and downwind from the traffic (more than
25 m from kerb) account for about 36-44% of the total particle number concentrations.
At first site, the particle number concentration average over the sampling period were
9.5±3.5×10$^4$ cm$^{-3}$ in the ranged >7 nm and 1.7±0.6×10$^5$ cm$^{-3}$ in the range >3nm, while at
the second site (25 m away from the kerb), the particle number concentration average
over the sampling period were 9.0±2.9×10$^4$ cm$^{-3}$ in the ranged >7 nm and 1.4±0.6×10$^5$
cm$^{-3}$ in the range >3nm.

A study for pseudo-simultaneous measurements in a Cambridge street canyon by Kumar
et al, 2009a indicated that the particle number concentration at street level was 6.5 times
higher than at rooftop and this was attributed to favorable conditions for gas-to-particles
conversion.

1.6 Parameters affecting particulate concentration and other air pollutants

1.6.1 Meteorological parameters:

There are different parameters especially meteorological ones (such as wind speed and
temperature) which can play a major role in reducing air pollution concentration by
dispersion and dilution of air pollution through vertical mixing and horizontal transport
(Deacon et al, 1997). Among the major meteorological factors affect particulate matter
and other air pollutants (Zannetti, 1990) are:
- The horizontal wind speed and direction
- The atmospheric stability which affects the dilution rate of pollution
- The strength of the elevated temperature inversion which limits the boundary layer.
- The atmospheric vertical motion due to low/high pressure systems or complex terrain effects (hills, mountain ranges, etc.)

Chang-Jin et al. (2004) made an intensive measurement of particulate and gaseous materials during wintertime in an urban of Kansai, Japan. The results of this study show that the concentration of NOx and PM$_{2.5}$ fall right down to the lowest point during rain events. Contini et al (2010) found that the average PM$_{10}$ concentration in an urban background site in Lecce (Apulia region, Italy) decreased of about 23% during precipitation (larger than 0.8mm) due to mainly the decrease in crustal matter contribution and secondary inorganic aerosol. The author also noted that when the wind speed is high the concentrations of Pb and Cu decrease but the concentrations of Na!+, Cl!- and Mg$^{2+}$ increase due to more efficient transport from sea to the land as suggested by the study. Ma et al., (2001) also noticed that during rainfall the raindrops can take up gases such as SO$_2$, NO$_x$, HNO$_3$, and NH$_3$ and aerosols. DeGaetano et al. (2003) noticed that the hourly PM$_{2.5}$ within New York City reach its maximum values during the summer and morning hours (7:00-9:00a.m.) and minimum PM$_{2.5}$ concentrations are noted during morning hours (4:00-6:00a.m.) in winter. This study also showed that the majority of high PM$_{2.5}$ events occur with fairly high, 5.4ms$^{-1}$ wind speed. On the other hand, high PM$_{2.5}$ concentration is most pronounced when early morning summer temperature is high. Similarly, the majority of hours high particulate concentrations tend to be associated with high humidity levels. This result was supported by Jung et al. (2002) who found that high PM$_{2.5}$ concentrations were often associated with high daily temperature.

Deacon et al. (1997) noted that in winter months there is an inverse correlation between PM$_{10}$ and wind speed due to the influence generated by both increased dispersion and higher boundary layer depths but in summer months the PM$_{10}$ tends to correlate
positively with the wind speed because soil and urban surface become a source of resuspended material when they are dried out.

Singh et al (2010) studied the variation of air quality during Diwali festival, Delhi (India), from 2002 to 2007 and noted that the concentrations of PM_{10}, SO_{2}, and NO_{2} increased two to six times during the Diwali period due to adverse meteorological conditions, i.e., decrease in 24h average mixing height, temperature, and wind speed. Desqueyroux et al. (2002) noticed that there were seasonal patterns in daily levels of SO_{2} and O_{3} with an increase of SO_{2} in winter and of O_{3} in summer. Further, there was a highly significant positive correlation between PM_{10}, NO_{2} and SO_{2} whatever the season. In summer, O_{3} was correlated with PM_{10} and NO_{2} and not with SO_{2}. The temperature was generally associated positively with O_{3} but negatively with atmospheric pollutants SO_{2}, PM_{10}, and NO_{2}. Relative humidity was usually associated negatively with the other variables.

Wallance J and Kanaroglou P. (2009) investigated the effects of temperature inversions on the levels of NO_{2} and PM_{2.5} during daytime and nighttime over the Hamilton Census Metropolitan Area (CMA) in Canada and their results indicated that the NO_{2} and PM_{2.5} increased by 49% and 54% respectively during nighttime inversion episodes. However, during daytime inversions resulted in an increase of 11% in NO_{2} but a decrease of 14% in PM_{2.5} possibly because of lower humidity during day time which leads to lower particle formation as observed in this study that high concentrations of PM_{2.5} coincident with high humidity on summer and fall nights because of higher formation of some secondary particulate (ammonium nitrate) when conditions of high relative humidity and low temperature prevail.

Several other studies (Shi et al 1999 and Zhu et al., 2002; Longley et al., 2005) have addressed the affect of meteorological factors on particle number concentration within urban areas. For example studies by Shi et al 1999 and Zhu et al., 2002 have indicated a reduction in particle number concentration with distance from the roadside due to higher wind speed and higher particle number concentrations at the roadside during periods of
low wind speeds. However both studies have not indicated which particle size is more affected by the wind speed. On the other hand, Charron and Harrison (2003) indicated the important of segregation of particles of different sizes and particle behavior under different wind speed conditions on the basis of different sizes. The authors found that increase in wind speed did not affect the levels of nucleation mode particles (11-30nm), whereas there were significant reductions in larger sizes.

Vakeva et al. (2000) reported that the local wind direction plays an important role in shaping particle number size distribution in the urban background area of Helsinki, Finland. Wang et al (2010) suggested that constant wind direction might play a positive role in the growth of particle size. Cheng et al. (2010) noted that wind direction did not significantly affect ultrafine particle concentrations, because the measurements were conducted very close to the emission source (highway toll station). However, the wind direction may play an important role if the measurements taken at a downwind side.

Kumar et al (2007) studied the dispersion of particles at two levels (street and rooftop) in a Cambridge UK street canyon and noted at street level the particle number concentrations decreased with increasing wind speed and larger influence of wind speed on particles size of 30-300nm than on particles size of 5-30nm. Conversely at rooftop the particle size of 30-300nm did not vary with wind speed whereas the smaller particle size (5-30nm) increased with wind speed. On contrast, Agus et al (2007) noted that both nucleation mode (0-20nm) and Aitken mode (20-100nm) decreasing exponentially with increasing wind speed at roadside location whereas at elevated site (8.5m) the decrease was noted only for Aitken mode particle.

Agus et al (2007) and Wehner and Wiedensohler (2003) found the coincidence of peaks in nucleation particle number (mainly secondary organic aerosol) and solar radiation suggesting the influence of photolysis driven process. Both studies found peaks in nucleation mode number concentration during high level of solar radiation and decreases in accordance with the decrease in solar radiation due to less production of new particle.
As for the ambient temperature and relative humidity effect, Yao et al., (2007) investigated the relationship between the particle size distribution of on-road vehicles and the ambient temperature (T) and relative humidity. The authors suggested that low ambient temperature and/or low relative humidity will result in the increase in the concentration of 30-60nm particles due to cooling of vehicle plumes under such conditions but in contrast under high temperature and moderate to high relative humidity, the formation of 30-60nm particle will be decreased. Similar indications were found by Gidhagen et al. (2007) who studied the ratio between total particle number and NOx in a Stockholm street canyon environment (assuming NOx parameter to be temperature independent) and the results indicate that the total particle number emission factor during a cold day may be risen up to twice as high as during warm day. Wang et al (2010) studied the particle number concentration and size distribution of ultrafine particle near the city of Rome and noted there is close correlation between particle numbers with diameter 30 to 50nm and 50 to 70nm with NOx and relative humidity while there is good correlation between particle number of 4 to 10nm, 10 to 30nm and 4 to 70nm with solar radiation, temperature and wind speed.

1.6.2 Transformation and loss processes affecting particle number and sizes

Particles in air increase in size by coagulation and growth. Growth can occur by condensation, vapor deposition, dissolution, or chemical reaction. However, some of these processes (such as growth and deposition) can be considered as important loss processes where as other process (chemical transform) is considered as gain process.

Coagulation:
Coagulation occurs when two particles collide and stick together to form larger particles and reducing the total particle number concentration in the atmosphere but conserving the volume concentration of particles in the air (Jacobson, 2002). Coagulation can occur between two small particles, or between a small and a large particle, or between two large particles. Gidhagen et al., (2005) utilized a three dimensional Eulerian model to calculate particle number distribution over Stockholm and the results showed that the
overall loss due to coagulation is up to 10%. This process is more efficient between different particles sizes. The speed of coagulation is a function of both size and diffusion coefficient where large particles (i.e. accumulation size) provide a large absorbing surface and the small particles (nano-particle size) have a rapid diffusion. For example a particle of 10 nm size coagulates 170 times faster with a 1 μm particle than with another similar size particle. Further it is suggested that the highest particle loss rate is noted for sizes of 8-20nm. Coagulation processes remove the nano-particles most efficiently since this size (~10nm) has a larger part of the size spectrum available to coagulation with. Consequently, the coagulation timescale for 10 nm particles (2×10^4s) is 10 times lower than that for 50 nm particles (2×10^5s) and time scale is generally increases with particle size.

Jacobson (2002) suggests that there are five important mechanisms that derive particles to collide are Brownian motion, enhancement to Brownian motion due to convection, gravitational collection, turbulent inertial motion, and turbulent shear. Among all five coagulation processes Brownian motion is the dominate process when at least one of the two colliding particles is small. When both particles are large (but not exactly the same size), gravitational collection (settling) is the dominant coagulation process. Brownian motion is the random movement of particles suspended in a fluid (Jacobson, 2002). Gidhagen et al (2005) suggested that the coagulation is only effective when the particle number concentration is very high such as those found near to vehicle exhaust pipe or in the car tunnel and the contribution of this process (coagulation) to reduce the total number concentration is of little important on urban scale not exceeding 3% but losses could go up to 10% for the smallest Nucleation size mode (3-10nm) during peak episodes.

The rate of change of the number concentration for monodisperse spherical particles can be expressed as mentioned in Hinds (1999):

\[
\frac{dN}{dt} = -K_tN^2
\]

---

(1.1)
Where $K_0$ is the coagulation coefficient and it has units of m$^3$/s in SI units. Value of $K_0$ can be calculated from

$$K_0 = 4\pi d_p D = 4kTCc/(3\eta) \quad \text{For } d_p>0.1\mu m \quad \text{-----------------------------------} \quad (1.2)$$

$D$ is the Brownian diffusion coefficient for the particles and $N$ is the number concentration of particles. For air at ambient temperatures (Colls, 1998), $K_0 = 3 \times 10^{-16} C_c$

The coagulation rate for polydisperse particles is more complicated and the reader is referred to Hinds (1999) for more details.

Condensation/Evaporation:
Coagulation is a process that involves two particles, whereas condensation, vapor deposition, dissolution, and surface reaction are gas-to-particle conversion processes. Jacobson (2002) indicates that condensation and evaporation occur only after homogeneous or heterogeneous nucleation. On a nucleated liquid surface, gas molecules continuously condense (change state from gas to liquid) and liquid molecules continuously evaporate (change state from liquid to gas). In equilibrium, transfer rates in both directions are equal, and the resulting partial pressure of the gas immediately over the particle’s surface is gas’s saturation vapor pressure. Zhang and Wexler (2002) indicated that both condensation and evaporation does not change the total particle number, but it changes the particles sizes, which is important for coagulation and deposition rate. Further, the authors suggested that the condensation will be a leading process for particle size of larger than 50nm and smaller than 2$\mu$m whereas coagulation will be important for particles below 50nm.

Deposition and chemical transformation of particulate matter
There are three main processes which play role in removal mechanisms: dry deposition; wet deposition and chemical transformation (Schnelle et al., 2000). Aerosols are removed from the atmosphere by dry and wet processes (Raes et al., 2000). Particles of size ($D_p<1\mu$m) diffuse to the Earth’s surface but this process becomes less efficient as
the particle size increases. On the other hand, large particles \((D_p > 1 \mu m)\) settle gravitationally and this process becomes less efficient as the particle size decreases. In the size range of \(0.1 < D_p < 1 \mu m\), dry removal process tends to be very slow, and both the formation and growth processes tend to accumulate the aerosol in this size range. When these particles have the right hygroscopic properties, they will be removed by activation in clouds and subsequent by wet deposition (Raes et al., 2000).

The removal processes (dry and wet deposition, chemical transformation) are usually taken in account in the Gaussian model by multiplying Gaussian equation (will be discussed in the latter subsection) by the following decay exponential terms such as:

\[
\exp\left(-\frac{t}{T}\right) \quad \text{(1.3)}
\]

Where \(t\) is the travel time

\[
t = \frac{x}{\bar{u}} \quad \text{(1.4)}
\]

and \(T\) is the corresponding time scale. \(\bar{u}\) is mean wind speed and \(x\) is the downwind distance from the source. More discussion on the above formula is presented in (Zannetti, 1990).

**Dry Deposition:**

Dry deposition is a process by which gases and particles are carried by molecular diffusion, turbulent diffusion, or advection to different surfaces (such as tree, buildings, grass, or car windows) then rest on, bond to, or react with the surface. Dry deposition is more efficient for particles than for gases because particles are heavier than gases. As such, particles fall and tend to stay on a surface more readily than do gases, unless wind speeds are high. Gases, especially if they are chemically unreactive, are more readily resuspended into the air (Jacobson, 2002).

Many studies (Gidhagen et al 2005; Kumar et al., 2008c; Kumar et al 2010) highlight the importance of dry deposition as loss processes that reduce the total particle number concentration. Gidhagen et al., (2005) suggested that deposition is more important than coagulation and found that dry deposition can cause up to 25% loss of total particle
number in the range of 3-400nm size and up to 60% for the smallest Nucleation size mode (3-10nm). As indicated earlier aerosol particles are removed from the air by sedimentation, dry deposition, and rain-out. Gases also sediment, but their weights are so small that their sedimentation velocities are negligible (Jacobson, 2002). A typical gas molecule has a diameter of 0.5 to 1nm (nanometer). Such diameters result in sedimentation (fall) velocities of only 1 to 3km per 10,000 years. Particles smaller than 0.5µm in diameter can stay in the air several years before falling even 1km. For these and smaller particles, sedimentation is a long-term removal process (Jacobson, 2002). If small particle are near the ground, dry deposition can usually remove them more efficiently than can sediment. For example, Kumar et al., 2008c estimated dry deposition losses of vehicle emitted particle number onto a road surface in a Cambridge street canyon. The author concluded that the removal of total particle number concentrations in the range of 10-30nm was about 19% higher than that particles in the range of 30-300nm at road surface compared to concentrations at 1m above the road level.

The time scale of dry deposition, $T_d$, can be expressed (Zannetti, 1990) as a function of the deposition velocity $V_d$ as following:

$$\frac{1}{T_d} = \frac{V_d}{\Delta_p}$$

(1.5)

Where $\Delta_p$ is the vertical thickness of the plume:

$$\Delta_p \approx 4\sigma_z$$

(1.6)

Where the $V_d$ is referred to as the dry deposition velocity. The deposition velocity for particles is calculated following Seinfeld and Pandis (1998):

$$V_d = \frac{1}{r_s} = \frac{1}{(r_a + r_b + r_a r_b v_s + v_s)}$$

(1.7)

With $r_a$, $r_b$, respectively, are the aerodynamic and quasilaminar resistance for particles and $v_s$ the sedimentation velocity.
**Wet Deposition:**
The particles can be removed from the atmosphere by incorporating into cloud droplets, raindrops deposited back to land and water bodies. If the particles are incorporated into cloud droplets which then turn into raindrops, it is called rainouts whereas if the particles are collected by raindrops as the latter fall through the atmosphere, it is called washout. However, it is difficult to distinguish between the two routes in practice. Rainout is an important removal process for aerosol particles. Because rain clouds occur only in the atmosphere, rainout is not a process by which stratospheric particles are removed (Jacobson, 2002).

There are two methods of modeling wet deposition. First method assumes the concentration decrease exponentially with time. The second method uses the washout ratio. The exponential method is strictly applicable only to particles of a single size. The time scale of the wet deposition, $T_w$, can be expressed (Zannet, 1990) as

$$T_w = \frac{3.6 \times 10^6 \, P_L}{S_r \, P_R} \quad (1.8)$$

Where $P_L$ is the thickness of the precipitation layer (an average climatologically value of $P_L$ is 4000m), $P_R$ is the precipitation rate in mm/hr, and $S_r$ is the scavenging ratio of the pollutant (a typical value for SO$_2$ is $4.2 \times 10^5$).

**Chemical transformation:**
Primary pollutants (such as sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$)) are emitted directly into the atmosphere from the source. Secondary pollutants are formed through chemical reactions – the conversion of SO$_2$ to sulfate and NO$_x$ to nitrates. The time scale of the chemical transformation, $T_c$, is a function of the reactivity of the pollutant (Zannet, 1990). For example, a typical value for SO$_2$ is 28 hours.
1.7 Dispersion modeling of particulate matter and gases:

There are many types of dispersion models (Computational Fluid Dynamic (CFD), Gaussian, Lagrangian, Eulerian) which are available for particle matter and gaseous prediction but very few are applicable for particle number prediction (such as the Multi-scale atmospheric transport and chemistry model (MATCH) and Multi-plume Aerosol dynamics and Transport model (MAT)). Gidhagen et al (2003) used MATCH model to assess the special distribution of total particle number in the size of 3-400nm and the authors noted that the particle number concentration in the urban background of Stockholm is 10,000#/cm$^3$ whereas the concentration close to a major highway is three times higher and in the vicinity of street canyon is seven times higher. Matthias and Berkowicz (2005) developed MAT model to study the dispersion and dynamics of particle size distribution (2nm to 2μm) in urban background. General review on these models and others can be found in Holmes and Morawska (2006). However, none of these studies have predicted the particle number distribution of different sizes. Prediction of particle number of different sizes seems to be difficult due to the complexity of processes (such as dilution, aerosol dynamics and chemical reaction and transformation processes) which the ultrafine particles undergo after their release into atmosphere. Further, the information on particle number emission factors for individual sources (vehicles, industries) is not abundantly available for routine applications. Under such difficulties and challenges modeling of particle number of different sizes may require further research and investigation.

Alternatively, Air dispersion models (such as AERMOD, ADMS, CALPUFF) can be applied to predict the particle number of different sizes indirectly based on the strong correlation between NOx and particle number as suggested by many studies (Morawska et al., 1998b; Thomas and Morawska, 2002; Marconi et al, 2007; Emily et al, 2007; Roth et al, 2008; Wang et al., 2010). The air quality dispersion models incorporate different factors including meteorology, terrain, physical and chemical characteristics of the effluent and source design to simulate the formation and transport of pollutant plumes and others if needed. Air dispersion models can be divided based on the complexity
(Screening, Refined and advanced) or based on the techniques used. The air modeling techniques are mainly divided into three approaches:
- Gaussian models
- Lagrangian models
- Eulerian models

Each of these has advantages and disadvantages in the treatment of atmospheric phenomena. Gaussian models (such as AERMOD) are the most commonly used models for air pollutant prediction due to its simplicity in usage and fast to compute the exact solution of a simplified mass conservation equation (the mass does not change as it is transported by the air). But such models have the following drawbacks: (1) they consider constant wind and turbulence over time and space (steady state assumption); (2) they will work only over short distances of up to 50km from the source of the pollutant to the receptor; and (3) they will also not work well in areas where the terrain is very complex.

Lagrangian models (such as CALPUFF) follows plume parcel as it moves in the atmosphere and such models have small numerical error and take into account the heterogeneity of the wind and turbulence. The drawback of Lagrangian model is that they need much information to run and take a relatively long time for computation especially when the number of sources is high and they may not fully represent the interactions between particles. On the other hand, Eulerian model is similar to a lagragian model in that it tracks the movement of plume parcels as they moves from the initial location. the advantage of Eulerian models that they take into account all the phenomena involved in air pollution but such model require long time for computation and have numerical errors.

However, the other difference between the Eulerian and Lagrangian models as defined by Colls, J., (1998) is that Eulerian models are based on the concept of a fixed reference point, past which the air flows. In other words, the Eulerian derivative is the rate of change at fixed position. By definition, this is the usual partial derivative ($\frac{\partial}{\partial t}$). Whereas
Lagrangian models, in contrast, are based on the concept of a reference point that travels with the mean flow (Zannetti P., 1990) and it can be expressed as \( \frac{D}{Dt} \).

In this part, two models will be discussed and compared: (1) steady state Gaussian model (AERMOD) and (2) non-steady-state Lagrangian model (CALPUFF). The reason for choosing these two models is because both of them are the most commonly used models and recommended by US-EPA for regular application.

### 1.7.1 Comparisons between CALPUFF and AERMOD:

The AERMOD (AMS/EPA Regulatory Model) model and CALPUFF (California Puff) will be compared in this subsection. CALPUFF, which is an advanced 3D Lagrangian-Gaussian non-steady-state model, is programmed to simulate continuous puff of air pollutants being emitted from a source into the atmosphere. As the wind flow changes with time, the path of each puff also takes changes to the new wind direction. Whereas AERMOD are Gaussian plume steady-state models that treat emissions from a source as a continuous mass.

AERMOD model was developed in 1995, reviewed in 1998 and formally proposed by the US EPA as a replacement for ISCST in 2000. Initial comparison between both models showed that AERMOD has improvements over ISCST3 prediction versus observations for flat and elevated terrain conditions. However, the disadvantage with AERMOD that it does not have a lake breeze model to assess shoreline fumigation conditions nor is it capable of considering coastal and over-water interaction (e.g. thermal internal boundary layer development). The model can be applied to various emission sources (point, line, area and volume) and has a module applicable to motor vehicle emissions in street canyon situations.

A comparison between main features of CALPUFF and AERMOD is shown in table 1.1. One of the main differences between the two types of models that Gaussian model is steady state model which assumes spatial uniformity in the meteorology and constant emission rates, but CALPUFF is non-steady-state puff dispersion model that simulates...
the effects of time-and space-varying meteorological conditions on air pollution transport, transformation, and removal. Further, CALPUFF model allows the plume trajectory to be deflected or modified by terrain features. On the other hand, AERMOD produces a straight-line plume trajectory based on the wind flow at a single location. However, there is an increased level of effort in moving from AERMOD to CALPUFF.

There are several studies which aimed to determine how well the two models predict compared to the observed values. Hanna et al., (1999) evaluated the predictions of ADMS, AERMOD and ISC3. The results of this study suggest that ISC3 generally overpredicts with a scatter of about a factor of three, and has 33% of its predictions within a factor of two of observations whereas both ADMS and AERMOD underpredict by about 20% and 40% respectively and both models have a scatter of about a factor of two. ADMS and AERMOD have about 53% and 46% of their predictions within a factor of two of observations, respectively. By comparing the highest predicted concentrations with the observations, ISC3 overpredicts by a factor of seven, while ADMS and AERMOD underpredict by about 20%, on average. This study concluded that the models can be ranked with ADMS on top, followed by AERMOD and then ISC3 on the bottom. McHugh et al, 1999 and CERC (2000) also shows that AERMOD gives overall underestimation with the predicted mean 50% of the observed and standard deviation 61%.

Kumar et al (2006) used AERMOD to predict the ground level concentration of SO2 for 1-, 3-, and 24-h average using emission source data for Lucas County, Ohio and noted that the model had generally tendency to underpredict in both the stable and convective conditions and did not show a satisfactory performance for 1-hour and 3-hour prediction but slightly better prediction for 24-hour concentration when the urban option is chosen.

Earth Tech., (2001) showed that the peak values predicted by ISCST3 and AERMOD are usually higher than those predicted by CALPUFF. Henderson et al., (2008) employed the CALMET/CALPUFF package to model the dispersion of the particles throughout a 325,000 km2 area with complex terrain and the authors noted moderate agreement (mean r = 0.61) between predicted and measured PM10 concentrations at five of six sites.
Table 1.1 Side-by-Side Comparison between CALPUFF and AERMOD

<table>
<thead>
<tr>
<th>Main Features</th>
<th>CalPuff</th>
<th>AERMOD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of model</strong></td>
<td>Non-steady-State Lagrangian-Gaussian model</td>
<td>Steady-State Gaussian model</td>
</tr>
<tr>
<td><strong>Meteorology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Input Meteorological data</strong></td>
<td>Time-dependent three-dimensional meteorological fields generated by diagnostic model (such as CALMET)</td>
<td>Assumes spatial uniformity in the meteorology and use two meteorological input data (surface and profile)</td>
</tr>
<tr>
<td><strong>Treatment calm condition</strong></td>
<td>Can handle calm wind</td>
<td>Does not apply during calm conditions</td>
</tr>
<tr>
<td><strong>Dispersion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Plume Rise</strong></td>
<td>Can simulate both (a) gradual rise of a buoyant and (b) partial penetration of elevated inversions</td>
<td>Simulate only partial penetration of elevated inversions</td>
</tr>
<tr>
<td><strong>Complex Effects</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Complex Terrain</strong></td>
<td>Can handle Complex terrain that permits the plume to flow both around and over terrain obstacles</td>
<td>Can handle Complex terrain to some extend by controlling hill elevation and point elevation at each receptor</td>
</tr>
<tr>
<td><strong>Chemical Transformation</strong></td>
<td>Chemical transformation of SO$_2$ conversion to SO$_4$ and NO conversion to NO$_2$, HNO$_3$, NO$_3$ and organic aerosols formation</td>
<td>Treat chemical transformation using simple exponential decay</td>
</tr>
<tr>
<td><strong>Other Features</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Model Range</strong></td>
<td>Appropriate for short and long range transport (tens of meters from a source to hundreds of kilometer)</td>
<td>Less than 50km</td>
</tr>
</tbody>
</table>
### Source-Receptor Relationships

<table>
<thead>
<tr>
<th>Source-Receptor Relationships</th>
<th>No fundamental limitation on the number of receptors or sources</th>
<th>Maximum number of receptors and sources allowed are 1500 and 1000 respectively</th>
</tr>
</thead>
</table>

| Horizontal Wind              | Non-steady state wind is dealt for each hour                  | A steady state wind is assumed for each hour                                   |

More details on features for CALPUFF can be obtained from Scire (2000a) and for AERMOD from Cimorelli et al., (1998).

Chang et al (2003) evaluated the performance of CALPUFF using two mesoscale field datasets and concluded that 50-60% of CALPUFF predictions were within a factor 2 of observations at site#1 whereas it was 25-30% within a factor of 2 of observations at site#2. The model underpredicted the observation at site#1 by a factor of 2-3 on average. The study suggested that large error (one-two orders of magnitude) in CALPUFF predictions were due to the predicted puff missing the sampling lines because of the problem in the derived wind field.

Yim et al (2010) employed the coupling of the MM5/CALMET system with the CALPUFF to analyse the contribution of major SO\(_2\) sources in the Pear River Delta Region in Hong Kong. The comparison results between predictions and observations showed that CALPUFF can reproduce the characteristics of SO\(_2\) concentration in summer and the model simulated mean, number of peaks and standard deviation of SO\(_2\) is consistent with the observed data. However, in winter, the observations are not fully represented in the model results although the model still captured the highest concentration in episode events. Another study by MacIntosh et al (2010) was to predict the deposition of cadmium (Cd), lead (Pb), and zinc (Zn) as a result of emissions from a zinc smelter using the CALPUFF model. The simulation results compared with observations demonstrated that CALPUFF can provide reasonably accurate predictions and can be a reliable model for prediction of long-term air pollutant deposition in the near-field ambient air concentrations in complex terrain.
Basic Gaussian Equation:

The three-dimensional Gaussian Plume formula is given by Zanneti (1990) as follows:

\[
C(x, y, z) = \frac{Q}{2\pi \bar{u} \sigma_y \sigma_z} \exp\left[ -\frac{1}{2} \left( \frac{y_r}{\sigma_y} \right)^2 \right] \exp\left[ -\frac{1}{2} \left( \frac{h_e - z_r}{\sigma_z} \right)^2 \right]
\]  \hspace{1cm} \text{(3.1)}

Where:

- \(C\) is the pollutant concentration, expressed in \(g/m^3\)
- \(Q\) is the pollutant source emission rate, expressed in \(g/s\),
- \(\bar{u}\) is the average horizontal wind speed (m/s) at release height,
- \(h_e\) is the effective emission height (i.e., \(h_e = z_s + \Delta h\)) expressed in m, \(z_s\) is the stack height from ground and \(\sigma_y\) and \(\sigma_z\) are the horizontal and vertical standard deviation of the plume concentration, expressed in m.

A simplified Gaussian equation for the maximum concentration at ground level \((z=0.0)\) under the plume center line \((y=0.0)\) is given by Barratt (2001) as follows:

\[
C = \frac{Q}{\pi \bar{u} \sigma_y \sigma_z} \left[ \exp\left( -\frac{(h_e)^2}{2\sigma_z^2} \right) \right]
\]  \hspace{1cm} \text{(3.2)}

For a steady-state Gaussian plume, the hourly predicted concentration of a substance at downwind distance \(x(m)\) and crosswind distance \(y(m)\) is given by Schnelle and Dey (2000) as follows:

\[
C = \frac{Q K V D}{2 \pi \bar{u} \sigma_y \sigma_z} \left[ \exp\left( -\frac{(y)^2}{2\sigma_z^2} \right) \right]
\]  \hspace{1cm} \text{(3.3)}

Where

- \(K\) = scaling factor to convert calculated concentration to desired values
D = decay term vertical term

On the other hand, when there is an instantaneous release or a burst of material, a puff model should be used. The Gaussian puff model assumes that each pollutant emission of duration $\Delta t$ injects into the atmosphere a mass $\Delta M = Q \Delta t$, where $Q$ is the emission rate. The center of the puff containing the mass $\Delta M$ is advected according to the local time-varying wind flow. If, at time $t$, the center of a puff is located at $p(t) = (x_p, y_p, z_p)$, then the substance concentration due to that puff at the receptor $r= (x_r, y_r, z_r)$ can be estimated using the following basic Gaussian puff formula (Zannetti, 1990):

$$
\Delta C = \frac{\Delta M}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp\left[ -\frac{1}{2} \left( \frac{x_p - x_r}{\sigma_x} \right)^2 \right] \exp\left[ -\frac{1}{2} \left( \frac{y_p - y_r}{\sigma_y} \right)^2 \right] \exp\left[ -\frac{1}{2} \left( \frac{z_p - z_r}{\sigma_z} \right)^2 \right] \quad (3.4)
$$

It is noted the above puff equation differs from the plume equation mainly because an extra horizontal diffusion term has been substituted for the transport term, with the consequent disappearance of the wind speed $\bar{u}$. In other words, in a puff model, the wind speed affects the concentration only by controlling the density of puffs over the study domain (i.e., the lower the wind speed, the closer a puff is to the next one emitted by the same source). Therefore, at least in theory, a puff model can handle calm or low-wind conditions, and this approach represents one of the most advantage and powerful application of the Gaussian Puff formula.

The basic equation for non-steady-state Lagrangian Gaussian Calpuff model for the integrated puff sampling function is given by Schnelle and Dey (2000) as following:

$$
C = \frac{Q}{2\pi \sigma_x \sigma_y} \exp\left[ -\frac{1}{2} \left( \frac{d_x}{\sigma_x} \right)^2 \right] \exp\left[ -\frac{1}{2} \left( \frac{d_y}{\sigma_y} \right)^2 \right] \quad \text{------------------ (3.5)}
$$

And

$$
g = \frac{2}{\sqrt{2\pi \sigma_z}} \sum_{n=-\infty}^{\infty} \exp\left[ -\frac{1}{2} \left( \frac{H_e + 2n h}{\sigma_z} \right)^2 \right] \quad \text{------------------ (3.6)}
$$
where

\( C = \) the ground level pollutant concentration (g/m\(^3\))

\( Q = \) the mass of pollutant (g) in the puff

\( \sigma_x = \) the standard deviation (m) in the along-wind direction

\( \sigma_y = \) the standard deviation (m) in the cross-wind direction

\( \sigma_z = \) the standard deviation (m) in the vertical direction

\( d_a = \) the distance (m) from the puff center to the receptor in the along-wind direction

\( d_c = \) the distance (m) from the puff center to the receptor in the cross-wind direction

\( h = \) the mixing layer height (m)

\( g = \) the vertical term (m\(^{-1}\)) of Gaussian equation

\( H_e = \) the effective height (m) above ground of the puff center

**Which dispersion model is more appropriate for prediction of the gases and particle number over YIC:**

It is understood that the most important factors that affect the quality and accuracy of the predicted results are:

- The suitability of the model for the task
- The availability of accurate meteorological data
- The availability of accurate source information

The first point will be addressed hereunder but the second and the third points will be discussed in chapters 4 and 5.

Based on the comparison and review of the technical specifications for the above two indicated models and the meteorological conditions and terrain and other factors for YIC, it seems that non-steady state CALPUFF model may be more appropriate to be utilized in this study for predicting the NO\(_x\) and particle number over YIC rather than AERMOD due to the following reasons:
- CALPUFF utilizes fully three-dimensional, time-dependent meteorological data (i.e. non-steady state) over the entire domain, which are provided by advanced meteorological models such as WRF (prognostic model) and CALMET (diagnostic model), rather than measurements at a single point, and an assumption of spatial uniformity as for the case of AERMOD.

- CALPUFF can simulate the effects of various meteorological conditions (such as coastal fumigation, sea/land breeze recirculation) and complex terrain (mountain and valley winds) on pollution transport/dispersion in a much more realistic way than a Gaussian-plume model (AERMOD).

- CALPUFF has ability to retain a memory of the preceding hour’s emissions to allow plumes to meander through modeling domain.

- CALPUFF model can compute concentrations for calm or low wind speed (<0.5m/s) by using its specific algorithms to deal with them as such. But AERMOD model assumes that concentrations of pollutants are inversely proportional to wind speed and therefore predicted concentration become unrealistically high as wind speeds approach calm condition.

- CALPUFF is able to track the puff emitted before, during and after wind shifts and reversals through the modeling domain while the other models (such as AERMOD) is only concerned with the current hour transport of its plum(s).

- CALPUFF allows for variable and curved trajectories (i.e., relies on non-steady-state dispersion) whereas AERMOD assumes a straight line trajectory.

- CALPUFF allows for first-order chemical transformation mechanisms which can simulate atmospheric chemistry in details, including transformation between ozone, NO, NO2 and conversion of NO2 to nitrate (NO3), and SO2 to sulphate (SO4).
1.8 Particulate matter and NOx Ambient Air Standards:

Based on the results of epidemiology-based studies which show an association between adverse health effects and the concentration of atmospheric particulate matter, especially fine and ultrafine particulates, the United States Environmental Protection Agency (USEPA) and other international organizations has developed standards for both PM$_{10}$ and PM$_{2.5}$ (particles smaller than 10$\mu$m and 2.5$\mu$m aerodynamic diameter respectively). These standards would maintain allowed levels of 150$\mu$g/m$^3$ as daily average and of 50$\mu$g/m$^3$ as annual average concentration of PM$_{10}$ and another standard of 65ug/m$^3$ as daily average and 15ug/m$^3$ as annual average concentration of PM$_{2.5}$. The annual averages of both sizes are not to be exceeded more than once per year. On the other hand, the European Union set 'Stage-I' ambient limits for PM$_{10}$ at 50$\mu$g/m$^3$ as 24-hour average and 40ug/m$^3$ as annual average standards to entered into force by 1$^{st}$ of January 2005. Further, EU set 'Stage-II' values for PM$_{10}$ at 50 and 20$\mu$g/m$^3$ for daily and annual mean limits respectively with target date of 1$^{st}$ January 2010. Later, the EU set a new limit for PM$_{2.5}$ of 25$\mu$g/m$^3$ as annual average to be targeted value enter into force by January 1$^{st}$ 2010 and as limit value into force by January 1, 2015.

It is obvious that the indicated ambient standards are based on the total mass of particulate matter collected. These present mass-based air quality standards cannot be applied to describe the levels of ultrafine particles which contain the majority of particle number but negligible mass concentration. Unlike mass, particle number is not conserved. It may change significantly by some important processes (such as nucleation and coagulation) during dilution and sampling which make it very difficult to set a standard although it is more important than mass-based concentration. Therefore, there is no legal threshold for particle number concentration in ambient air set by US-EPA or EU. Alternatively European countries set particle number standards for source emission (vehicles) included in Euro-5 and Euro-6 (EU, 2008: see Section 7 for details) which limit number emissions to $6.0 \times 10^{11}$/#/km and this value was based on the
recommendation by the UK Department of Transport on a number basis for light and heavy duty compression ignition vehicles (Parkin, 2008). This particle number limit ($6.0 \times 10^{11}#/\text{km}$) will be effective from 1st September of 2011 for the approval of any new types of vehicles and from 1st January of 2013 for all new vehicles sold, registered or put into service in the community (EU, 2008).

On the other hand, the ambient air quality 1-hour average standards for NO$_x$ (as NO$_2$) nationally and internationally are as follows:

- National (Saudi Arabia) ambient standard = 660ug/m$^3$
- European Commission ambient standard = 200ug/m$^3$ and not to be exceeded more than 18 times per year
- United State national ambient= 100ppb (188.6ug/m$^3$)
1.9 Summary and Conclusion:

This literature review has covered several important aspects related especially to particulate matter (number and mass) including the characteristics and sources of particles, chemical composition, health effects, their relationship with gaseous pollutants (NOx) and their modeling and regulatory implications. This review can be summarized in the following points:

- The particulate matter can be divided into three different particle size ranges: ultrafine (particle sizes below 100nm), fine (below 1000nm) and coarse particle (above 1000nm) (Oberdorster et al., 2005a). The fine particle mode can be further broken down into particles with diameters between 0.1 and 1µm, known as the accumulation range, and those with diameters between 0.01 and 0.1µm, known as the transient or Aitken nuclei range (Raes et al., 2000) and less than 20nm as nucleation mode (Emily et al., 2007).

- The health effects of particle matter depend on mainly the particle size and the chemical composition. The lower particle size, the higher health effect on human. Many studies (such as Dockery et al., (1993), Pope et al., (1995a); Yeh et al., (1997); Lingard et al (2005)) have shown that the correlation between particle concentration and health effect increases as particle diameter decreases. Donaldson et al., (1998) suggested that the particle number concentration may be more relevant for human health effects than the particle mass. For example, some studies (Weichen et al., 2007 and Sioutas et al., 2005) found that human health effects appear to better correlate with submicrometer particle number concentration rather than particle mass concentration. However none of these studies have discussed in detail the importance of chemical composition of different particle sizes on human health. For example, 10µg/m3 of particle mater made of sea salt and water are probably less harmful than same mass of particles made up of carbonaceous species derived from anthropogenic sources. Therefore,
comprehensive study includes chemical composition, particle number size distribution and health impact is highly recommended.

- There are two main sources for particle matter: combustion (anthropogenic) and non-combustion sources. The combustion sources (automobiles, industries) usually contributes significantly to particle number (dominated by particle fraction <1µm) while non-combustion sources including natural ones (such as dust storm, sea salt, tire and brake wear etc.) is responsible for particle mass concentration (dominated by particulate with diameter of greater than 1µm). Studies (Harrison and Maricq, (2001) Laakso et al., 2003; Charron et al. (2003)) indicated that particles with different sizes come from different sources. For example, nucleation mode particles generated by gas-to-particle conversion of different chemical compounds (such as sulphuric acid and ammonia) or formed in the atmosphere during cooling and the dilution of semi-volatile compounds from vehicular emissions. Murawska et al. (1998) and Ristovski et al. (1998) indicate that the majority of particles from vehicle exhaust are in the size range 20-130nm for diesel engine and 20-60nm for gasoline engines. Aitken mode particles are also produced from condensational growth of nucleation mode particles. Accumulation mode particles are emitted by industrial combustion and resuspended from the road surface by traffic. Charron et al. (2003) indicated that accumulation mode particles are associated with emissions from heavy-duty traffic (mainly diesel vehicles) while smaller particles (30-60nm diameter) show a strong correlation with light duty vehicles. Some accumulation particles also generated by natural sources such as sea spraying and cloud processing of particles and vapors while one-micron particle may be emitted by natural sources, resuspension and combustion sources. Particles of 1-10µm diameter are mainly mechanically generated; dust, resuspension, industrial processes and sea-salt.

- The chemical composition of aerosol particle varies with particle size. Colls J. (1998) suggested that the nuclei mode consists primarily of the volatile organic and sulphur compounds and the accumulation mode contains mainly
carbonaceous agglomerates and their adsorbed materials. Other studies (Pakkanen et al. 2001a; Berner et al., 1996 and Hughes et al., 1998) suggested that highest contribution to UFP was the non-analysed fraction assumed to contain mainly carbonaceous material (70%) and some water content (10%) and the water amount could reach up to 50% in larger particles (≥2.5µm). The contribution of sulfate, nitrate, and ammonium could make up to 10% of fraction of UFP mass. Trace metals (such as Ca, Na, Fe, K, and Zn) and heavy metals (Ni, V, Cu, and Pb) usually made negligible contribution to the mass and could reach up to 1% in some cases. Hughes et al. (1998) found that water soluble inorganic Ionic species (mainly nitrate and sulfates) are commonly found in particles larger than 0.2-0.3 µm diameter, with the highest concentrations present in particles larger than 0.5µm diameter. By contrast, particles with size range 0.1<d_p<0.3µm are largely carbonaceous, particles with size of d_p<0.1 µm are found to consist of 46-62% elemental carbon and organic compounds. Very limited work has been done so far to simultaneously measure both particle number distribution of different sizes and their chemical composition in urban areas and therefore this area of research needs more investigation.

- Particle number concentrations vary from place to place depending on how much the impact from anthropogenic sources on those places. Hussein et al. (2004) indicated in his study that in rural areas typical particle number concentrations are between 1,000 and 10,000 cm⁻³ whereas in urban environments air quality, which is strongly influenced by traffic emissions, the particle number concentration usually exceeds 10,000 cm⁻³. Other several studies (Waller, (1967), Putaud et al (2010)) found 10,000 particles cm⁻³ at background locations, 30,000-50,000 particles cm⁻³ in street and 160,000 particles cm⁻³ in road tunnels and during fogs. Jaenicke (1993) gives for the total number concentration (nucleation, Aitken and accumulation) for remote continental areas about 6,000cm⁻³ and for urban (street canyon) more than 10⁵ particles cm⁻³ whereas Laakso et al. (2003) show 2,000 and 17,000cm⁻³, respectively. However, very limited numbers of studies that have addressed the particle number size distribution in industrial areas. In this study
this particle number of different particle size starting from 7nm up to 10um will be discussed in detailed.

- Scientific studies (Hitchins et al., 2000; Morawska et al., 1999; Marconi et al 2007; Zhu et al., 2009) have focused on the emission of particle from traffics and have correlated the increase in particle number (especially particle with <100nm size) with the increase in traffic density. Pey et al., 2009 conclude that the contribution of road vehicles can be up to 86% of the total particle number concentrations in the 13-800nm size range whereas the contribution from other sources (photochemically induced nucleation, industrial sources, mineral dust) are minor.

- The correlation between the particle number concentrations and the concentration of NOx and CO was addressed by many studies (Morawska et al., 1998b; Thomas and Morawska, 2002; Marconi et al, 2007; Emily et al, 2007; Roth et al, 2008; Wang et al., 2010) have addressed. Ketzel et al. (2003) found that the particle number concentration highly correlated (R>0.83) with NOx through a wide range of particle sizes. The results suggested the Pearson correlation coefficient between NOx and particle number is higher than 0.85 for particle diameter between 30 and 100nm and slightly lower for diameter less than 30nm. Roth et al., 2008 tested the correlation between number of particles on each ELPI plate and gas concentrations (SO2 and NOx) and the results indicates that the particle number with diameter between 0.10 and 0.62μm are highly correlated with the NOx levels (correlation coefficients>0.5) whereas the correlation between SO2 and particles number is less clearly correlated. In this study the correlation between different particle sizes and gaseous pollutants at three urban sites will be addressed.

- Meteorological parameters (such as wind speed and temperature) can play a major role in decreasing or increasing particle matter and gases concentrations. Several studies (Charron and Harrison (2003); Kumar et al (2007)) concluded that
the concentration of nucleation mode particles (11-30nm) were not affected by the wind speed, whereas there were significant reductions in larger sizes. Wang et al (2010) suggested that constant wind direction might play a positive role in the growth of particle size. Agus et al (2007) and Wehner and Wiedensohler (2003) found peaks in nucleation mode number concentration during high level of solar radiation and decreases in accordance with the decrease in solar radiation due to less production in new particle. Yao et al., (2007) suggested that low ambient temperature and/or low relative humidity will result in the increase in the concentration of 30-60nm particles due to cooling of vehicle plumes under such conditions but in contrast under high temperature and moderate to high relative humidity, the formation of 30-60nm particle will be decreased. On the other hand, there are other processes (such as coagulation, vapor deposition, dissolution, or chemical reaction etc) which may increase or decrease the particle number in the air. Gidhagen et al., (2005) suggested that the coagulation is only effective when the concentration is very high such as those found near to vehicle exhaust pipe or in the car tunnel and the contribution of this process (coagulation) to reduce the total number concentration is of little important on urban scale not exceeding 3% but losses could go up to 10% for the smallest nucleation size mode (3-10nm) during peak episodes. Zhang and Wexler (2002) indicated that both condensation and evaporation does not change the total particle number, but it changes the size of the particles and that the condensation will be a leading process for particle size of larger than 50nm and smaller than 2μm whereas coagulation will be important for particles below 50nm. Gidhagen et al., (2005) suggested that Deposition is more important than coagulation and found that dry deposition can cause up to 25% loss of total particle number in the range of 3-400nm size and up to 60% for the smallest nucleation size mode (3-10nm).

- Two types of air dispersion models were compared in this chapter: steady state Gaussian model (AERMOD) and non-steady-state Lagrangian model (CALPUFF). It was concluded that CALPUFF model is more appropriate to be applied for this study to predict the NOx and derive the particle number concentrations over YIC due to several reasons. Firstly CALPUFF allows for
variable and curved trajectories whereas AERMOD assumes a straight line trajectory. Secondary, CALPUFF can simulate concentration for calm wind speed. Thirdly CALPUFF utilizes meteorological data that varies in space and time. Fourthly, CALPUFF retains information on emissions from the previous hour to allow plumes to meander through the modeling domain.

- Current ambient air quality standards for particle matter (PM$_{10}$ and PM$_{2.5}$) are based on mass concentration at national and international levels. Toxicological and epidemiological studies have demonstrated that ultrafine particles are more toxic and harmful to human health than larger particle because ultrafine particle able to enter into blood stream, whereas most of the PM$_{10}$ and PM$_{2.5}$ mass may be retained in the respiratory tract. High ultrafine particles (mass or number) concentration does not necessary mean high PM mass concentration and vice versa. Therefore, current air quality standards may not be sufficient to conclude the relationship between particle number and the observed health effects. Thus, it is important to introduce ambient air quality standard for particle number as it is necessary to protect human health in more efficient.

Based on the above investigations, it seems that the number concentrations of fine and ultra-fine particle are more important to study than the mass concentration with regard to impact of particulate on human health and environment. Therefore it was decided to address in this study the particle number concentration and chemical composition of particulate of different sizes and their predictions over industrial area due to emission of different sources.
1.10 Aims and Objectives:
The main aims of this work are to develop and evaluate the correlation between particle number of different sizes and some trace gases, especially NO\textsubscript{x}; to determine the chemical composition of different particle sizes in terms of inorganic ions and trace metals and to predict the particle number concentrations of two sizes (7-40nm and 7nm-10\textmu m) over YIC based on CALPUFF NO\textsubscript{x} prediction and the linear regression between NO\textsubscript{x} and PM\textsubscript{no} observations.

This thesis will be divided into the following chapters:

- **Chapter 1**: provides introduction and literature review which was discussed earlier
- **Chapter 2** discusses the methodology and the measurements of particulate number and trace gases at three sampling sites of YIC (Yanbu Industrial City) and find out the correlationship between these particle number sizes and some of the trace gases (namely SO\textsubscript{2}, NO\textsubscript{x}, CO, H\textsubscript{2}S and O\textsubscript{3})
- **Chapter 3** address the chemical composition of different particle sizes in terms of inorganic ions and trace metals at one sampling site and the anticipated sources for each particle size will be addressed.
- **Chapter 4** evaluates the prediction of WRF model compare with the surface and upper air observations. The SODAR technique was used to provide the wind speed and direction observation while RASS and Radiosonde to provide the temperature profile at one sampling site. The surface observations from 3 sites were compared with WRF outputs.
- **Chapter 5** demonstrates CALPUFF/CALMET predictions for ground level NO\textsubscript{x} concentration due to emissions from industries and traffic during weekdays and weekends. The particle number concentrations were derived based on NO\textsubscript{x} predictions and linear regression of PM\textsubscript{no} onto NO\textsubscript{x}. Prediction of NO\textsubscript{x} and PM\textsubscript{no} will be evaluated using hourly observations at two sampling sites. The caveats of NO\textsubscript{x} and PM\textsubscript{no} predictions will be discussed at the end of this chapter.
- **Chapter 6** addresses the overall conclusion and recommendation.
Chapter 2: Methodology and Experimental Set-Up of Measurements at YIC, Saudi Arabia

2.1 Introduction:

There are numerous studies on aerosol number size distribution and number concentration which have been conducted in urban environmental sites of developed countries (such as Wehner et al. 2002, Longley et al., 2003 and Kumar et al., 2010). However, studies that examine the number size distribution or number concentration in Middle-east or in Asia or Africa are relatively very few (such as Mitra and Sharma 2002, Monkkonen et al., 2005). Some of these studies suggested that NOx and ultra-fine particle have good correlation which indicates the possibility for predicting the particle number based on NOx measurements. In this study the particle number concentration and size distribution has been interpreted in terms of three modes. (1) Nucleation mode or sometimes call Aitken nuclei (<90nm) mostly originates from condensation of hot vapors during combustion processes (Seinfeld and Pandas, 1998); from nucleation and growth from gaseous precursors involving reaction products of sulfates, nitrate, ammonium and organics leads to the formation of lower size range of this mode (<20nm); and also by coagulation of freshly formed particles with larger particles. (2) Accumulation mode (90-1000nm) is formed from the coagulation of nano–particles and from heterogeneous nucleation of secondary ions (such as sulfate, nitrate, ammonium and organics) generated by atmospheric reactions (Whitby and Sverdrup, 1980). (3) Coarse mode (particles>1000nm in diameter) is generated mainly by mechanical processes, both natural and anthropogenic.

The purpose of this chapter will be to: (1) address the measurements of particulate numbers and mass concentration, air quality and meteorological parameters during sea and land breeze at three different sites in Yanbu Industrial City, Saudi Arabia and (2) examine the correlation between trace gases and various particle sizes covering the range of 7nm up to 10μm.

2.2. Description of Measurement Program:

2.2.1 Sampling Site Description:

The measurements were taken at Yanbu Industrial City (YIC) which is located on the western coast of Saudi Arabia (23° 57' 10" N, 38° 17' 22" E). YIC of 143,000 inhabitants is situated in the Yanbu Sub-Region on the Red Sea 11km southeast of the
original settlement of Yanbu (Yanbu Al-Bahr) and 330 km northwest of Jeddah as illustrated in figure 2.1. This city is characterized by the following distinguished features:

- The population of this city is about 143,000 during daytime and 92,000 during night-time because about 35% of the population living in the other near by areas.
- It is considered as the second largest industrial city in Saudi Arabia because it has a high density of various heavy (such as refinery and petrochemical industries) and light industries (such as paint, carpet and gypsum plants) as well as traffic which both constitute main sources of anthropogenic air pollution in urban area.
- It is very much affected by natural sources (sandstorm) which represent an important source of mineral dusts.
- It is affected by sea and land breeze. Sea breeze is normally witnessed during the day time whereas the land breeze occurred during night hours.

Within this city, three sites were selected for this study as shown in figure 2.1 and the distance between one site and the other and to the main road (King Abdul Aziz Road) are shown in table 2.1.

| Table 2.1: Distance (m) between each sampling site and the other and main road |
|--------------------------------------------------|--------|--------|--------|--------|
| Site 1 | Site 2 | Site 3 | Main Road |
| Site 1 | 0.0 | 18,987 | 5,241 | 100 |
| Site 2 | 18,987 | 0.0 | 14,166 | 4050 |
| Site 3 | 5,241 | 14,160 | 0.0 | 1100 |

The descriptions of these three sites are as follows:

**Sampling Site 1:** The sampling at this site was collected during spring months (March 28 to May 30, 2008). This site is downwind location of industries during day time. The location of this site is very close (about 100m) to the main road which is a major road with four lanes (two lanes in both direction and 4 m area between the directions). This highway provides significant source of traffic emissions. Therefore, this sampling site is very much influenced by fresh traffic emission besides the emissions from industries (refineries, petrochemical, power plant, chemical plants and others). Actually it is more affected by the transportation emissions than industries with regards to NOx level especially during night times when the wind blowing from the road towards this site.
Chapter 2  
Methodology and Experimental Set-Up of Measurements at YIC

Figure 2.1: Location of sampling sites (Marked with Red Color).

**Sampling Site 2:** This site is upwind location of all industries emissions during day times but downwind during night times. This site can be considered as urban background level since it is very affected by marine air during sea breeze (day times) and slightly affected by traffic and industries during land breeze (night time). Measurements at this site began on July 14 and continued until September 15, 2008. Air masses encountered at this site represent either aged polluted outflow from Yanbu Al-Bhar town, or relatively clean background air masses transported across the Red Sea by westerly wind.

**Sampling Site 3:** The third site is located downwind of industries and traffic emissions. The distance between this site and the major road is about 1100m and this sampling point is mainly affected by industries and traffic emissions during sea breeze (day times). The measurements period at this site was conducted in spring period (March 14 to April 11, 2009).

It should be noted that the measurements at the three sites were collected non-simultaneously.
2.2.2 Instruments

A mobile laboratory was equipped with all necessary instruments to measure simultaneously trace gases, meteorological parameters, particulate mass concentration and particle size distribution (figure 2.2) at the same sampling point.

![Figure 2.2: mobile laboratory used for this study](image)

Details of equipments used in the study are shown in table 2.2. All gases, particles and meteorological data had a time resolution of 10 minutes at site 1 and 2 but 15 minutes at site 3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Detector Type/Detection Limit</th>
<th>Instrument/manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx (=NO+NO2)</td>
<td>Chemiluminescence Limit: 0.5ppb</td>
<td>NO/NO2 analyser, model AC-32M, Environment-SA, France</td>
</tr>
<tr>
<td>SO2/H2S</td>
<td>UV Fluorescence Limit: 1ppb</td>
<td>SO2/H2S analyzer, model AF-21M, Environment-SA, France</td>
</tr>
<tr>
<td>O3</td>
<td>UV Photometric D. L.: 0.5ppb</td>
<td>O3 analyzer, model O3-42M, Environment-SA, France</td>
</tr>
<tr>
<td>CO</td>
<td>NDIR</td>
<td>CO analyzer, model CO-12M, Environment-SA, France</td>
</tr>
</tbody>
</table>
Chapter 2 | Methodology and Experimental Set-Up of Measurements at YIC

<table>
<thead>
<tr>
<th>PM$_{10}$ gravimetric mass concentration</th>
<th>Limits: 0.05ppm Environment-SA, France</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta Gauge D.L.: 5ug/m$^3$</td>
<td>PM analyzer, model BAM1020, Met One, USA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number size distribution</th>
<th>Electrical Low Pressure Impactor with Corona Charger and multi-channel electrometer Limits: 7&lt;D$_p$&lt;10000nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELPI, Model EFSI 90, (Dekati, 2007) Finland</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Meteorological parameters</th>
<th>Meteorological station, model Lastem, Environment-SA, France</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp., R. Humidity</td>
<td>Solid State Thermistor Transducer</td>
</tr>
<tr>
<td>Atmospheric Pressure, Wind Speed</td>
<td>Anemometer (Cup type) Potentiometer</td>
</tr>
<tr>
<td>Wind Direction</td>
<td>Tipping bucket</td>
</tr>
<tr>
<td>Precipitation</td>
<td></td>
</tr>
<tr>
<td>Global Solar Radiation</td>
<td></td>
</tr>
</tbody>
</table>

The main instrument used in this study was outdoor Air Electrical Low Pressure Impactor (ELPI) as shown in figure 2.3. This instrument was manufactured by Dakati Ltd., (Tampere, Finland) with filter stage to measure a real-time airborne particle size distribution in the size range of 0.007-10μm at all three sites. The principle operation of ELPI is based on particle charging, inertial classification in a cascade impactor, and electrical detection of the aerosol particles (for more detailed description of this instrument, the reader is referred to Keskinen et al. (1999) and Marjamaki et al. (2000)). The main components of the instrument are a unipolar corona charger, low-pressure cascade impactor and multi-channel electrometer (Fig. 2.3). Although the time resolution of the ELPI was one second, the data were averaged over ten minutes to make the data handling easier. The ELPI sampling was set at a constant aerosol flow rate of 10lpm and equipped with a pre-impactor (cut-off diameter 10μm), 12 impaction stages with filter (7-10,000nm) as details in table 2.3. The general set-up of ELPI is to collect and detect particle in 12 stages covering a size range from 30nm to 10μm aerodynamic diameter. The lower size limit can be extended to a cut-off diameter of 7nm by removing stage#12 to make a room for the filter stage.

To minimize particle bounce effect, greased aluminum foils were used as particulate impaction and sample substrates on the impactor stages to prevent particle bounce. Before particles entering the impactor stages, their surfaces are charged with well-
defined positive charges by corona charger according to their Stokes diameter. After charging, these particles are introduced in the low pressure cascade impactor with 12 size stages in order to be classified owing to their inertia and their aerodynamic diameter. Each stage is electrically insulated from each other. The multi-stage electrometer is used to simultaneously measure the total charges in each stage due to the collected particles. These raw data from each ELPI stages are in the form of electrical current versus aerodynamic diameter versus time. Raw current distribution for the 12 impactors stages are then directly converted to particle number and mass distribution using mathematical algorithms (Marjamaki et al. 2000). Due to the dependence of the particle charging efficiency on Stokes diameter, the particle density must be defined for accurate conversion. The particle density in this study was estimated 1.5gcm\(^{-3}\) based on the measurement from both DEKATI and PM\(_{10}\) Gravimetric analyzer (see section 3.3).

The ELPI software calculates the different parameters (such as surface area and volume) simply by taking the number count and particle size and assuming that all particles are spherical and using the following formulas:

- **Number distribution** is formed by multiplying the current distribution \((C_i)\) with the conversion factor \((1/X_i(D_i))\):

\[
dN = C_i \left( \frac{1}{X_i(D_i)} \right)
\]  

(2.1)

- **Aerosol distribution** is normally given in the \(1/d\log(D_p)\) mode. It is formed by dividing the stages measured value by the logarithmic width of the stage. In \(1/d\log(D_p)\) mode the area of the histogram gives the value in each size range:

\[
\frac{dN}{d\log(D_p)} = dN \times \left[ \frac{1}{d\log(D_p)} \right]
\]  

(2.2)

- **Diameter distribution** gives the total diameter of all particles in each size range. It is calculated by multiplying the current distribution by the conversion vector and by a vector formed from the midpoint values \((D_i)\) of each stage:

\[
\frac{dD}{d\log(D_p)} = dN \times D_i \times \left[ \frac{1}{d\log(D_p)} \right]
\]  

(2.3)

- **Area distribution** gives the total surface area of all particles in each size range. It is formed by multiplying the current distribution by the conversion vector and by a vector formed the surface areas of spheres having diameter equal to midpoint values \((D_i)\) of each stage:
Chapter 2 Methodology and Experimental Set-Up of Measurements at YIC

\[
\frac{dA}{d \log(D_p)} = dN \times (\pi \times D_i^2) \times \left[ \frac{1}{d \log(D_p)} \right] 
\]  \hspace{1cm} (2.4)

- **Volume distribution** gives the total volume of all particles in each size range. It is formed by multiplying the current distribution by the conversion vector and by a vector formed from the volumes of spheres having diameters equal to midpoint values (\(D_i\)) of each stage:

\[
\frac{dV}{d \log(D_p)} = dN \times \left( \frac{1}{6} \times \pi \times D_i^3 \right) \times \left[ \frac{1}{d \log(D_p)} \right] 
\]  \hspace{1cm} (2.5)

- **Mass distribution** gives the total mass of all particles in each size range. It is formed by multiplying the current distribution by the conversion vector and by a vector formed from the masses of spheres having diameter equal to midpoint values (\(D_i\)) of each stage:

\[
\frac{dM}{d \log(D_p)} = dN \times \left( \frac{1}{6} \times \pi \times D_i^3 \times \text{Density} \right) \times \left[ \frac{1}{d \log(D_p)} \right] 
\]  \hspace{1cm} (2.6)

The instrument also contains a flush pump, a high-voltage power supply for the charger, which is used to zero the electrometer by pumping clean air through the instrument. During the measurements periods, the electrometer channels were automatically calibrated every three hours by flushing the low pressure impactor with particle free air. After each calibration process and signal stabilization, all electrometer channels were set to zero.

![Electrical Low-Pressure Impactor instrument (left) and impactor with 12 stages used for collecting samples](image)

**Figure 2.3:** Electrical Low-Pressure Impactor instrument (left) and impactor with 12 stages used for collecting samples
Table 2.3: properties of the impaction stages of the ELPI

<table>
<thead>
<tr>
<th>Stage#</th>
<th>Aerodynamic diameter Dₐ (μm), 50% cut size</th>
<th>Number of hole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter</td>
<td>0.007 (smallest cut particle diameter)</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.028</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>0.057</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>0.095</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>0.157</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>0.264</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>0.384</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>0.617</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>0.954</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>1.610</td>
<td>17</td>
</tr>
<tr>
<td>10</td>
<td>2.410</td>
<td>14</td>
</tr>
<tr>
<td>11*</td>
<td>4.020</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>9.970 (largest cut particle diameter)</td>
<td>1</td>
</tr>
</tbody>
</table>

* Stage # 12 (6.67μm stage) was removed to make a room for the filter stage

The main instrument (ELPI) limitation is that it cannot observe the very smallest ultrafine particles (<3 nm in diameter) during nucleation bursts. Particles usually start to be observed at an instrumental detection limit of round 7nm, which means that these particles have already grown for sometime starting from the size of a nucleated cluster of around 1nm. Therefore, the instrument has limitation in detecting nano-particles in the size range 3-7nm which is regarded as evidence of newly formed particles.

2.2.3 Air Pollution Sources:

There are three main pollution sources in the city: (1) industries; (2) traffic and (3) natural sources. The emissions from first two sources can be estimated based on well know emission factors but the emission from third source (natural) cannot be identified.

The air emissions from major industries in the city were determined based on either actual measurements or by an approved method (United State Environmental Protection Agency Method-42). Emissions from traffic were also estimated based on some well know emission factors and traffic count.

Emission from traffic sources will mainly depend on traffic density and vehicle type at each site. There are two methods for collecting traffic volume data: manual and
automatic. In this study, we used both methods to count the traffic volume and classification. Automatic counting (equipment name: PEAK ADR-2000) was used to obtain the traffic volume at site 1 and site 3 for one week and manual counting method was used at site 1 for a specific time interval (ten-minutes during peak hours (8-10am)) to determine the vehicle classification.

**Figure 2.4**: Typical vehicle density at sites 1 and 3 during normal days and weekend (15 minutes interval)

The information on vehicle counting at 15 minutes interval is shown in figure 2.4. As clear from this figure that peak hour is between 06:30 and 07:30am but during weekend the peak hours are in the afternoon (15:30-21:30pm). The average daily traffic density on TAMA Road (Tariq Al-Maliq Abdulaziz) nearest to site 1 and site 3 is more than 20,000 cars/day. The contributions of different car types to the total number vary.
depending on the time of the day. For example, during morning and afternoon hours the
dominant traffic type is small cars (gasoline/diesel cars) whereas during late morning and
evening the main contributors are the trucks and Lorries.

The estimated/actual emissions from these sources (traffic and industries) will be
addressed in more detail on chapter-5.

2.2.4 Data Quality and Data Assurance
Trace gases measurements were carried out based on approved methodology as shown in
Table 2.2. A side by side comparisons test was made for NOX, SO2 and O3 at site 1 only
because the laboratory was parked near a fixed air quality monitoring station. The results
showed that the systematic difference between the instruments was less than 10% and the
correlation coefficient for each pollutant was higher than 0.95.

The particulate mass concentrations from Dekati were calculated based on the measured
particulate number and assumed particle density of 1.5gcm⁻³. The comparison results
between Dekati and Met-One measurements for particle mass concentration were quite
good with a correlation coefficient of about 0.67 with an assumed density of 1.5gcm⁻³,
but when the particle density was decreased or increased this correlation becomes weaker
(less than 0.65). However, such comparisons (side by side) for trace gases as well as for
particulate matter were made at site 1 only.

The following steps were followed at all sites to obtain quality assured data:

- Zero/Span Calibrations were carried out for all trace gases analysers once every
  week and multi-point calibration was carried out at the beginning and at the end
  of each measurement program and during any maintenance work.
- During any maintenance work the data from the secondary analyzer was used as
  replacement for any missing data
- Analyzers parameters (such as flow rate, UV lamp efficiency, Ozone conversion)
  for each trace gases analysers were checked once every week as recommended by
  the analyzer manufacturer.
- Particle number instrument (Dekati) was automatically calibrated every 3 hours
  by flushing the impactor with zero air (particle free air).
- Finally all collected data were checked for quality assurance according to the
  reliability of the measurements (e.g. water vapor interfere the trace gases
  concentrations).
2.2.5 Meteorological and Air Quality Conditions

Meteorological data (temperature, pressure, relative humidity, solar radiation, wind speed and direction and rainfall) were measured at 10m tower during the measurements program as well as for the last five years (2004-2008) at site#1. Throughout the five years data which will give a broad picture of the weather over the city, the following finding can be concluded:

- The coldest period usually occurs in January and the warmest period in June. The maximum hourly temperature recorded during the last five years (2004-2008) was 47.7°C (June, 2006), the minimum hourly temperature was 9.5°C (January, 2005).
- The hourly wind speed was between 0.1 and 15.8 m/s. The maximum and minimum wind speed recorded during the last five years are 15.8 m/s (May 2004) and about 0.1 m/s (occurred more than one time).
- Yanbu Industrial City is very much affected by the phenomena of sea and land breeze (see figure 2.5). It was clear from the wind direction measurements during last five years data as well as from the measurement programs at all sites that the dominant wind direction over YIC is westerly to south-westerly during day time (from 12:00 to 22:00), and easterly and north-easterly wind during night time (from 24:00 to 08:00). This phenomenon is called sea-land breeze. On the other hand these data also showed that the sea breeze is much stronger (four times or higher) than the land breeze. The times from 0900 to 1200 hrs are periods of transition from land breeze to sea breeze and the wind is south-easterly to southerly.
- The hourly pressure varied between 1073 mb and 993 mb during last five years but during this measurement program the pressure was varying between 1013 and 997 mb.
- The lowest relative humidity usually occurs at noon time and the highest relative humidity usually occurs in the early morning hours. The maximum and minimum hourly values recorded during the last five years (2004-2008) at site 1 are 96% (occurred in October, 2008), 0.1% (occurred more than one time) respectively.
- The incoming solar radiation during summer months starts around 0700 hrs, forming a normal distribution pattern with a peak radiation of about 800 W/m² at about 1300 hrs. During winter months, the pattern is similar to that of summer, with a peak of 500 W/m² and shorter duration.
- The highest total monthly rainfall received at YIC area was 19 mm (January, 2005). During 2008 there was one day with rain of 3.5 mm in December 2008. However during measurements programs at all three sites, there was no rain fall recorded.
For the measurement periods at site 1, 2 and 3, the meteorological statistical results are shown in table 2.4. As is clear from this table the average 10-minutes temperature varied from 44.6 to 18.6°C with a mean of about 30°C. However, daily variations were generally large, up to 12°C. The typical daily pattern is, maximum in temperature in the afternoon accompanied by minimum in relative humidity whereas minimum temperature in early morning (before sunrise) and accompanied by maximum in relative humidity. Maximum relative humidity was about 97.5% observed at site#2 and the minimum was 6.7% recorded at site 1. The maximum wind speed at all sites was higher than 13.8m/s whereas the minimum was almost calm (0.1m/s). As explained above and shown in figure 2.5 the wind conditions followed a similar pattern for most of the days during last 5 years and during measurement program periods. The prevailing wind direction during all program measurements at all sites (1, 2 and 3) was westerly to northwesterly during daytime (Sea breeze) and easterly to northeasterly during night time (Land Breeze).

### Table 2.4: Meteorological measurements (10-minutes interval) at three sites during program periods

<table>
<thead>
<tr>
<th></th>
<th>Maximum</th>
<th>Minimum</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
<td>Site 2</td>
<td>Site 3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>44.6</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>Relative Humidity%</td>
<td>96.2</td>
<td>97.6</td>
<td>97.5</td>
</tr>
<tr>
<td>Wind Speed m/s</td>
<td>15</td>
<td>14.8</td>
<td>13.8</td>
</tr>
<tr>
<td>Solar Radiation (w/m²)</td>
<td>775</td>
<td>823</td>
<td>876</td>
</tr>
<tr>
<td>Pressure (mb)</td>
<td>1009</td>
<td>1013</td>
<td>1012</td>
</tr>
</tbody>
</table>

With regard to air quality measurements, the following pollutants were measured at sites 1 and 2: nitrogen dioxide, sulfur dioxide, particulate matter, ground level ozone, carbon monoxide, BTEX. The results of these measurements at sites 1 and 2 are shown in table 2.5. As clear that the level of all pollutants (except ozone) at site 1 are much higher that those at site 2.
Figure 2.5: Frequency distribution of Wind direction and wind speed measured during sea and land breeze and transition period for the last five years (2004-2008) and for measurements program at sites 1, 2 and 3.
Table 2.5: Air Quality measurements (10 minutes interval) at downwind (site#1) and upwind (site#2) locations during program period

<table>
<thead>
<tr>
<th></th>
<th>Site 1 (Downwind) Urban Location</th>
<th>Site 2 (Upwind) Urban Background</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>NO\textsubscript{x} (ppb)</td>
<td>270</td>
<td>0.71</td>
</tr>
<tr>
<td>SO\textsubscript{2} (ppb)</td>
<td>477</td>
<td>0.9</td>
</tr>
<tr>
<td>H\textsubscript{2}S (ppb)</td>
<td>389</td>
<td>0.6</td>
</tr>
<tr>
<td>O\textsubscript{3} (ppb)</td>
<td>122</td>
<td>4.3</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzene (ppb)</td>
<td>47</td>
<td>0.1</td>
</tr>
<tr>
<td>Toluene (ppb)</td>
<td>23</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethyl Benzene (ppb)</td>
<td>19.8</td>
<td>0.1</td>
</tr>
<tr>
<td>M,p-xylene (ppb)</td>
<td>24</td>
<td>0.1</td>
</tr>
<tr>
<td>O-Xylene (ppb)</td>
<td>23</td>
<td>0.1</td>
</tr>
<tr>
<td>PM\textsubscript{10} (µg/m\textsuperscript{3})</td>
<td>1122</td>
<td>10</td>
</tr>
<tr>
<td>PM\textsubscript{2.5} (µg/m\textsuperscript{3})</td>
<td>366</td>
<td>6</td>
</tr>
<tr>
<td>PM\textsubscript{1} (µg/m\textsuperscript{3})</td>
<td>271</td>
<td>4</td>
</tr>
</tbody>
</table>

The reason behind high pollution levels at site 1 is because this site is affected by both industries as well as traffic. During daytime the sea-breeze will blow the pollution from industries towards this site and during night the land-breeze will blow the emissions from traffic toward this site. The average ratio urban background (site2)/urban concentration (site1) is 0.66 for NO\textsubscript{x} and 0.015, 1.02, 0.95, 0.85, 0.73 and 0.74, respectively, for SO\textsubscript{2}, O\textsubscript{3}, Benzene, PM\textsubscript{10}, PM\textsubscript{2.5} and PM\textsubscript{1}. (The contributions from different sources are discussed later sections).

2.3 Instrument comparison and particle density determination:

Two instruments (ELPI and Met-One) were utilized to measure simultaneously the particulate mass concentration (PM\textsubscript{10}) at site 1 with 10-minutes interval during 28 March to 31 May 2008. This step was carried out in order to evaluate the Dekati performance under different particle density and relate the two measurements of particle mass as eventually one has to make assumption on the particle 'effective density', which depends mainly on particle composition and shape. Our reference for this comparison between the two instruments was Met-One analyser which uses US-EPA approved method (Beta
Gauge) for measuring mass concentration of PM$_{10}$. Further, Hock et al. 2008 suggest that determination of a mass concentration by a gravimetric method (such as Met-One instrument) can be considered more reliable than converting a number distribution into a mass concentration. As explained earlier in this chapter that in order to obtain mass concentration in Dekati instrument, particle number distribution is converted into volume distribution assuming spherical particles and then converted volume to mass concentration assuming a defined density.

Two Studies by Morawska et al. (1999) and Pitz et al. (2003) reported a wide range of apparent particle density from less than 1gcm$^{-3}$ to greater than 3gcm$^{-3}$. In this study four different particle densities were assumed starting from 1gcm$^{-3}$ to 2.5gcm$^{-3}$. The ELPIVI 4.4 software (DEKATI) was used to determine the mass concentration of PM$_{10}$ based on these different particle densities. Having calculated the mass concentration from Dekati instrument and compare it with Met-One measurements, it has been noticed that the correlation coefficient between the two instruments was 0.61, 0.66 and 0.62 when the density was set to 1, 2 and 2.5gcm$^{-3}$ respectively. However, the correlation improved slightly to 0.67 when the density was set to 1.5gcm$^{-3}$. This result is in good agreement with the study of McMurry et al. (2002) and Virtanen et al. (2006). The former study by McMurry et al. (2002) found that the density of 0.1μm urban aerosol particles in Atlanta, USA, varied between ~ 1.4-1.7gcm$^{-3}$ whereas Virtanen et al. (2006) found the effective density for 72.0±14.3nm urban aerosol particle was 1.45±0.1gcm$^{-3}$ and 1.87±0.3gcm$^{-3}$ for summer and wintertime respectively.

Therefore, we assumed the particle density of 1.5gcm$^{-3}$ in all ELPII calculations during our measurements program at the three sites although particle density may vary from one site to another. In figure 2.6 the mass concentration of PM$_{10}$ from both instruments (Dekati and Met-One) are compared. It is clear from this figure that both instruments are in a relatively good agreement with correlation coefficient of 0.67 although Dekati instrument usually record higher level than Met-One instrument but the general trend is similar. However, the difference in concentrations between both techniques could be due to various possible reasons (e.g. heating system of gravimetric instrument (Met-One) which will remove the humidity from the inlet sample but also will remove volatile organic compounds which means it will reduce the mass concentration whereas this component is monitored in ELPI).
Figure 2.6: Comparison of Dekati and Met-One particle mass concentration (1-Hour average PM$_{10}$) at site 1 during March 28 to May 31 2008

The linear regression between both instruments is given in figure 2.7, which shows the regression slope (1.12), the intercept (85) and the correlation coefficient ($r^2$) of 0.444. The average PM$_{10}$ concentration for Met-One instrument is 199$\mu$g/m$^3$ while the average for Dekati is 102.6$\mu$g/m$^3$. The ambient temperature during these measurements was varying between 18.6 C as minimum and 44 C as maximum with an average of 30.7 C. This correlation may become less or more significant depending on the sampling site and chemical composition of particles.
Chapter 2                        Methodology and Experimental Set-Up of Measurements at YIC

2.4 Particle measurements

2.4.1 PMx mass concentration:

Particle mass concentrations of different sizes at all three sites were determined using ELPI particle number concentration and assuming spherical particles and a density of 1.5g/cm³. The highest PM₁₀ mass concentration at site 1, site 2 and site 3 were 1122, 962 and 1312 μg/m³ respectively whereas the PM₂.₅ concentrations at these three sites were 366, 269 and 435 μg/m³ respectively and the level of PM₁ at these sites were 271, 202 and 249 μg/m³ respectively. Extremely high PM₁₀ values compared to other sizes (PM₂.₅ and PM₁) indicate a large contribution of coarse particles with diameter above 2.5 μm to the total particle mass concentration although this size portion plays negligible role in particle number concentration.

It is clear from figure 2.8 that the particulate mass concentration levels may reach extremely high values at all sites due mainly to the influence of sandstorms blowing from desert or local heavy construction rather than by true long range transport episodes. It can also be noticed that the concentrations at downwind location (Site 1 and 3) are higher than that at upwind location (site2) for all particle sizes because site 1 and 3 are more affected by sand-storm winds (especially during day times) and other sources such as resuspension particles from road, emission from industries as well as due to some local construction activities which all affect these two sites unlike site 2.

During this measurements program, it has been noted that the coarse mode (>1μm) particle concentration accounted for about 70-80% of the total mass concentration whereas accumulation mode (90nm-1um particle size) and nucleation mode account for 20-29% and less than 1% respectively of the total mass for the entire study period. The average ratios between the various sizes are as follows: PM₂.₅ and PM₁ make up of 37% and 19% of PM₁₀ respectively; PM₁ comprises 52% of PM₂.₅. These results clearly indicate that the coarse fraction of PM₁₀ (PM₁₀-PM₂.₅) control PM₁₀.
Chapter 2  Methodology and Experimental Set-Up of Measurements at YIC

Figure 2.8: Particle Mass Concentration measured at (a)Site 1 (b)Site 2 and (c)Site 3
2.4.2 Particle number concentration:
Total particle number concentrations (particle in the size range of 7nm-10μm) were measured at all three sites using the ELPI. The measurement results at these sites are shown in figure 2.9 and table 2.6. It is clear that Site#1 recorded the highest maximum, minimum and average particle number concentration among other sites because this site is very close to major road in the city and very much affected by traffic emission. The maximum 10-minutes total number concentration (333,971 cm\(^{-3}\)) at site 1 was more than 2.5 times higher than that recorded at site 2 (123,842 cm\(^{-3}\)) and about 1.2 times higher that the value (263,572 cm\(^{-3}\)) at site 3. The lowest concentration (123,842 cm\(^{-3}\)) was noted at site 2 because this site is not as much affected by local traffic emission as other sites and it is also generally less influenced by industries emissions although during the night time the wind direction was towards this site from the industries. Further site#2 is located to the upwind of the industries during day times but it is downwind of other sources (marine air masses and other far sources from Yanbu old city) which means it is affected by long-range transported aerosols. Therefore, Site#2 can be considered as an urban background location. The minimum particle number concentration value at all three sites was ranging between 18 cm\(^{-3}\) and about 500 cm\(^{-3}\) and as noted the lowest minimum recorded at site 2 and the highest minimum was at site 1.

It is a good idea to compare our measurement results for urban industrial environment with other pervious studies for different environments. For example, Jaenicke (1993) gives for the total number concentrations for remote continental areas about 6000 cm\(^{-3}\) and for urban (street canyon) area more than 10\(^5\) cm\(^{-3}\). On the other hand, Hussein et al. (2004) suggested that the typical particle concentrations in rural areas are between 1000 and 10,000 cm\(^{-3}\) whereas in urban environment where the air quality is very much influenced by road traffic emissions, the aerosol number concentrations usually exceed 10,000 cm\(^{-3}\). The average values at site 1 and 3 are much higher than the above indicated background level for an urban environment by Hussein (2004) but less than the suggested value by Jaenicke (1993). However, the average value at site#2 is similar to what has been suggested by both authors for rural areas although the level at site 2 sometimes gets very high. The average total number concentration at the upwind (site 2) and downwind (site 1) sites differs by a factor of 7. Further, it is clear that the maximum values at all sites are much higher than the typical level for urban environment as suggested by Jaenike (1993) and Hussein et al. (2004).
### Table 2.6: Statistical comparison of particle number concentration between the three sites

<table>
<thead>
<tr>
<th></th>
<th>Site 1 (Downwind)</th>
<th>Site 2 (Upwind)</th>
<th>Site 3 (Downwind)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>44,118</td>
<td>6,833</td>
<td>23,070</td>
</tr>
<tr>
<td>Maximum</td>
<td>333,971</td>
<td>123,162</td>
<td>263,572</td>
</tr>
<tr>
<td>Minimum</td>
<td>483</td>
<td>18</td>
<td>242</td>
</tr>
<tr>
<td>SD</td>
<td>43,885</td>
<td>8,002</td>
<td>21,241</td>
</tr>
</tbody>
</table>

Ruuskanen et al. (2001) reported that the hourly total number concentrations at an urban site of Helsinki and other European cities (Alkamaar in Netherlands and Erfurt in Germany) was about 145,000 cm\(^{-3}\) which is lower than our short-term (10-minutes) measurements at urban locations (site 1 and 3) of this study ranging between 260,000 and 333,000 cm\(^{-3}\). Comparing both results for these studies will be more reliable if they have same measurements time interval.

Our values are in agreement with the results by Monkkonen et al. (2005). A field experiment by Monkkonen et al. (2005) at highly polluted place in New Delhi, India for Aerosol particle number concentrations with 10-minutes time resolution showed the number concentrations were varying between 20,000 and 250,000 particle cm\(^{-3}\).

The contributions of the three particle sizes (Aitken or nucleation; accumulation and coarse) to the total number concentration at each site are shown in figure 2.9. It is clear that the total number concentrations were dominated at sites 1 and 3 by aitken mode because both sites are very much affected by transportation emissions as well as industries whereas at site 2 the Aitken mode contribution is about 57% of the total number and this is because site 2 is more influenced by long-ranged transported aerosols. The contributions of ultrafine particle (smaller than 100nm in aerodynamic diameter) to the total particle number concentration are between 80-87% at site 1 and 3 and only 57% at site 2. These results are in agreement with other previous studies (Wichmann et al., 2000 and Rodriguez et al., 2007, Mejia et al., 2008) which suggest that 80% of the total number of particles in urban areas belong to nucleation mode. Further, it is clear that the fraction of aged accumulation mode particle is noted at site 2 because this site is more influenced by aged transported particles from the marine air and long distance sources. It is suggested by Kulmala et al., (2000b) that the accumulation mode is related to LRT particle material from combustion and coagulation of smaller particles.
Figure 2.9: Total particle number concentration (left plots) and Contributions of three sizes to the number concentration at site 1, 2 and 3 (Aitken+nucleation) mode: 7-90nm; Accumulation:90nm-1um and Coarse:>1um) (right plots)

The results for site 1 and 3 indicate that the high values of number concentration are due to local sources (anthropogenic sources) because Aitken mode particles do not transport over long distance and they are usually formed close to the observation point (Laakso et al., 2003).

The contribution of coarse mode to the total number concentration is negligible -less than 0.2% at all sites. This very low value may not represent the actual scenario due to particle bounce-off in cascade ELPI impactor which has been documented by several authors (Hinds 1998). Some particle can bounce from their respective collection stage and are collected on stages corresponding to small sizes. Experimental data by Hinds (1998)
show that once a large particle bounces-off its proper stage it is likely to continue bouncing-off other stages in the impactor and may not be collected at all.

2.4.3 Average Size Distribution during Sea and Land Breeze

As Yanbu Industrial City located at the coast line of the Red Sea, it is very much affected by sea and land breeze. This phenomenon is very much influencing the measurements at all sampling sites. During the day times, sea breezes tend to blow most of the urban pollution from all anthropogenic sources (industries and traffic) towards the land (sites 1 and 3 in particular) and this pollution builds up after midday till midnight. However, after midnight when the wind changes its direction land breeze may recirculate this polluted air back into the sampling sites and towards the sea.

Based on this fact, particle size distributions were classified according to wind direction which is considered as a crucial parameter indicating the origin of the air mass. As stated earlier that the wind direction can be divided into three clusters: sea breeze (wind blowing from the Red Sea towards the three sites); transition period (wind direction shifting from land breeze to sea breeze) and land breeze (wind blowing from the land towards the sea). Therefore, the average size distributions were plotted based on these three wind-directions.

In this study all calculations from the ELPI measurements and graphs are plotted using aerodynamic diameters and density of 1.5gcm$^{-3}$.

2.4.3.1 Site#1 (Downwind location)

Based on the measurement results at site 1 shown in figure 2.10, it can be concluded the following:

- Site 1 is more influenced by traffic emissions than industries as it is very close to the major road in the city. Therefore, during land breeze when the wind blowing directly from the traffic towards the sampling site (downwind of the traffic and upwind of the industries), the average number distribution is about triple than that during sea breeze and it is about double than that during transition period. The lower range size of Aitken mode is clearly noted at this site but the upper range size of Aitken mode and accumulation mode are not observed.

- During sea breeze (upwind of the traffic and downwind of the industries) the particle size distribution has less maximum than that during land breeze because
the nucleation mode particles emitted from industries will be removed by deposition and coagulation on their way to the sampling point. Further during sea breeze at this site the impact from industries will be higher than that from traffic which will be minor.

- The analysis of the data at site 1 shows clearly that the particle number distribution has only one mode (nucleation mode with diameter less than 20nm) during all wind direction clusters. The nucleation mode represents the fresh nucleation mode and produced directly by traffic emissions and by gas to particle conversion. This result is supported by other previous studies. For example, Wehner et al., (2003) also noticed that traffic emission produced a peak in the number size distribution at around 20nm particle diameter during rush hours. Further, Longley et al. (2003) suggested that traffic has been observed to be one major primary source of nucleation mode ($D_p<20$nm) particles.

- The difference in particle number distribution (66,000cm$^{-3}$) of Aitken mode between sea breeze (wind blowing from industries) and land breeze (wind blowing from major road) is probably the impact of the traffic at site 1.

It is clear from figure 2.10 that the average number concentration generally decreases as the particle diameter increases, while particle surface area (fig 2.10 b) and particle mass and volume (fig 2.10 c and d) concentrations exhibit a distinct maximum in the accumulation mode from 200nm to 500nm aerodynamic diameter and in the coarse mode of about 2$\mu$m respectively. Further, the particle mass and volume distributions are elevated during sea breeze compared to land breeze and dominated by coarse particles with size of larger than 1$\mu$m because during sea breeze the wind blowing from the industries carrying relatively larger particle towards the site. The emitted particle from the industries will grow by coagulation from nucleation mode and condensation of condensable vapor and those particles will reach site 1 with accumulation mode diameter.

On the other hand, the area size distribution had two modes for all wind clusters: one dominant mode in the submicron size range peaking at around 300nm and the other minor mode in the coarse size range and peaking at around 1.9$\mu$m. However, during wind transition period the peak is higher than those during sea and land breeze. It is clear from Figure 2.10b and 2.10d that the accumulation mode accounts for most of the surface area of particles whereas the coarse mode account substantially to particle mass.
Accumulation mode particles are generally too small to be removed by gravity and too large to be coagulated into larger particles, and therefore their atmospheric lifetimes are in the range of a few days or slightly longer.

**Figure 2.10:** Mean size distribution of particle number, area, volume and mass at site 1 during March 28 to May 31, 2008.

### 2.4.3.2 Site#2 (Upwind location):

The particle distribution at site#2 is different from that at other site (sites 1 and 3) because this location is less affected by local anthropogenic sources but more influenced by natural marine air masses and long-range transport particles. During sea breeze, this site is more influenced by either "aged polluted" air masses outflow from old city of Yanbu (Yanbu Al-Bahar); or relatively "clean marine" air masses originating from the Red Sea transported to the sampling site; or relatively polluted air had been built up during night times over the sea shore. During land breeze this site is affected by air pollution from industries and some local traffic.

Based on the results shown in figure 2.11, it can be noticed that the number size distribution has two modes (unlike other two sites: 1 and 3) especially during land breeze and transition period (wind blowing from industries towards this site): the first mode in the nucleation range (less than 20nm) and the second in the accumulation size (400nm). However, during sea breeze when the air mass originated from north-west (marine air), the particle size distribution shifted to larger values which clearly indicate that the site is
affected by long range transported particle. The maximum in the size distribution is shifted to about 200nm in comparison to the anthropogenic (industrial and traffic emissions) distribution with a maximum at less than 20nm. Clearly the long-range transport is apparently the dominating source at this site. However, the other explanation for this larger particle that during the night times, land breezes tend to blow most of the urban pollution (particle with ultra-fine particles) over the sea which builds up after midnight till sunrise, blows much of the air pollutants into the coastal plain. After sunrise and early morning sea breeze may recirculate this built-up polluted air back into this site but with larger size particles.

During sea breeze there was only one clear mode (accumulation mode) unlike during land breeze. The maximum number size distribution during land breeze is about five times higher than that during sea breeze due to higher emissions caused by fossil fuel combustion (refineries, petrochemical industries, traffic and other sources).

The maximum volume and mass size distributions occurred at two size ranges: around 500nm and another maximum at around 6μm or higher. The maximum volume/mass value during sea breeze (volume:100μm³/cm³; mass:0.15mg/m³) exceeded that of land breeze (volume:55μm³/cm³; mass:0.08 mg/m³) by a factor of two. On the other hand, the particle area distribution has only one peak of 400nm during all wind clusters although there is very small other mode in the range of 2μm.

Figure 2.11 Mean size distribution of particle number, area, volume and mass at site 2 during July 14 to September 15, 2008
2.4.3.3 Site#3 (Downwind location):
Both sites 1 and 3 are affected by traffic as well as industries emissions and therefore these two sites have relatively similar particle number distribution pattern and have one peak in the nucleation mode (20nm) as shown in figures 2.10 and 2.12. However, the difference between these two sites that site 3 is located relatively far from the major road (about 1100m away) unlike site 1 which is very close to the traffic emission (30m). It is understood that as the distance between sampling point to the traffic emission becomes larger, the removal of small particles (Aitken mode) can take place during a longer transport time of the air mass. Aitken mode particles do not transport over long distances so they have to be formed relatively close to the emission source (Laakso et al. 2003)

Based on average size distribution for site 3, we can conclude the following:
- The particulate number distribution at downwind Sites (1 and 3) consist of one distinguishable mode (nucleation mode<20nm) due to the influence of local sources (industries as well as traffic)
- Site 3 has the highest particle number distribution (42,000cm$^{-3}$) during sea breeze when the wind direction blows most of the urban air pollution from all anthropogenic sources (mainly industries) towards this site. It is interesting to note that the peak value at site 3 (42,000cm$^{-3}$) is similar to that occurred at site 1 during same wind direction (sea breeze). However, these values during sea breeze are much lower than that during land breeze at site1 (108,000cm$^{-3}$) and the reason behind this drop in the maximum particulate number distribution during land breeze at site 3 is moving away from the traffic emission which causes more dilution with background air and coagulation that both processes are considered as the main mechanisms for drop in number concentration.
- During transition period the particle number decreased to 27,000cm$^{-3}$ because during this time the site affected partially by industries as well as traffic emissions.
- The average number size distribution dropped to 20,000cm$^{-3}$ during land breeze because the wind blows from the desert towards this site.
- The surface area at site 3 has two modes: one distinguished peak in accumulation (about 0.5μm) and the other in the coarse mode. The highest peak mode was observed during sea breeze whereas the lower peak was during land breeze because of less affect of large particles. High surface area means relatively poor visibility.
- At site 3 the volume/mass distribution has a clear peak in the coarse mode because this site is more affected by desert aerosols. The volume/mass distributions of the coarse mode are higher during sea breeze than those during land breeze and transition period.

Figure 2.12: Mean size distribution of particle number, area, volume and mass at site 3 during March 21 to April 11, 2009

2.5 Diurnal Variation of particle number and gases

Diurnal variation of particle number; trace gases concentrations and some meteorological parameters were plotted for site 1 (downwind of industries) and site 2 (upwind of industries) as shown in figure 2.13 (diurnal variation for site 3 was not plotted at this section since it has almost as same pattern as site 1). All readings have been rounded to the nearest hour and each plotted point (10-minutes time interval) shows the mean of all readings obtained at that hour during the period of observations at each site. It can be noticed from figure 2.13 that the diurnal variations in particle number (PM$_{10}$) and NO$_x$ concentrations show distinct peaks between 7-8am, which coincide with the peak morning traffic as shown in earlier section (figure 2.4). The close relationship between NO$_x$ and PM$_{10}$ indicated that the traffic on the highway directly influencing particle
number concentrations at sampling site. Based on the findings shown in figure 2.13, it can be concluded the following facts:

- Particle number of all sizes increase during early morning hours (7-9a.m.) when there is a very clear traffic-generated morning rush hour peak and the emissions are blown towards the sampling sites (1 and 2). The rise in particle count is approximately coincident with the rise in NOx from the road traffic. Our findings agree with the results by Hitchins et al (2000) who conclude that when the wind blowing directly from the highway, the particle number concentration most influenced whereas the level decreases during the afternoon when the wind blowing from the station towards the highways.

- After morning peak hours both PM_{no} and NOx declined rapidly. The aerosol number concentrations decreased because of dilution within the developing boundary layer (mixing height is rapidly increasing after 8a.m.) and also because small particle created earlier in the day grow to larger sizes by coagulation and condensation whereas NOx level decrease mainly due to ozone formation.

- A substantial reduction in particle number and trace gases in the afternoon appears to be occasioned by an increase in wind speed and a rise in temperature which will have promoted vertical mixing. Usually higher wind speed tends to lower the levels of pollution in general due to higher dilution while lower wind speed lead to higher concentration.

- The diurnal variation of SO2 has two peak concentrations (first peak was 41 μgm^-3 and the second was 72 μgm^-3) during morning hours due to diminishing the inversion layer after sunrise which will bring all pollution from above to near the ground and second peak during after noon due to wind direction which blows SO2 from the power plant towards this site. However, it is clear that there is a poor correlation trend between particles number and SO2 or H2S diurnal variation.

- The average particle number concentrations at site 1 during morning and evening times (78,000cm^-3 and 40,000cm^-3 respectively) were about four times higher than that at site 2 (20,000cm^-3 and <10,000cm^-3 respectively) because site 1 is very much affected by traffic emission whereas site 2 is not. Hussain et al. (2004) reported rather similar nighttime background concentration values of 8,000cm^-3 and 10,000cm^-3 during the summer and winter seasons, respectively. Our average results for site 1 during peak rush hours agrees with the finding by Virtanen et al (2006) who showed that the average roadside concentration during morning rush hours at Itavayla (main road in Helsinki) were approximately 100,000cm^-3 in the winter and 50,000cm^-3 in summer.
Figure 2.13: Average diurnal variation of particle number, gaseous pollutants (NOx, SO2, H2S) and meteorological variables (wind speed, temperature) for site 1 (left plots) and site 2 (right plots)
The possible chemistry of particle formation and furnish are not discussed in this study but the reader is referred to Stanie et al. 2004 who has discussed the formation of nucleation events associated with photochemical processes.

2.6 Effect of wind direction on particle number and NOx concentration:
It is interesting to study the effect of wind direction, which plays a major role, on particle number of 7-200nm size (this size is mainly emitted from combustion sources such as traffic) and NO\textsubscript{x} at all three sites. It is clear from Figure 2.14 that at site 1 both parameters (particle number and NO\textsubscript{x}) increase dramatically when the wind direction is easterly to southeasterly which blows from the major road towards the sampling site and again a relative increase in both parameters when the wind is westerly- blowing from industrial areas towards site 1 whereas these parameters (particle number and NOx) decrease when the wind is southerly to south-westerly. This result shows clearly the impact of traffic and industrial emission on the level of particle number and NOx concentration measured at site 1.

At site 2, higher particle and NO\textsubscript{x} concentration were observed when the wind direction is northerly to north-westerly and north-easterly which blows from the road towards this site whereas lower particle number and NO\textsubscript{x} is observed when the wind is blowing from other direction. It can be concluded from this result that there are no major sources of particles which cause higher particulate number concentration with smaller size.

At site 3 the particle number and NO\textsubscript{x} concentration increase when the wind direction is westerly to south-westerly which blows from industries as well as major road towards the sampling site as shown in figure 2.14.
Figure 2.14: Relationship between wind direction, particulate Number (7-200nm) and NOx at the three sites: a) Site 1 during March 28 - May 30, 2008; b) Site 2 during July 15 - September 14, 2008 and c) Site 3 during March 22 - April 10, 2009

2.7 Correlations between particle number and trace gases

The correlation between particle number of different sizes and trace gases concentrations measured at the three sites were determined and discussed in this section. Since not all instruments were always in operation, the number of samples, that are available for the correlation estimate, is variable with the parameter combination. A set of 4500, 7000 and 2016 instantaneous samples of particle numbers and gases concentrations were taken at site 1, site 2 and site 3 respectively to have a good accuracy in the correlation coefficient determination. These sets of data were taken every 10 minutes time interval at site 1 and 2 and 15 minutes at site 3 during the sampling periods. Particle numbers at each site were taken simultaneously with trace gases.
Table 2.7: Correlation coefficient (r) between trace gases and particle number concentration of different size ranges

<table>
<thead>
<tr>
<th></th>
<th>7-40nm</th>
<th>40-200nm</th>
<th>200nm-10μm</th>
<th>7-200nm</th>
<th>0.1-1μm</th>
<th>7μm-10μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>0.54</td>
<td></td>
<td></td>
<td>0.51</td>
<td>0.58</td>
<td>0.56</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0.72</td>
<td>0.65</td>
<td>0.4</td>
<td>0.73</td>
<td>0.45</td>
<td>0.74</td>
</tr>
<tr>
<td>NO</td>
<td>0.73</td>
<td>0.59</td>
<td>0.3</td>
<td>0.72</td>
<td>0.32</td>
<td>0.73</td>
</tr>
<tr>
<td>SO₂</td>
<td>-0.1</td>
<td>0.15</td>
<td>0.52</td>
<td>-0.05</td>
<td>0.19</td>
<td>-0.04</td>
</tr>
<tr>
<td>O₃</td>
<td>-0.55</td>
<td>-0.49</td>
<td>-0.22</td>
<td>-0.55</td>
<td>-0.19</td>
<td>-0.55</td>
</tr>
<tr>
<td>H₂S</td>
<td>-0.08</td>
<td>0.155</td>
<td>0.54</td>
<td>-0.025</td>
<td>0.22</td>
<td>-0.014</td>
</tr>
<tr>
<td>Site 2</td>
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<td>NO₂</td>
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<tr>
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<td>0.72</td>
<td>0.31</td>
<td>0.71</td>
</tr>
<tr>
<td>NO</td>
<td>0.65</td>
<td>0.56</td>
<td>0.13</td>
<td>0.66</td>
<td>0.27</td>
<td>0.65</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.12</td>
<td>0.045</td>
<td>-0.18</td>
<td>0.1</td>
<td>-0.15</td>
<td>0.091</td>
</tr>
<tr>
<td>O₃</td>
<td>-0.42</td>
<td>-0.3</td>
<td>0.13</td>
<td>-0.41</td>
<td>0.03</td>
<td>-0.4</td>
</tr>
<tr>
<td>H₂S</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
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<td>0.75</td>
<td>0.63</td>
<td>0.77</td>
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</tr>
<tr>
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<td>0.32</td>
<td>0.34</td>
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<td>0.35</td>
</tr>
<tr>
<td>NO</td>
<td>0.3</td>
<td>0.17</td>
<td>0.24</td>
<td>0.15</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.01</td>
<td>0.09</td>
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<tr>
<td>O₃</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>H₂S</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

A summary of the correlation coefficient (r) between particle number concentrations of different sizes and the criteria air pollutants measured at the three sites is given in table 2.7. As is clear from the table that correlation coefficients between the particle number with diameter less than 200nm and between 7nm and 10μm are highly related to the NOₓ and NO concentration at sites 1 and 2. The reason behind good correlation between NOₓ/NO and the total range (0.007-10μm) is because the aitken mode is the dominant part of the total number. This result indicates that particles are traffic induced since NOₓ is mainly emitted by vehicles in particular at upwind and downwind locations (sites 1 and 2). According to Harris and Maricq (2001) the particle size distribution corresponding to automobile emissions is in the range of 20-300nm with a maximum between 6-100nm. Further, other previous studies suggested that particle in the range of 20-130nm mostly emitted from diesel engines (Morawska et al., 1998a) and 40 to 80nm from petrol engines (Ristovski et al., 1998). These results indicate that both ultrafine particles numbers and NOₓ gases are emitted from same source type- Motor vehicle which is considered as the common source of NOₓ and particles (Ketzel et al., 2004).

Furthermore, it is noted from table 2.7 that there is a high correlation between NOₓ/NO and particle number concentration through a wide range of size classes (7-40; 7-200nm and 7μm-10μm) for sites 1 and 2. The highest values of (r) are observed for the parameter combinations particle number of ultrafine particle (7-40nm) and NOₓ and this
high correlation is caused by the fact that both compounds originate mainly from road traffic emissions. Moreover, the correlation at site 1 is generally better for the size of 7-40nm than those at sites 2 and 3 because site 1 (kerb-site) is very close to the traffic road (20m) whereas other sites (in particular site 3) is relatively far (1100m) from this source which means some particles get removed by deposition and coagulation on their way from the sources (traffic or industries) to site 3.

However, the correlation decreases towards larger particle sizes (accumulation mode and coarse modes) at sites 1 and 2 due to the contribution of other sources in the area (such as stand-storm and resuspension particles from the road). Further, it is observed from table 2.7 that as particle size diameter increases the correlation between NO\textsubscript{x}/NO and number concentration decrease from "r" 0.7 for diameter <200nm (a fraction which account for >80% of the total number concentration) to 0.3 for 200nm-10\mu m (a fraction which account for <20% of the total number concentration) at sites 1 and 2 (near traffic road locations). These results are in agreement with the observations by Ketzel et al., 2003 who noticed high correlation (R>0.83) between particle number concentration and NO\textsubscript{x} through a wide range of particle sizes at street level in Jagtvej, Copenhagen whereas the correlation between NO\textsubscript{x} and size segregated particle number reduced substantially above 200nm. Further, in a 2-year study in the city of Brisbane (Morawska et al.,1998) showed that particle number concentration in the range of 5-1000nm was moderately correlated with NO\textsubscript{x} (R=0.63). A 4-year study of urban background number concentration in Leipzig (Wehner and Wiedensohler, 2003) showed a high correlation between total particle number concentration in the range of 20-800nm and both NO and NO\textsubscript{2} concentration especially in winter months when ventilation of the urban canopy layer is reduced by increased atmospheric stability.

The correlation of particle number with NO and NO\textsubscript{x} are generally stronger than with NO\textsubscript{2} at sites 1 and 2 (very close to traffic road) because at the beginning traffic emit NO and particles of different sizes simultaneously and after several minutes this component (NO) will be converted to NO\textsubscript{2}. Therefore NO is better tracer for close traffic than NO\textsubscript{2}. On the other hand for site 3 the scenario is different- the correlation coefficient between NO\textsubscript{2} and particle number of Aitken mode and accumulation mode are fairly better than with NO because NO will be converted to NO\textsubscript{2} when it reach site 3 and the emitted ultrafine particles will become larger till arrive at the sampling site. Further, the correlation between NO\textsubscript{x} and particle number of Aitken mode is weak compared to accumulation and coarse modes for site 3 because particles get larger in sizes by coagulation on their way from the sources (traffic or industries) to site 3. Our results are
in contrast with the study by Roth et al. (2008) who found there is high correlation between NO\textsubscript{x} and particle number with diameter between 0.1 and 0.62\textmu m in sampling site very close (less than 10m) to the road in the center of Strasbourg.

As for the other air pollutants, the particle number concentration has a generally weak correlation with the SO\textsubscript{2} at all sites because this pollutant (SO\textsubscript{2}) originates mainly from the sulphur present in the fossil fuel (heavy fuel oil, diesel oil) which mainly consumed by some facilities (such as power plant) in the city that are relatively far (>3km) from the sampling site. The contribution of traffic is very little to SO\textsubscript{2} emissions as suggested by Citepa (2005). Further, the lack of correlation between the particle number concentration (especially for ultrafine and coarse modes) and SO\textsubscript{2}/H\textsubscript{2}S data implies that the two are not from the same source type. However, the correlation between particle number of accumulation mode and SO\textsubscript{2} has been found relatively better at site 1 because this site is the most affected location by power plant emissions. Our results are in agreement with the findings by Roth et al., 2008 who noted that the particle number with diameter between 0.10 and 0.62\textmu m are highly related to the NO\textsubscript{x} concentration with correlation coefficients of higher than 0.5 whereas the correlation between SO\textsubscript{2} and particles number is less clearly correlated. Williams et al., (2000) found that the nucleation mode (3-7.5nm) had a stronger correlation with SO\textsubscript{2} than with NO\textsubscript{x}. However, our measurements did not cover the nucleation mode to compare with this study.

Negative correlation (-0.31) has been identified between particle number and the O\textsubscript{3} concentration which can be explained by the chemical balance between NO\textsubscript{x} and O\textsubscript{3} leading to anti-cyclical pattern of these species. There was poor correlation between CO and PM\textsubscript{no} (<0.02) and CO and NO\textsubscript{x} (-0.01) because CO has other different sources (such as incomplete fuel combustion from flares) than NO\textsubscript{x} and PM\textsubscript{no} in industrial areas.

Based on the above results, linear regressions were performed for three different size ranges at the three sites. The slope of the regression line NO\textsubscript{x} vs. particle number concentration of different sizes for both sites are shown in figure 2.15 and table 2.8. The slope for lower size range of 7-40nm was the highest at site#1 (834 #/cm\textsuperscript{3}/ppb of NO\textsubscript{x}) because this site is very close to the main traffic road but the slope for the size range of 7nm-10\textmu m was the highest at site#3 (1225 #/cm\textsuperscript{3}/ppb of NO\textsubscript{x}).
Chapter 2  Methodology and Experimental Set-Up of Measurements at YIC

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a. Site 1 (size range: 7-40nm)
y = 834.21x + 4069.4
R² = 0.5251

b. Site 1 (size range: 7-200nm)
y = 909.71x + 8289.2
R² = 0.5428

c. Site 1 (size range: 7nm-10μm)
y = 917.83x + 9273.6
R² = 0.5488

b. Site 2 (size range: 7-200nm)
y = 580.04x + 918.75
R² = 0.5872

c. Site 2 (size range: 7nm-10μm)
y = 587.91x + 2022
R² = 0.5858

b. Site 3 (size range: 7-200nm)
y = 1143x + 8814
R² = 0.3819

c. Site 3 (size range: 7nm-10μm)
y = 1225x + 9047
R² = 0.409

Figure 2.15: Correlation between NOx and particle number of different size ranges and linear regression lines for different particle sizes at sites 1, 2 and 3

Table 2.8: Results of linear regressions of aerosols sizes ranges onto NOx concentration at sites 1, 3 and 3

<table>
<thead>
<tr>
<th></th>
<th>7-40nm</th>
<th>7-200nm</th>
<th>7nm-10μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>b 4069</td>
<td>8289</td>
<td>9273</td>
</tr>
<tr>
<td></td>
<td>a 834</td>
<td>909</td>
<td>917</td>
</tr>
<tr>
<td></td>
<td>r² 0.52</td>
<td>0.54</td>
<td>0.55</td>
</tr>
<tr>
<td>Site 2</td>
<td>b -929</td>
<td>918</td>
<td>2022</td>
</tr>
<tr>
<td></td>
<td>a 495</td>
<td>580</td>
<td>587</td>
</tr>
<tr>
<td></td>
<td>r² 0.58</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>Site 3</td>
<td>b 7853</td>
<td>8812</td>
<td>9047</td>
</tr>
<tr>
<td></td>
<td>a 754</td>
<td>1143</td>
<td>1225</td>
</tr>
<tr>
<td></td>
<td>r² 0.26</td>
<td>0.38</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Note: Regression onto the line y=ax+b where y is aerosol concentration of certain size range and x is gas concentration

It is interesting to note that when the intercept of the slope is set to zero (b=0.0), the number concentration of particle as compared to NOx varies between 893 (<40nm) and 1029 (<200nm) particle cm⁻³ per ppb (NOx) at site 1 while at site 2 (upwind location) the emission factor varies between 451 (<40nm) and 623 (<200nm) particle cm⁻³.
2.8 Comparison of YIC linear regression with other UK sites:

Simultaneous measurements of particle number and NOx concentrations at three different characterized sites in UK were processed to determine the linear regression. These three sites are as follows: Tropospheric ORganic CHemistry (TORCH1) is located about 30km north-east of London, and therefore it is semi-urban site, TORCH2 is located on the North Norfolk coastline near Weybourne without large population centers or industrial areas and therefore it is considered as semi-rural area, and G6 site is located in Greater Manchester in the north west of England approximately 600m to the south of the Piccadilly rail-station and therefore, it is considered as urban site. The measurements at TORCH 1 conducted from July to August 2003, at TORCH 2 during 25th of April and continued until the 25th of May, 2004 and at G6 during May 24 to July 28, 2005. The linear regressions of three different aerosol size ranges onto NOx at each of these sites were calculated and shown in table 2.9.

<table>
<thead>
<tr>
<th>Site</th>
<th>Size Range</th>
<th>7-40nm</th>
<th>7-200nm</th>
<th>7-650nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TORCH 1</td>
<td>b</td>
<td>6150</td>
<td>8620</td>
<td>8715</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>485</td>
<td>576</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
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<td>b</td>
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<td>3604</td>
<td>3805</td>
</tr>
<tr>
<td></td>
<td>a</td>
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</tr>
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<td></td>
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<td>G6</td>
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<td>16300</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>138</td>
<td>204</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.10</td>
<td>0.15</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The above analysis revealed the correlation between particle number and NOx at UK sites are relatively poor ($r^2$ ranging between 0.0 and 0.16) as compared to the three YIC sites ($r^2$ ranging between 0.3 and 0.59). TORCH 1 is located at downwind of London emissions plume under prevailing wind conditions which has similar characteristic of site#3. The slopes at site#3 of 754 and 1225 #/cm³/ppb of NOx for size range of 7-40nm and 7nm-10μm, respectively, were much higher than those at TORCH1 of 485 and 580, which suggests that YIC is more affected by anthropogenic sources than TORCH1. One
difference is that the measurements at TORCH1 for the higher size range went up to 650nm, but those at Site#3 went up to 10μm. However, the contribution of upper size (higher than 650nm) can be negligible to the particle number compared to lower size. The intercept at both TORCH 1 and Site#3 at YIC is relatively close to each other and it is ranging from 6150 (7853 at site#3) to 8715 (9047 at site#3) at TORCH1.

The correlation coefficient ($r^2$) between the particulate number concentration and the NOx concentration at TORCH 1 and G6 sites is relatively better than that at TORCH 2 as shown in table 2.6. However, by comparing all six sites (tables 2.8 and 2.9) it can noted that YIC sites (especially sites#1 and 2) have much better correlation coefficient than those at UK sites and the correlation coefficient ($r^2$) at TORCH 2 for all size ranges were very poor with a maximum of 0.05 in the range of (7-200nm). Further, the slope and intercept at TORCH 2 are the lowest among these sites. The main reason for poor correlation and low slope and intercept at TORCH 2 is because most of the particles at this site are Long-range transport particles. Further, the particulate matter at TORCH 2 represents either "aged polluted" air masses outflow from London or relatively "clean marine" air masses originating from the Norwegian Sea or the Northeastern Atlantic Ocean transported across the North Sea region by northerly to north-easterly wind to the sampling site which may take several days.
2.9 Summary and Conclusion:
Particulate number and mass concentration, gas pollutants and meteorological parameters were measured at three different characteristic sites in YIC. The particulate matter as well as trace gases at downwind of industries location (Site 1 and 3) are generally higher than that at upwind location (site2) for all particle sizes. The measurements showed good correlation (0.67) between Dekati and Met-One measurements for particle mass concentration when particle density of 1.5gcm$^{-3}$ was assumed, but when the density was decreased or increased this correlation becomes weaker (less than 0.65).

Site#1 recorded the highest maximum, minimum and average particle number concentration among other sites because this site is very close to major road in the city and very much affected by traffic emission. The maximum total number concentration (333,971 cm$^{-3}$) at site 1 was more than 2.5 times higher than that recorded at site 2 (123,842 cm$^{-3}$) and about 1.2 times higher that the value (263,572 cm$^{-3}$) at site 3. The coarse mode at all sites accounted for about 70-80% of the total mass concentration whereas accumulation mode and aitken mode account for 20-29% and less than 1% respectively. On contrary, the contributions of aitken mode particle to the total particle number concentration are between 80-87% at site 1 and 3 and only 57% at site 2 while accumulation mode is less than 20% at sites 1 and 3 but it is more than 40% at site 2. The contribution of coarse mode to the total number concentration is negligible -less than 0.2% at all sites.

The average particulate number distribution at downwind Sites (1 and 3) consist of one distinguishable mode (nucleation mode<20nm) due to the influence of local sources (industries as well as traffic) whereas site 2 has two modes (the first in the nucleation range and the second in the accumulation) because this site is affected either by long range transported particle or recirculation of built-up polluted air back to this site from the sea. The highest particle number distribution at all sites (site1: 108,000; site2: 10,000 and site3: 42,000cm$^{-3}$) occurred when the wind blows directly from industries or traffic side towards these sites while the lowest number distribution take place when the wind blows from the desert or sea.

It is interesting to note that the peak value of average size distribution at site 3 (42,000cm$^{-3}$) is similar to that occurred at site 1 during same wind direction (sea breeze) which is inferred that the impact of the traffic on site 3 is negligible. The difference in
particle number distribution (66,000 cm\(^{-3}\)) of Aitken mode between sea breeze and land breeze is probably the impact of the traffic at site 1.

The diurnal variation of particle number of all sizes increase coincidently with NO\(_x\) during early morning hours (7-9a.m.) when there was a very clear traffic-generated emission blown towards the sampling sites (1 and 2) and afterward both parameters decreased remarkably because of dilution within the developing boundary layer (mixing height is rapidly increasing after 8a.m.). Further, particle number and NO\(_x\) concentration increased at all sites when the wind direction is blowing from traffic road and/or industries towards the sampling locations whereas the concentrations decreased when the wind is blowing from other direction

The correlation of particle number with NO and NO\(_x\) are generally stronger than with NO\(_2\) at sites 1 and 2 (very close to traffic road) because at the beginning traffic emit NO and particles of different sizes simultaneously and after several minutes this component (NO) will be converted to NO\(_2\). Therefore NO is better tracer for close traffic than NO\(_2\). On the other hand for site 3 the scenario is different- the correlation coefficient between NO\(_2\) and particle number of Aitken mode and accumulation mode are fairly better than with NO because NO will be converted to NO\(_2\) when it reach site 3 and the emitted ultrafine particles will become larger when arrive at the sampling site. Further, the correlation between NO\(_x\) and particle number of the Aitken mode is weak compared to accumulation and coarse modes for site 3 because particles get larger in sizes due to coagulation on their way from the sources (traffic or industries) to site 3

The correlation coefficient (r>0.7) between NO\(_x\) and particle number at sites 1 and 2 is generally better for the sizes of 7-40nm; 7-200nm and 0.007-10 \(\mu\)m than that at site 3. However, the correlation decreases towards larger particle sizes (accumulation mode and coarse modes) at sites 1 and 2 due to the contribution of other sources in the area (such as stand-storm and resuspension particles from the road). Further, it is observed from table 2.7 that as particle size diameter increase the correlation between NO\(_x\)/NO and number concentration decrease from "r" 0.7 for diameter <200nm (a fraction which account for >80% of the total number concentration) to 0.3 for 200nm-10 \(\mu\)m (a fraction which account for <20% of the total number concentration) at sites 1 and 2. On the other hand, however, the correlation coefficient at site 3 is better in the upper end of aitken mode (40-200nm) and accumulation mode (0.1-1\(\mu\)m) than other sites because ultrafine particles get removed by deposition and coagulation on their way from the sources (traffic or industries) to site 3.
As for the other air pollutants, the particle number concentration has generally weak correlation with the SO\textsubscript{2} at all sites because this pollutant (SO\textsubscript{2}) originates mainly from the sulphur present in the fossil fuel. However, the correlation between particle number of accumulation mode and SO\textsubscript{2} has been found relatively better at site 1 because this site is the most affected location by power plant emissions.

Negative correlation (-0.31) has been identified between particle number and the O\textsubscript{3} concentration which can be explained by the chemical balance between NO\textsubscript{x} and O\textsubscript{3} leading to anti-cyclical pattern of these species. There was poor correlation between CO and PM\textsubscript{no} (<0.02) and CO and NO\textsubscript{x} (-0.01) because CO has other different sources (such as incomplete fuel combustion from flares) than NO\textsubscript{x} and PM\textsubscript{no} in industrial areas.

Comparison of linear regression between YIC and UK sites showed that the slopes at YIC site#3 of 754 and 1225 #/cm\textsuperscript{3}/ppb of NO\textsubscript{x} for size range of 7-40nm and 7nm-10\textmu m, respectively, were much higher than those at UK TORCH1 of 485 and 580, which suggests that YIC site is more affected by anthropogenic sources than TORCH1. The intercept at both UK TORCH 1 and YIC Site#3 is relatively close to each other and it is ranging from 6150 (7853 at site#3) to 8715 (9047 at site#3) at TORCH1. Further, by comparing all six sites in Saudi Arabia and UK it was noted that YIC sites (especially sites#1 and 2) have much better correlation coefficient than those at UK sites and the correlation coefficient (r\textsuperscript{2}) at TORCH 2 for all size ranges were very poor with a maximum of 0.05 in the range of (7-200nm). The possible reason for the poor correlation and low slope and intercept at UK is because these sites are relatively far from particle number sources (such as road) and they are more affected by Long-range transport particle.
Chapter 3: Chemical Composition of Size Fractioned Particulate at YIC,

3.1 Introduction:

The inorganic fraction generally comprises 70-80% of the total particle mass in the atmosphere whereas the remainder is organic compounds (NEERI2000). Inorganic ions and trace metals are released into the atmosphere both from natural and anthropogenic sources, namely: combustion of fossil fuel, traffic and resuspended surface dust. The fuel combustion sources (industries as well as traffic) are major contributors for emitting directly or indirectly the inorganic ions (such as SO$_4$, NO$_3$). On the other hand, the combustion of fossil fuels constitutes the principle anthropogenic source for many elements (such as Be, Hg, Mo, Cu, Zn, Cd) as well as a large contributor of As, Cr, Cu, Mn and Zn (Pacyna, 1998). Exhaust emissions from gasoline and diesel fuelled road vehicles contain variable quantities of Pb, Fe, Cu, Zn, Ni, and Cd (Pacyna, 1986). Trace metals are found in almost in all particle sizes and therefore this has a great effect on the toxicity of metals when inhaled by human beings because the degree of respiratory penetration and retention are particle size dependent.

Very few studies on precise chemical characterization of ultra fine particles (with diameters less than 0.1μm) in terms of trace metals and inorganic ions concentrations are available. Although these ultrafine particle are not the major contributor to the total mass concentration, they largely dominate in number and may be main responsible for some adverse health effects. Ultra fines get deposited in the lower lung area where the adsorption efficiency for trace metals is relatively high 60-80% (Becker et al., 2005).

Yanbu Industrial City (YIC) as second largest industrial complex in Saudi Arabia has various industrial facilities as well as traffic which may emit inorganic and trace metals. It is interesting to determine the chemical composition of particles of different sizes in such industrial place. In this chapter the different size particles captured on 12 ELPI stages during spring period (March 14-April 11, 2009) were chemically analysed by IC for inorganic ions and by ICP-MS for trace metals.
3.2 Sampling location and Experimental Procedures:

3.2.1 Sampling Location:

The particle samples were collected during March 14 to April 11, 2009 at site 3. This coastal site is considered as urban location as it is located inside Yanbu Industrial City. It is affected by natural source (e.g. sand storm) as well as by anthropogenic sources (industries and traffic emissions). The distance between this sampling site and main road is 1100m and about 2km from the heavy industries (for more detail on Chapter 2).

3.2.2 Experimental Procedures:

The ELPI with 12 stages were used to collect the particle samples in the sizes (0.007-10 μm). The ELPI inlet was operated at a constant flow rate of 10 Lmin⁻¹. Polycarbonate filter papers (Whatman Inc.) were used to collect the samples. Grease was not used on the collection substrates to avoid any contamination of samples although some recommend for using grease to reduce the possible particle bounce-off. The sampling time was increased from 24 hour to one week, in order to obtain sufficient amount of sample for chemical analysis. After each sample collection, ultrasonic bath was utilized to clean the 12 stages (figure 3.1). The net mass of each particle size collected on each filter paper were measured by weighing the polycarbonate filter before and after each sampling using a semi-micro balance (model: AB204 Mettler Teledo with a minimum resolution of 0.1mg). After mass determination, the sample filters were kept in a dry sealed plastic capsule and stored in a refrigerator till for further analysis. After sampling, all samples were kept in a special cool keeper at less than 4°C and shipped from YIC (Saudi Arabia) to Manchester University laboratory (UK) for extraction and chemical analysis.

Figure 3.1: Ultrasonic Bath (left photo) and ELPI 12 stages (right photo)
Before starting the chemical analysis, a series of calibration standards was prepared using a mixture of anion stock solutions to cover the maximum and minimum expected range and calibration curve was obtained for each component. The chemical analysis procedures applied in this study is similar to those used by other authors (Pakkanen et al., 2001).

A blank (unexposed) polycarbonate filter was chemically analyzed to check the background contamination. The results of the analysis of blank samples were used to estimate the element/ions concentrations produced by the filter and/or the plastic tube and/or during sample preparation or transportation. The results of the blank filter test in this study for each ion are as follows: Chloride (1.7ngm⁻³), Nitrite (0.8ngm⁻³), Nitrate (1.8 ngm⁻³), Sulphate (0.5 ngm⁻³) and for the remaining ions values were not detected. In this blank tube except chloride and nitrite (below 0.4 ngm⁻³) no other ions were detected.

Our analysis was started with the lowest particle size filter (7-40nm) for one week to check if the instrument can clearly detect the ions but it was observed that the concentration of ions in the sample solution for one week was too low to be detected at this certain particle size and therefore it was decided to combine the samples of 4 weeks for each size and make a composite sample.

All 4 filters (for 4 weeks) from each plate were placed in a plastic sample tube using forceps and extracted in 5mL ultra-pure water. Tube was treated in an ultrasonic bath for 15 minutes and gently agitated. The liquid extracts were filtered using a disposable 0.45μm syringe filter. All filtered extract was stored in another plastic tube ready for chemical analysis (see figure 3.2).

For IC analysis, 600μl of the diluted sample for each particle size was taken for ion chromatographic (IC) analysis and the remaining portion was used for trace metals using inductively coupled plasma mass spectrometry (ICP-MS). The inorganic ions (Sulphate, Nitrate, Nitrite, Bromide, chloride, Oxalate, Phosphate) were analyzed by IC (Dionex DX-600 (figure 3.3)). The anion separation column was an AS9-HC (High Capacity), with NaCO₃ 9Mm as mobile phase running at 1.4mL min⁻¹. The injection volume was 200μl. The detection limits for ions was variable but typically around 0.1ppm in solution. The uncertainties (at the 95% confidence level) for all the measured ions ranged from 1% for sulfate to 7% for chloride (Prichard, 2001).

The ammonium was analysed using UV-VIS Spectrophotometry with wave length of 420nm. The minimum detection limit for this instrument is 0.5ppm.
The ICP-MS (Inductively Coupled Plasma Mass Spectrometer) instrument (see figure 3.3) was used for determining the concentrations of the following elements: Na, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Zn, Ag, Ti, V, Hg and Sn. The detection limit of ICP-MS may be as low as 0.01ppb under normal operating conditions although 0.1 is more commonly achieved level. The results of blank filter test for trace metals were as follows: 0.3ngm$^{-3}$ for Na, 0.1ngm$^{-3}$ for Zn and less than 0.01 for the remaining metals. All metals considered in this study are soluble in water.

The calibration curves for IC (sulphate as an example) and for ICP-MS (Zn as an example) are shown in figure 3.4 and as an example for IC chromatogram results for particle size of 900nm-4000nm is shown in figure 3.5.
Fig 3.4: Calibration curves for IC (top-Sulphate) and ICP-MS (bottom-Zink)

Fig 3.5: IC chromatogram for particle size of 900nm-4000nm at site 3 (note: unknown peak is possibly organic acids and/or carbonate/bicarbonate)
3.3 Results and Discussion:

3.3.1 Wind Direction against different particle size number and NOx:
Wind direction is an important parameter especially for air pollution studies as it indicates the origin of air mass and the relative position of the sampling site to the main sources. Therefore, the particle number concentrations of each impactor stage (12 sizes) as well as NOx concentrations were plotted against the wind direction (figures 3.7 and 3.8) to determine the likely source of each particle size.

When wind direction data is analysed for site#3, it is found that the prevailing wind direction is westerly to south-westerly blowing from the industries and from the Red Sea (marine air masses) towards this site and this represent more than 51% of the total wind data whereas only 12% of the total wind data is primarily from road traffic and 37% from desert region as shown clearly in figure 3.6. This means site3 is more affected by industrial emissions sources (power plant, refineries, petrochemicals and others) and marine air masses than other sources.

![Wind Direction: 51% blowing from industries; 37% from desert and 12% from traffic](image)

**Figure 3.6:** Wind Direction distribution (left) at site#3 (Brown color: wind blowing from industries towards the site; bright green: wind from traffic and blue color: wind from desert) and site map (right)

Therefore, in order to pinpoint the sources of each particle size, wind direction was plotted against the particle number at each stage (figure 3.7). Wind direction can be classified into three clusters as noted earlier based on source type: (1) sea breeze-wind blowing from industrial area towards site#3; (2) transition period-wind blowing from traffic towards site#3 and (3) land breeze-wind blowing from desert towards site#3.

**Cluster 1 (Sea breeze—marked with yellow color):** Wind direction from south-south-east to west-west-north (140°-310°) is dominant wind and brings high particle number of
almost all particle sizes (especially accumulation mode) due to emission from industries (refineries, power plant, petrochemical facilities) as well as marine air. Particles emitted from industries in aitken mode (<0.1μm) will transform to larger particles (mainly in accumulation mode) as they move away from the source due to a combination of dilution, coagulation, condensation and chemical reactions processes until reach site#3. Moreover, there is no clear increase in nuclei mode particle concentration (plate 1 and 2: 7-55nm) although the wind blowing from combustion sources because these particle sizes (nano-particle) do not transport over long distance so they have to formed very close to the emitting source. For example, the distance between particles emitting sources (industries) and site#3 is ranging between 2.5km and 9km and the distance between main traffic road and this sampling site is 1.1km which causes these nano-particles to become larger. However, the difference between the two different sources (industries and traffic) is the emitting source height, for the case of industries the stack height is ranging between 80m and 150m above the ground whereas in case of traffic it is less than 2.5m on average.

Cluster 2 (transition period-marked with gray color): For south-easterly and north-westerly (110°-140°&300°-315°) relatively high particle number concentrations in plate 3 and 4 were observed due to primarily contribution from traffic. It is clear from figure 3.7 that site#3 is not much affected by the traffic emissions because when the wind (SE&NW) blowing from the traffic road the NOx is not remarkably increased but when the wind direction (S-WNW) from the industrial area the level of this pollutant is increasing. It is clear that aitken mode particle emitted from traffic and industries are removed or become larger due to longer distance from the emitting sources to the sampling point

Cluster 3 (land breeze): Wind from north-north-west to north-east (335°-0°&0°-110° clockwise) blowing from the desert is associated with lower particle number concentration of all sizes although there is small increase at plate 8 and 9.

In summary it can be concluded that site 3 is mainly affected by industries emissions although there is minor contribution from automobile sources and natural sources (marine air masses). The sampling site recorded higher concentration in aged non-traffic related accumulation mode particles. It is suggested by previous study the fraction of aged accumulation mode particle can be remarkable especially when traffic level is low (Virtanen et al., 2006).
Figure 3.7: Time series over 4 weeks period (March 14 to April 11, 2009) for particle number at each impactor stage plotted against wind direction at site#3.
3.3.2 Inorganic Ions:
The ionic analysis results (shown in figure 3.9) reveal that the data at site 3 can be classified into two groups based on each particle size range: first ionic group (sulfate and ammonium) concentrated on particle size less than 0.38 μm and the second group (nitrate and chloride) concentrated on particle larger than 0.38 μm although sulfate and other ions are present.

As in figure 3.9 and table 3.1 that the major ions in the collected samples are sulfate, nitrate, ammonium and chloride. Sulfate was detected in all plates 1 to 12 but this ion is concentrated in lower end of accumulation mode (101-380 nm). The concentration of sulfate ranged from 10.75 ng m⁻³ as minimum in nuclei mode (0.028 μm) to a maximum of 702 ng m⁻³ in accumulation mode (0.16-0.38 μm). The next highest concentration amongst anions was nitrate and this ion was detected in plates 6 to 12 and dominates the particle mode between 0.6 μm and 4.0 μm. The highest concentration of nitrate was 485 ng m⁻³ and detected in particle size of 2.41 μm and the lowest concentration (<1 ng m⁻³) was in the size of <0.06 μm. Ammonium was also observed clearly in most of stages especially in small particles (<0.61 μm) size but it was in minor quantity in the larger particle (>0.95 μm). The highest (275 ng m⁻³) ammonium concentration was detected at plate 6 and the lowest (<4 ng m⁻³) was noted at plate 1 (0.028 μm) and plate 9 (1.6 μm).

There are two possible reasons for being sulfate in aitken mode particle and nitrate in accumulation mode particle: firstly that sulfate is emitted from sources nearby to the sampling site while nitrate from relatively far away source. The other reason is that sulfate ion tends to accumulate in relatively small size particles as sulfate is essentially non-volatile ion and has a size distribution controlled by gas-diffusion. On the contrary, nitrate is more volatile ion than sulfate and therefore it will tend to evaporate from
smaller particles and deposit on large particles where curvature effects on vapor pressure are minimal (Zhang et al., 2000)

Moreover, it is worth noting that generally sulfate and ammonium present in the same particle sizes (mainly aitken mode) whereas chloride and nitrate appear in the same plates (mainly accumulation mode).

![Graph 1](image1)

**Figure 3.9**: Distribution of inorganic ions (with non-sea salt sulfate) mass concentration according to the particle size (top) and % distribution of ions according to the particle size (bottom)

Chloride and nitrate were found in particle sizes between 0.61 and 9.9 μm. Oxalate is mostly correlated with diameters larger than 0.61 μm. Bromide and phosphate were also...
detected in the accumulation mode but with very low concentrations. Generally speaking, 
nitrite, Bromide, Phosphate and Oxalate are found in very low concentration.

Table 3.1: Mass distribution (ng m\(^{-3}\)) of inorganic ions (with non-sea salt sulfate) in 
plates 1 to 13 (aerodynamic diameter of 0.28 to 9.9\( \mu m \))

<table>
<thead>
<tr>
<th>Plate#</th>
<th>Cut point D50% (( \mu m ))</th>
<th>Cl</th>
<th>NO2</th>
<th>Br</th>
<th>NO3</th>
<th>PO4</th>
<th>SO4</th>
<th>OX</th>
<th>NH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.028</td>
<td>1.86</td>
<td>0.93</td>
<td>0.00</td>
<td>0.00</td>
<td>10.75</td>
<td>0.00</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.057</td>
<td>1.46</td>
<td>1.19</td>
<td>0.00</td>
<td>0.93</td>
<td>0.00</td>
<td>41.22</td>
<td>0.00</td>
<td>14.59</td>
</tr>
<tr>
<td>3</td>
<td>0.095</td>
<td>2.39</td>
<td>0.93</td>
<td>0.00</td>
<td>1.10</td>
<td>0.00</td>
<td>170.62</td>
<td>0.00</td>
<td>47.75</td>
</tr>
<tr>
<td>4</td>
<td>0.157</td>
<td>2.39</td>
<td>1.19</td>
<td>0.00</td>
<td>1.46</td>
<td>0.00</td>
<td>468.70</td>
<td>0.00</td>
<td>127.32</td>
</tr>
<tr>
<td>5</td>
<td>0.264</td>
<td>4.38</td>
<td>0.00</td>
<td>0.00</td>
<td>4.64</td>
<td>1.86</td>
<td>702.64</td>
<td>0.00</td>
<td>196.29</td>
</tr>
<tr>
<td>6</td>
<td>0.384</td>
<td>3.85</td>
<td>1.06</td>
<td>0.40</td>
<td>10.08</td>
<td>2.52</td>
<td>701.33</td>
<td>8.09</td>
<td>275.86</td>
</tr>
<tr>
<td>7</td>
<td>0.617</td>
<td>28.38</td>
<td>1.19</td>
<td>0.27</td>
<td>106.10</td>
<td>1.06</td>
<td>251.45</td>
<td>7.56</td>
<td>42.44</td>
</tr>
<tr>
<td>8</td>
<td>0.954</td>
<td>137.93</td>
<td>1.72</td>
<td>0.00</td>
<td>343.50</td>
<td>0.00</td>
<td>180.71</td>
<td>13.66</td>
<td>6.63</td>
</tr>
<tr>
<td>9</td>
<td>1.610</td>
<td>216.18</td>
<td>0.93</td>
<td>0.00</td>
<td>449.60</td>
<td>0.00</td>
<td>206.34</td>
<td>16.18</td>
<td>3.98</td>
</tr>
<tr>
<td>10</td>
<td>2.410</td>
<td>299.73</td>
<td>1.06</td>
<td>0.00</td>
<td>485.00</td>
<td>0.00</td>
<td>280.30</td>
<td>16.31</td>
<td>14.59</td>
</tr>
<tr>
<td>11</td>
<td>4.020</td>
<td>241.38</td>
<td>0.80</td>
<td>0.00</td>
<td>320.95</td>
<td>1.06</td>
<td>297.87</td>
<td>12.47</td>
<td>14.59</td>
</tr>
<tr>
<td>12</td>
<td>9.92</td>
<td>10.74</td>
<td>0.53</td>
<td>0.00</td>
<td>15.92</td>
<td>0.00</td>
<td>78.66</td>
<td>3.98</td>
<td>11.94</td>
</tr>
</tbody>
</table>

Roth et al., (2008) reported that highest concentration of ammonium and sulfate were in 
aerodynamic diameter between 617 and 954nm but ammonium in ultra fine particles 
(diameter lower than 80nm) was measured below the limit of determination. On contrary, 
our findings showed that the maximum concentration of sulfate and ammonium were in 
diameter of <610nm and negligible ammonium in particles with diameter between 
950nm-4\( \mu m \). However, both studies showed that maximum nitrate concentrations were in 
aerodynamic diameter of 954nm. It is important to highlight that the chemical 
composition of any particle depend mainly on site location and the type of pollution 
sources affecting the sampling site.

The marine sulfate and non-sea salt sulfate were calculated from the total measured 
sulfate based on the typical ratio of sulfate to sodium in sea water (2.7/10.6). The total 
sulfate and non-sea salt sulfate are calculated for each particle size and shown in figure 
3.10. It is clear from this figure that the non-sea salt sulfate is dominant in all particle 
sizes and the contribution of marine sulfate is minor. The contribution of marine sulfate 
to total sulfate is ranging from 0.2% in Aitken mode size to 18% in coarse mode particle. 
As is clear from this figure that the natural sources (marine) play negligible to minor role 
in sulfate level but industries play the major role especially sulfate in aitken mode and 
accumulation mode particle size.
The total sulfate and nitrate contributed 51% and 23.7% of the total ionic mass respectively followed by chloride (13.3%) and ammonium (10.6%) as can be noted from figure 3.11. Oxalate accounted for only 1.2% of total ionic mass and less than 0.5 for the remaining ions. The total ionic mass includes only those analysed in this study (sulphate, nitrate, nitrite, bromide, ammonium, chloride, oxalate, phosphate) but not all ions.

![Figure 3.10: Total sulfate and non-sea salt sulfate level at each particle size](image)

![Figure 3.11: Percentage contribution of each Inorganic ions to the total mass concentration (particle size<10µm) of anions and NH₄](image)

It might be interesting to compare the mass concentrations for inorganic ions for this study with other measurements at sites around the world (table 3.2). In comparison with
the results measured at urban sites in the world, the ionic levels at YIC is relatively low and the concentrations (except nitrate) are very close to that at Sapporo in Japan. As noted that the highest concentrations for sulfate (20,600ngm$^{-3}$) and chloride (2,460ngm$^{-3}$) were observed in the eastern Asia coastal areas showing the characteristics of marine aerosol and coal burning emission. On the other hand, the highest concentration of nitrate (13,480ngm$^{-3}$) and ammonium (5,520ngm$^{-3}$) were recorded at Bakersfield, an urban site in San Joaquin Valley, which is characterized by vehicle emission pollution.

Table 3.2: Mass concentration of ions (ngm$^{-3}$) at YIC compared with other measurements at site around the world.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>$SO_4^{2-}$</th>
<th>$NO_3^-$</th>
<th>$NH_4^+$</th>
<th>$Cl^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YIC, Saudi Arabia</td>
<td>3590</td>
<td>1739</td>
<td>757</td>
<td>952</td>
</tr>
<tr>
<td>Bakersfield, San Joaquin V., USA, (Chow et al, 1993)</td>
<td>5000</td>
<td>13480</td>
<td>5520</td>
<td>420</td>
</tr>
<tr>
<td>Leeds, UK (Quality, 1996)</td>
<td>6800</td>
<td>2800</td>
<td>2400</td>
<td>1500</td>
</tr>
<tr>
<td>Sapporo, Japan (Kaneyasu et al., 1995)</td>
<td>3898</td>
<td>898</td>
<td>815</td>
<td>849</td>
</tr>
<tr>
<td>Honk Kong (Qin et al., 1997)</td>
<td>9535</td>
<td>1624</td>
<td>2319</td>
<td>1160</td>
</tr>
<tr>
<td>HKIT, Central Taiwan (Fang et al., 1999)</td>
<td>20600</td>
<td>7580</td>
<td>--</td>
<td>2490</td>
</tr>
</tbody>
</table>

3.3.3 Trace Metals
The concentrations of the following trace metals were determined with ICP-MS at 12 impaction stages (cut-off D50% aerodynamic diameter 7nm to 10μm): Na, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Ba, Hg, Pb. The chemical analysis results (shown in figure 3.12 and 3.13) indicate that the dominant trace metals in all particle sizes (7nm-10μm) are Na, Al, Ti, V, Fe, Zn, Sr and Cr. The most abundant metal is Na which represents more than 94% of the total mass of trace metal in PM$_{10}$.

The trace metals concentrations results (figure 3.12) shows that in the lower particle size range (7-380nm) high levels of Fe (3.7ngm$^{-3}$), V (4ngm$^{-3}$), Zn (3.6ngm$^{-3}$) and Al (2.7ngm$^{-3}$) associated with this particle size range. Also, low concentrations of Ti (1.1ngm$^{-3}$), Cr (1.2ngm$^{-3}$), Mn (0.4ngm$^{-3}$), Pb (0.7ngm$^{-3}$), Ni (1.0ngm$^{-3}$) were observed in the same particle size range. The remaining metals (Sn, Hg, Ag, Mo, As, Cu) were in negligible concentrations. On the other hand, in the upper particle size range (>380nm) there are other metals which were higher in this size: Al (7.5ngm$^{-3}$), Cr (2.7ngm$^{-3}$), Sr (5.2ngm$^{-3}$), Mn (1.4ngm$^{-3}$), Ba (0.6ngm$^{-3}$) and the remaining metals are either in very low concentration or in negligible level.
The highest total mass concentration (8.5 ng/m³) for trace metals was observed at particle size of 0.38 μm (cut-point 50% aerodynamic diameter).

It is worth noting that the sodium ion (Na) was detected in all plates (7 nm-10 μm) with very high concentration compared to other metals and therefore this ion was plotted separately (shown in figure 3.13). As might be expected, the predominance of sea breeze during the sampling period enhanced Na⁺ level, especially in the accumulation and coarse fractions as clear from figure 3.13. Cl⁻ and Na⁺ are major components of marine aerosols. Considering the geographic location of the YIC, which is very close to the Red sea a high concentration of Na⁺ is expected. Na⁺ holds more than 94% of the total mass of trace metals in PM₁₀. Our result for Na⁺ (796 ng/m³) is very close to other measurement (746 ng/m³) by (Orlic et al., 1999) at AJC, Singapore but it is much lower than other result at Manchester (1300 ng/m³) by (QUARG, 1996) and Hong Kong (1480 ng/m³) by (Qin et al., 1997).
Figure 3.13: Distribution of Na$^+$ mass concentration according to the particle size

The contribution and mass concentration of each trace metals in the PM$_{10}$ is illustrated in figure 3.14. It is clear that the main contributors in mass concentration are Al (25%), Sr (13%), Zn (13%), V (10%), Cr (10%) and Fe (10%). Mn, Ti, Ni, Cu, Pb and Ba account for less than 5% of total metal mass. The remaining each metals either holds <1% or negligible mass of total trace metals.

Figure 3.14: Contribution and mass concentration (ng/m$^3$) of each trace metals to the total mass concentration (particle size<10µm).
By comparing our results with others measurements around the world, it is clear (table 3.3) that the Na value at YIC is very close to the value measured at coastal site of Singapore but it is lower than the measurements at other sites. Metals like Pb, Zn and Cu that originate from anthropogenic sources were much lower at YIC than that measured at other urban sites around the world. The total mass concentrations of Zn and Cu at YIC were 5.7 and 0.6 ng/m$^3$ respectively. These values are very low compared to measurements at Hong Kong (Zn=111 and Cu=123ng/m$^3$) and those at Singapore (Zn=80 and Cu=54.6ng/m$^3$). The relatively high of Ni at YIC compared to other coastal site (Oki island in Japan) implies site#3 is affected by emission of fuel oil combustion sources.

**Table 3.3:** Mass concentrations (ngm$^{-3}$) of some trace metals in PM$_{10}$ at YIC compared with other measurements at sites around the world.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Na</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>YIC, Saudi Arabia</td>
<td>796</td>
<td>0.9</td>
<td>1.4</td>
<td>5.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Point Reyes, San Joaquin Valley, USA, (Chow et al, 1993)</td>
<td>1604</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Manchester, UK (Quality, 1996)</td>
<td>1300</td>
<td>360</td>
<td>13.2</td>
<td>237</td>
<td>-</td>
</tr>
<tr>
<td>Oki island, Japan (Mukai et al., 1990)</td>
<td>430</td>
<td>12</td>
<td>0.9</td>
<td>15</td>
<td>1.7</td>
</tr>
<tr>
<td>Honk Kong (Qin et al., 1997)</td>
<td>1480</td>
<td>71</td>
<td>4.2</td>
<td>111</td>
<td>123.8</td>
</tr>
<tr>
<td>AJC, Singapore (Orlic et al., 1999)</td>
<td>746</td>
<td>69</td>
<td>11.8</td>
<td>80</td>
<td>54.6</td>
</tr>
</tbody>
</table>

It is interesting to point out that our measurements for some trace metals and inorganic ions in large particles could be underestimated because polycarbonate filter was used without placing grease on each collection plate to avoid contamination to the sample. This step may cause particle bounce-off in cascade impactors as has been documented by several authors (Hinds, 1998) and it is more common in the upper stages of the impactors. Experimental data show that once a large particle bounce off their intended stage in the impactors it is likely to continue bouncing away from the other stages and may not be collected at all.

**3.3.4 Sources analysis for ions and trace metals:**

Sampling site (Site#3) is very much affected by several anthropogenic and natural sources which have significant influence on the concentrations of ions and trace metals. The possible contributing sources present within 10km radius from sampling site are: power plant, petrochemical facility, refineries, gas plant, traffic, crustal and marine sources.
As noted previously in section 4.3.1 that when the wind is blowing from industrial side, all particle sizes (mainly accumulation mode) increased remarkably but when the wind blows from the desert side or traffic road the increment of particle number either low or minor because site 3 is relatively far from traffic road which cause freshly emitted particles below 100nm to coagulate and taken by large particle and therefore its number rapidly drops with distance from the road as reported by many studies (Ketzel et al. (2003); Zhu et al. (2002); Hitchins wt al (2000)). Therefore, it is inferred that industries are the main contributor for number concentration and chemical composition of particles at site 3 although there are other sources (such as marine).

In order to identify the impact of each industrial source on the sampling point, a simple USEPA (United State Environmental Protection Agency) SCREEN3 model (EPA, 1995a) was utilized. SCREEN3 model uses a Gaussian plume equation incorporating source related factors and meteorological parameters to estimate the ground level concentration from individual sources. It is assumed that there is no chemical reaction or removal processes (such as dry or wet deposition) act on the plume during its transport from the source to the sampling point. This model was applied based on actual emission rate (g/s) and plume characteristics (such as exit gas velocity and temperature, stack height) provided by each facility or calculate using an approved method (US-EPA method 42). The emission rate from traffic was calculated based on the traffic count and some well know emission factor. It was assumed that the traffic emission is volume source. The emission details will be discussed in chapter 5. The estimated distance between each source and sampling site are shown in table 3.4 and the modeling results are shown in figure 3.15.

Table 3.4: Estimated distance between sources and sampling point

<table>
<thead>
<tr>
<th>Source name</th>
<th>Air Pollutants emitted</th>
<th>Downwind distance to site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Plant 1</td>
<td>SO₂, NOₓ, PM, Fly ash, Metals</td>
<td>9.1km</td>
</tr>
<tr>
<td>Power Plant 2</td>
<td>SO₂, NOₓ, PM, Fly ash, Metals</td>
<td>14km</td>
</tr>
<tr>
<td>Petrochemical</td>
<td>NOₓ, VOC</td>
<td>8.8km</td>
</tr>
<tr>
<td>facility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinery 1</td>
<td>SO₂, NOₓ, PM, Metals</td>
<td>3.4km</td>
</tr>
<tr>
<td>Refinery 2</td>
<td>SO₂, NOₓ, PM, Metals</td>
<td>2.4km</td>
</tr>
<tr>
<td>Gas Plant</td>
<td>NOₓ, VOC</td>
<td>4.9km</td>
</tr>
<tr>
<td>Traffic</td>
<td>NOₓ, CO, VOC</td>
<td>1.1km</td>
</tr>
<tr>
<td>Sea Shore</td>
<td>SO₂, Metals</td>
<td>7km</td>
</tr>
</tbody>
</table>
Figure 3.15: Downwind concentration of NOx (top graph) and SO2 (bottom graph) from main polluting sources in YIC

It can be inferred from figure 3.15 and table 3.4 that the main affecting sources at site#3 for NOx (and accordingly nitrate) are power plants and gas plant as well as refinery whereas the main sources for SO2 (and accordingly sulfate ion) are power plants and refinery 2. However, the impact from traffic emission (a near ground source) seems to be minor or negligible on the measurements at site#3 but this source has large affect on areas within 50-150m downwind distance as clear from this figure.
In order to determine the initial and final particle size emitted from these main sources in YIC and ions mass concentrations when it reaches site#3, the following factors were considered:

- It was suggested by Morawska et al., (1998a) that the emitted particles from diesel engines will be in the size range of 20-130nm and from gasoline engine will be 40nm to 80nm. Another study (Harrison and Maricq, 2001) for size distributions of diesel agglomerates emitted from a heavy-duty diesel engine showed that the mean particle diameter is 60-100nm. Earlier study by Moisio et al. (1998) for size distributions of different combustion plant types showed that the dominant particle number concentration is in the size range of 100nm. Based on the above findings it can be assumed that the particulate emission due to fuel oil combustion by power plant and refinery in the range of 20-130nm (as initial emitted size) and particulate emission due to usage of fuel gas combustion source by petrochemical facility and gas plant will be in the range of 40-80nm (as initial emitted size).

- The average wind speed during sea breeze (wind blowing from industries towards site#3) is 9km/hr. The relative humidity during day time was varying between 40% up to 70%.

- Kulmala et al. (2004) indicated that the typical growth rate by condensation and coagulation in a range of different environments vary between 1-20 nmh⁻¹ although this growth rate may vary dramatically in coastal areas. Growth rate as high as180nmhr⁻¹ have been observed close to the coastal source region at Mace Head (Dal Maso et al., 2002; O'Dowd et al., 2007). Further, Kulmala et al. (2004) indicated that some estimates in coastal areas give growth rates as high as 200nmhr⁻¹ and the smallest growth rate are about 0.1nmhr⁻¹ in clean polar areas. Based on the above findings it can be assumed that growth rate in YIC is as high as 180nmhr⁻¹.

- Sulfate either emitted directly as primary sulfate or secondary sulfate produced in the atmosphere through gas to particle conversion of SO₂ and other sulfur containing gases. Sulfur oxides will be oxidized to sulfuric acid which in turn form sulfate particles and nitrogen oxides are oxidized to nitric acid in the atmosphere, which in turn form the nitrate particles (Matsumoto and Tanaka, 1996). The formation rate of sulfate and nitrate depends significantly on the amount of SO₂ and NOₓ present in air, background air composition (such as ozone level) and ambient condition (mainly water vapor and solar radiation). Forrest et al. (19981) found a daytime average conversion rate of 3% hr⁻¹ for SO₂ to sulfate during summer and an average of 0.5% hr⁻¹ at night for the coal-fires
Cumberland plume. Another study for Oil-fired plume by Garber et al (1981) found lower \( \text{SO}_2 \) conversion rate to sulfate of less than 1% hr\(^{-1} \) but this rate increased to 2.3% hr\(^{-1} \) when ambient temperature increased to greater than 13\(^{\circ}\)C. Further, Anlauf et al (1982) found an average summertime \( \text{SO}_2 \) to sulfate oxidation rate of 4% hr\(^{-1} \) in the plume of the Nanticoke coal-fired power station in Ontario at distance downwind from stack of 3-43km at relative humidity of 30-50%. With regard to nitrate formation rate, Gillani et al. (1998b) found nitrate formation rate in the range of 10-15%. Hewitt (2001) suggest that the maximum \( \text{SO}_2 \) conversion rate to sulfate of about 3% hr\(^{-1} \) and a maximum NOx conversion rate of about 30% hr\(^{-1} \) in sunny days. A recent study by Lin et al. (2007) suggests the formation rate of particle nitrate is 2.4±1.8%h\(^{-1} \). Based on these findings it can be assumed the formation rate is varying between less than 1 up-to 4% hr\(^{-1} \) (on average 2.5%) for sulfate and less than 2.4 up-to 15% hr\(^{-1} \) (on average 8.7%) for nitrate.

Based on the above information, it can be inferred that:

Fuel oil combustion facilities emit both sulfate and nitrate particulate with initial size range of 20-130nm as discussed above. Particulates (sulfate and nitrate) emitted from power plant 1 will reach site#3 after approximately one hour with final size between 200 to 310nm while particle emitted from power plant 2 will take one hour and half with final size between 300 and 410nm at site#3. On the other hand, particle emitted from refinery 1 will grow to the size between 88 and 198nm and from refinery 2 with final size of 68 and 178nm at sampling point (Site#3). This means that main sources of sulfate and nitrate (primarily or secondary) in the size range of 68-198nm (as shown in figure 3.9) are refineries 1 and 2 whereas sulfate and nitrate in the size range of higher than 200nm is power plants.

On the other hand, fuel gas combustion facilities will emit mainly nitrate and negligible amount of sulfate with initial size of 40-80nm. Nitrate particle emitted from gas plant will reach site#3 after 30 minutes with final size of 130-170nm while particle emitted from refineries will reach site#3 with final size of 88-128nm. This means that nitrate in the lower end of accumulation mode is associated with emission from refineries and/or gas plant. Power plant will be main contributor for nitrate with size of >220nm. These sources are considered as main contributor for NO\(_2\) emissions and in turn main sources of nitrate because nitrate ions present in the air originate from the reaction between NO\(_2\) and O\(_3\) and from hydrolysis of N\(_2\)O\(_5\) (Rakesh et al., 2006)
Although sulfate, nitrate and ammonia may be directly emitted into atmosphere by some natural processes (e.g., sulfate in marine aerosols), the major portion is generated by chemical reactions of gaseous precursors (SO$_x$, NO$_x$ and NH$_3$) as proved in previous section. However, it would be recommended in any future study to take measurements at remote area near YIC to determine the background level of these ions and compare them with the levels of sulfate and nitrate in this study.

With regard to mass concentration of sulfate and nitrate, as clear from figure 3.15 that power plants are the main sources of SO$_2$ but as for NO$_x$ power plants as well as other sources (Gas plant and refineries) are the major contributors. The formation rate as mentioned above can be on average 2.5% hr$^{-1}$ for sulfate and 8.7% hr$^{-1}$ for nitrate. Based on the prediction values, assumed formation rate and distance between these sources and site#3, the mass concentration at site#3 will be 51$\mu$g/m$^3$ for sulfate due to emission from power plants and 24$\mu$g/m$^3$ for nitrate due to power plants, Gas plant and refineries emissions. However, these mass concentrations for sulfate and nitrate are much higher than what has been collected in ELPI plates and analyzed by IC (3.6$\mu$g/m$^3$ for sulfate and 1.7$\mu$g/m$^3$ for nitrate). The large discrepancy between the two results (the calculated and measured values) could be due to several reasons such as the formation rate might be much lower than assumed (for example it was suggested by Forrest et al (1979a) that sulfate formation rate is less than 0.25% whereas for nitrate is 1% as reported by Lin et al. (2007)). However, the other possible reason is the efficiency of collecting samples by ELPI instruments was poor during measurements or because the predicted values by SCREEN model is over-predicted as many physical processes (dry deposition and wet deposition) and chemical processes were not considered in this model or due to other reasons as discussed in the following section.

With regards to other ions, chloride (Cl$^-$) and sodium (Na$^+$) contents in PM$_{10}$ are mostly affected by sea aerosols (Rakesh et al., 2006). Moreover, Kaneyasu et al., (1995) noticed 30 times more chloride and 20 times more Na in a town near the ocean compared to other characteristics sites. He observed low concentration of Cl$^-$ at the city of Strasbourg which is far from the sea. However, Cl$^-$ is also released by anthropogenic sources (e.g., industrial emissions) mainly in the form of HCl, which later reacts with ammonia to form NH$_4$Cl in the fine mode. The Oxalate ion is originated mainly from long-range transport and there is no obvious source for this ion.
Trace Metals:
Concentration of metals (such as Zn, V and Fe) in Aitken modes turned out to be useful indicators of local or nearby sources. The high concentrations of some elements are suggesting a common local combustion source for these elements, possibly natural gas combustion or heavy fuel oil combustion. The other group (such as Mn and Ba) has high concentration in accumulation and coarse modes, the likely source being relatively far sources such as combustion of heavy fuel oil.

It is interesting to note from previous figures (3.9, 3.12 and 3.13) that the Na, Cl and Sr are very much correlated and concentrated in the accumulation and coarse mode (>0.61μm) which means these ions can be attributed to marine sources as suggested by (Pakkanen et al., 2001b) that these ions are the typical sea-salt ions. However, Echelar et al., (1998) linked the presence of sodium (Na) in fine particle to biomass fuel burning.

Ni, Cu and Zn are concentrated in particle size range of less than 0.61μm which may indicate that the source of these metals from sources close to the sampling site such as refineries. An experiment (Desboeufs et al., 2005) for natural and anthropogenic aerosols showed that more than 80% of Ni, Cu, Zn are associated with anthropogenic sources as fly ashes.

Mo and Co were detected in particle size less than 0.61 and the likely sources for these elements are also fuel oil combustion (such as refineries). Earlier study (Dzubay et al., 1988) indicated that Mo and Co had their highest correlation with Ni which points to oil combustion and also noted that Sr, Ni, Co and Mo may originate from combustion of heavy fuel oil.

As clear that Fe and V are highest in particle diameter of less than 0.61μm pointing to traffic emission or natural gas combustion (Fe) sources such as petrochemical facilities and to combustion of heavy fuel oil (V) as likely local sources. Some other elements (As and Se) with negligible concentration, it is not possible to identify its emission source, although possibility of industrial origin for this source cannot be excluded.

The crustal sources dominantly made up of typical soil components (Al, Mn, Sr, Ti); marine sources made of the typical marine species (Cl and Na) and petrochemical sources as inferred from sulfate, ammonia, Ni, V, Co and Nitrate association (Querol et al., 2002)
Pakkanen et al. (2001b) suggested that Ba, Cu and Fe have been attributed to traffic and natural gas combustion (such as petrochemical facility) and Ti and Pb were attributed to LRT.

### 3.3.5 Comparison of different masses:

The masses at each impactor stage were obtained from three different approaches:

1. total net mass of polycarbonate filter before and after sampling using balance;
2. total inorganic ions and trace metals mass based on chemical analysis results and;
3. mass calculated based on particle number.

The comparison between these three different masses is shown in figure 3.16. As is clear the total mass of ions and metal is almost matching with the calculated mass based on particle number in the Aitken mode but there is large difference between these values and the calculated mass based on particle number for accumulation and coarse mode particle due to the following different reasons. Firstly, a significant portion of particles (especially large particles) are trapped in the ELPI charger and they don’t end up in the impactor stages. However, these particles number were taken into consideration during calculations. Secondly, there are many collected inorganic and organic components (mostly those from soil origin i.e. sand dust) are not considered in the chemical analysis although they play an important role in the total weight. Thirdly, the ELPI generally gives overestimation for large particles (PM-10 measurement). Fourthly, the grease was not used during collecting samples which may cause losses of many particles to the walls of the impactor and bounce-off from the collecting stages of ELPI (especially the upper stages).

On the other hand there is obvious differences between total mass of ions and metals and net mass from balance because the resolution of the balance is 0.1mg which means it cannot detect mass less than 1mg as minimum.
Chapter 3  
Chemical Composition of Size Fractioned Particles at YIC

Figure 3.16: Comparison between different masses (balance, calculated, ions & metals) at each impactor stage

3.4 Summary and Conclusion:
Particle samples from 12 ELPI stages during spring period (March 14-April 11, 2009) at site#3 of YIC were chemically analysed using IC for inorganic ions and ICP-MS for trace metals.

The ionic analysis results sulfate and ammonium concentrated on particle size less than 0.38μm while nitrate and chloride concentrated on particle larger than 0.38μm although sulfate and other ions are present. The concentration of sulfate ranged from 10.5ngm⁻³ as minimum in Aitken mode (0.028μm) to a maximum of 705ngm⁻³ in accumulation mode (0.16-0.38μm). The next highest concentration amongst anions was nitrate (485 ngm⁻³) in particle size of 2.39μm and the lowest concentration (<1ngm⁻³) was in the size of <0.06nm. The non-sea salt sulfate is dominant in all particle sizes but the contribution of marine sulfate is minor. The contribution of marine sulfate to total sulfate is ranging from 0.2% in Aitken mode size to 18% in coarse mode particle. The total sulfate and nitrate contributed 50.3% and 24.4% of the total ionic mass respectively followed by chloride (13.3%) and ammonium (10.6%)

The trace-metals analysis results indicate that the dominant metals in all particle sizes (7nm-10μm) are Na, Al, Ti, V, Fe, Zn, Sr and Cr. The most abundant metal is Na which represents more than 94% of the total mass of trace metal in PM₁₀ and detected in all plates (7nm-10μm) with very high concentration (796ng/m⁻³) compared to other metals. Further, the results showed that in the lower particle size range (7-380nm) high levels of
Fe (3.7ngm⁻³), V (4ngm⁻³), Zn (3.6ngm⁻³) and Al (2.7ngm⁻³). On the other hand, in the upper particle size range (>380nm) there are other metals which were higher in this size: Al (7.5ngm⁻³), Cr (2.7ngm⁻³), Sr (5.2ngm⁻³), Mn (1.4ngm⁻³), Ba (0.6ngm⁻³). The remaining metals are either in very low concentration or in negligible level in both size bands. Moreover, the main contributors in total mass concentration (excluding Na) are Al (25%), Sr (13%), Zn (13%), V (10%), Cr (10%) and Fe (10%). Mn, Ti, Ni, Cu, Pb and Ba account for less than 5% of total metal mass.

The main possible affecting sources for nitrate could be power plants, refineries, petrochemical facility and gas plant (main sources of NO₂) whereas the main possible sources for sulfate ion are power plants and refinery (main sources of SOx). The sources of other ions, chloride (Cl⁻) and sodium (Na⁺) contents in PM10 are mostly marine air.

Power plants are the main contributor for sulfate and nitrate with size of >200nm whereas refineries are the main sources of nitrate and sulfate in the size of <200nm. One the other hand, gas and petrochemical plants are sources of nitrate for sizes less than 120nm.

Sources of trace metals (such as Zn, V and Fe) are mainly from local combustion source, natural gas combustion or heavy fuel oil combustion whereas Na, Cl and Sr are attributed to marine sources. Sr, Ni, Co and Mo may originate from combustion of heavy fuel oil. Ba, Cu and Fe have been attributed to traffic and natural gas combustion (such as petrochemical facility) and Ti and Pb were attributed to LRT.

There was obvious difference between total mass of ions and metals and net mass from balance due to several reasons (e.g. some inorganic ions which were not considered in the analysis, losses of some large particles to the walls of the impactor and/or bounce-off from the collecting stages of ELPI during measurements). Moreover, as particle size is getting larger the difference in masses is widening.
Chapter 4: Evaluating three dimensional meteorological field over YIC using WRF model and observations

4.1 Introduction:
Some existing dispersion models (such as AERMOD) typically use hourly meteorological observations at a single site as input data and are not capable of simulating the transport and diffusion of air pollutants within spatially variable meteorological fields. On the other hand, other models such as CALPUFF (Scire et al 2000a,b) have this capability, but the success of such models is dependent in part on having as input meteorological data sets that can adequately resolve the synoptic, meso-scale and planetary boundary layer structures. The meteorological data plays an important role in simulating accurate dispersion and diffusion and thus its accuracy is essential for good air quality simulations.

In order to provide the various required surface and upper air meteorological data input for the air quality model (CALPUFF), the Weather Research and Forecast (WRF) meso-scale model was applied over Yanbu Industrial City (YIC). However, before using this model (WRF) for generating the three dimensional meteorological data as input for CALPUFF, it is necessary to evaluate WRF predictions with observations from some real case studies. WRF predictions, using both forecast and reanalysis data as initial conditions, were evaluated using surface data (10-m winds and 2-m temperature) as well as upper air profiles from RASS (Radio Acoustic Sounding System)/SODAR and Radionding systems. Our comparison will be focused on the wind and temperature observations with the predicted outputs as these parameters play the main role in air dispersion modeling.

Therefore, in this chapter WRF predictions will be compared with observations for two scenarios. First scenario will be for 24 hour simulations using forecast and reanalysis data as initial conditions while second scenario will be for 78 hours using reanalysis data
only. The purpose of these two scenarios is to determine if WRF predicts coastal surface and upper air temperatures, and wind speed and direction, accurately.

4.2 Upper air System Description and specification:
The model PA5 RASS/SODAR system made by REMTECH was used to evaluate the upper air predictions by WRF model for several case studies. This system is designed to measure over a range of up to 5000m, but the average range in typical conditions is a height of 3000m. The RASS system uses acoustic wave emissions to measure atmospheric virtual temperature profiles with resolution of 0.2°C as claimed by REMTECH. This system is sensitive to wind which displaces the return signal out of the receiving antenna. May et al. (1989) evaluated the accuracy of the RASS temperature measurement by using 50 radiosonde observations taken at Denver site for height up to 2500m and they concluded that the agreement between the two instruments is excellent and the overall RMS difference is about 1.0°C.

DOPPLER SODAR systems was used to measure remotely a vertical profile of wind speed and direction, thermal stratification, and turbulence parameters (sigma W, sigma Theta) with a range above ground of up to 3,000m in typical conditions. The measurement from the Sodar is accomplished by emitting a strong acoustic pulse in the audio band and detecting the Doppler frequency shift of the received backscattered echo. As claimed by the system manufacturer (REMTECH) that Sodar has horizontal wind speed range of 0 to 50m/s and horizontal speed accuracy of 0.2m/s or 3% for wind speed over 6 m/sec and horizontal wind direction accuracy of 3° or better for winds faster than 2m/s. The SODAR is especially sensitive to ambient acoustic noise: the less the noise level the better the performances. REMTECH recommends the following operating conditions for antenna: temperature of -40 to 60°C and humidity of 10 to 100%. These operating conditions were met during our measurements.

Vogt S. and Thomas P. (1995) tested the accuracy and reliability of different Doppler SODAR (PA0 and PA2) by long-term intercomparisons with in situ instrument at a 200m high meteorological tower and they conclude that the accuracy of wind speed and
direction is generally good. Further, the study showed that the correlation coefficient between Sodar and tower wind speed measurements is exceeding 0.9. Another study by Finkelstein et al (1994) compared the measurement of wind speed and direction from four different Doppler Sodars with similar measurements from in situ sensors on a 300m instrument tower and the results showed that the sodars measure wind speed and direction accurately and with reasonably high precision.

The RASS principle is based on the measurement of the temperature-dependent sound velocity by backscattering of electromagnetic waves. The following equation is usually used for deriving RASS temperature:

$$ T = \frac{C_a^2}{K} \quad \text{---------------------------------------- (5.1)} $$

In which $C_a$ is the sound speed in m/s, $K$ is a constant (=401.94 J g$^{-1}$K$^{-1}$) and $T$ is the absolute temperature in Kelvin degrees. $C_a$ is measured using Doppler effect which results from reflection of the radio waves emitted upwards on the acoustic wave train emitted by the Sodar:

$$ f_{dr} = \frac{(2 f_r \cdot C_a)}{C_o} \quad \text{---------------------------------------- (5.2)} $$

In which $f_{dr}$ is the radio frequency doppler shift in Hz, $f_r$ is the emitted radio frequency, $C_a$ is the sound speed, $C_o$ is speed of light. Having solving these two equations for every time interval and every height, $T$ is derived.

For the Sodar the Doppler effect is again used but this time the acoustic waves are reflecting on the air itself. Therefore the Doppler equation reads:

$$ f_{da} = \frac{(2 f_a \cdot v_r)}{C_a} \quad \text{---------------------------------------- (5.3)} $$

In which $f_{da}$ is the radio frequency doppler shift in Hz, $f_a$ is the acoustic emitted frequency in Hz, $v_r$ is the radial wind speed along the sodar beam in m/s and $C_a$ is the sound speed in m/s. By pointing into different directions (by phasing the antenna in lines and then in columns) the wind along different axis will be calculated by a geometrical transformation. A review of the theory of SODAR measurements is provided in Antoniou, et al. (2003).
4.3 Observations and data availability:

The RASS/SODAR upper air profiles were obtained from site#3 (explained in chapter 3). This site is located at Latitude (23° 58.160’N) and Longitude (38° 18.270’E), about 2 km from industries and away from any nearby noise sources (figure 4.1). On the other hand, radiosonde temperature profile data was taken from Jeddah King AbdulAziz Airport (Latitude: 21° 69.547’N and Longitude (39° 18.866’E) to verify the RASS data for scenario#1. The radiosonde station is the nearest available upper station at the western coast of Saudi Arabia to site#3. These data are available only two times a day at specified synoptic times (0UTC and 12UTC). Jeddah and YIC (site#3) are located on the east coast of Red Sea (west of Saudi Arabia) and both sites are affected by similar weather. The distance between the two cities (YIC and Jeddah) is about 310km.

The RASS/SODAR system was used to measure the hourly vertical temperature, wind speed and direction distribution at site#3 in the atmospheric boundary layer starting from the lowest reliable height of 100m up to 3000m above ground. The boundary layer has considerable influence on meteorological and environmental issues. The mixing height or boundary layer is the parameter which determines the volume of air through which the air pollution is diluted. During day time when there is maximum heat input from the solar radiation the boundary layer depth usually extend to the highest and the turbulent mixing near the ground surface will be maximum while during night time the earth surface losses its energy the boundary layer depth will be the lowest and the turbulent mixing reaches a minimum. The air pollution level is usually high when the boundary layer depth is low and the reverse is true.

The radiosonde data from Jeddah King AbdulAziz Airport were measured up to 12km. The surface observation data were taken from three sites at YIC as shown in figure 4.1. The data availability for each case study and for each site is shown in table 4.1. Cases#1 to 3 (scenario#1) are 24-hour simulation and Case#4 to 8 (scenario#2) are 78-hours simulation and these cases were chosen from each month and during which the instrument was operating reliably.
Figure 4.1: Observation sites 1, 2 and 3

Table 4.1 Data availability for surface and upper air observations

<table>
<thead>
<tr>
<th>Case#</th>
<th>RASS/Sodar At Site#3</th>
<th>Radiosonde Jeddah**</th>
<th>Surface data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Site 1</td>
</tr>
<tr>
<td>Case# 7</td>
<td>Not Available (WS, WD, T)</td>
<td>Available (T)</td>
<td>Available (WD, T)</td>
</tr>
</tbody>
</table>
Case# 8

|--------------------------|---------------|-----------------------|--------------------|--------------------|

* WS is Wind speed, WD is wind direction data and T is temperature data

** Radiosonde data were missing for the following hours:

- Hour 03, Jan 10 and 11, 2010
- Hour 03, Feb 12, 2010
- Hour 03, Mar 9, 2010
- Hour 03, Apr 26 and 28, 2008

5.4 Modelling system:

WRF, the newest generation of numerical weather prediction models, version 3.0.1 was used in this study to generate the three-dimensional meteorological field over YIC, Saudi Arabia for eight case-studies. This model has been developed by the joint efforts of the scientific community based on experience with its predecessor models. Skamarock (2008) highlight the major features of version 3 of this model. WRF is a fully compressible. It is an Eulerian non-hydrostatic model using a terrain-following hydrostatic pressure vertical coordinate, with vertical grid stretching such that the vertical level are closer together near the surface and more spread out aloft. The horizontal grid is an Arakawa C grid. A third-order- Runge-Kutta scheme with a smaller time step for acoustic and gravity wave modes is used to integrate the dynamical equations. Further the following schemes were selected: PRTM scheme for long-wave radiation; Goddard scheme for short-wave radiation; Eta scheme for surface layer physics; Noah land surface model for land surface.

In this study, all simulations use three nested grids with one-way nesting. A nesting ratio of 3 was used from domain 1 to 2 and from domain 2 to 3 and the innermost domain had a 1km horizontal grid spacing (see figure 4.2). All three domains have the same number of grid points of 61 by 61 and were centered at site#3 (Latitude 23° 58.160'N and Longitude 38° 18.270'E). The model used vertical grids of 28 levels from the surface up to 50hPa and ran with a time step of 100s.
4.4.1 Input Data:

WRF was run for the following two scenarios:

Scenario#1 (24 hour simulation): The aim of this scenario is to determine which initial data (forecast or reanalysis) will give better prediction compare with observation. This scenario consists of the following case studies:

- Case#1: Jan 11, 2010
- Case#2: Feb 13, 2010
- Case#3: Mar 08, 2010

For each case, the model was run twice with different initial and boundary conditions: once using 1.0°x1.0° NCAR/NCEP (National Center for Environmental Prediction) Global Forecast System (GFS) data and once using 1.0°x1.0° NCAR/NCEP reanalysis data. The boundary conditions from GFS data were applied in 3-hourly intervals, whereas the NCAR/NCEP reanalysis data were applied in 6-hour intervals. The reanalysis data is quality assessed/quality controlled using observational data from various sources such as synoptic station data, radiosondes and METEOSAT. The U.S.
Geological survey data was utilized in this study providing the land surface properties for WRF such as soil moisture availability, surface roughness, topography and land use.

**Scenario #2** (78 hours simulation): this scenario has the following cases:

- Case#4: Jan 10-12, 2010
- Case#5: Feb 12-14, 2010
- Case#6: Mar 7-9, 2010
- Case#7: Mar 25-27, 2009
- Case#8: Apr 26-28, 2008

The model set-up and source of input data for each case are exactly same as that of scenario#1 except each case of this scenario was run for 78 hours using reanalysis data only. The main purpose of this scenario is to determine if any errors will build up with time after the startup due to the model drifting away from the re-analysis (as it is only applied at the model boundary of domain 1). The outputs from this scenario will be used as input for running air dispersion model (CALMET/CALPUFF).

**4.4.2 Model Evaluation –Statistics**

To assess the overall WRF predictions compared with observations for surface and upper air temperature, wind speed and direction, the following standard statistic measures are used in accordance with Anthes (1983) and Anthes et al (1989): Bias (mean error); root mean square error (RMSE); standard deviation of error (SDE) and MicroSoft Excel's correlation coefficient function. The definition of each of these statistical measures is as follows:

Mean Bias $\phi = \frac{1}{n} \sum_{i=1}^{n} \phi_i$  

(5.4)

Where $\phi_i$ is the difference between the $i^{th}$ WRF prediction over domain#3 and the observed quantities and $n$ is the number of observations.

$$\text{RMSE} = \left[ \frac{1}{n-1} \sum_{i=1}^{n} (\phi_i)^2 \right]^{\frac{1}{2}}$$

(5.5)
Evaluation of Predicted 3-D Meteorological field over YIC

\[ SDE = \left[ \frac{1}{n-1} \sum_{i=1}^{n} (\phi_i - \tilde{\phi})^2 \right]^{1/2} \]  \hfill (5.6)

\[ Correl(X,Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}} \]  \hfill (5.7)

Where \( x \) and \( y \) are the observation and prediction values. Bias indicates systematic error resulting from model parameters, deficiencies, parameterizations and numerical approximations. For a perfect forecast the difference between \( i^{th} \) predicted and the observed quantity is zero for all i. Note that the bias can be zero if the sum of the negative differences equals that of the positive differences. For the case of wind direction, if the bias is \( >180 \) then 360 was subtracted from the bias, but if the bias is \( < -180 \), then 360 was added to the bias. RMSE evaluates the overall performance. Since bias and variance contribute to the RMSE, the RMSE is very sensitive to systematic and large errors. According to Von Storch and Zwiers (1999), a prefect forecast has \( F=P \), correlation coefficient=1 and RMSE=0.
4.5 Results and Discussion:

4.5.1 Comparison of WRF predictions with surface observations:

Scenario#1 (24-hour simulation): The purpose of this scenario is to determine which initial conditions (forecast or reanalysis) give better predictions compared to observations. WRF predictions for three different case-studies, initiated with both forecast and reanalysis data, were statistically compared with surface observation data (tables 4.2 and 4.3). The first notable thing for the forecast-initialized and reanalysis-initialized WRF predictions is that all cases studies have a very good correlation coefficient (except for wind speed for case#1 for the forecast-initialized case) compared with the observations for all parameters (>0.85 for temperature, >0.7 for wind speed and >0.6 for wind direction).

It is clear from tables 4.2 and 4.3, and figure 4.3, that WRF predictions underestimate the 2m air temperature for runs initiated with both forecast and reanalysis data. Overall the surface temperature bias is negative, ranging from less than -1 up to -3°C, except for the forecast initialized run for case#1. Figure 4.3 shows that the biases tend to be lower at the beginning and at the end of the day and higher at the middle, suggesting that the model may be poorly representing solar interaction with the surface. The temperature bias ranged between less than 1% and 13% of the overall average observation. On the other hand, WRF predictions perform better for the 2m air temperature during morning and evening (minimum temperature) than during noon and afternoon hours (maximum temperature) for all cases. The RMSE and SDE for surface temperature range from 1.6 up to 3.6°C and from 1.3 up to 2.1, respectively, for runs using both initial input data types (forecast-initialized and reanalysis-initialized). Based on the above results it seems that forecast initial data gives slightly better surface temperature prediction than reanalysis data.

For wind speed the mean bias for the WRF predictions is above zero in all cases for runs using both input data types (forecast and reanalysis initial data). The timeseries in figure 4.3 show that WRF overestimates the wind speed at most times, except for between 12 and 18 hours for the reanalysis run for case#2. The mean wind speed bias ranges from
0.2 to 1.5 m/s on average for all cases, which is 6% to 50% of the overall mean observed wind speed. Wind speed RMSEs are less than 2.8 m/s for forecast data and less than 1.6 m/s for reanalysis data. The wind speed SDEs is in the range of 1.1 to 2.4 m/s for the forecast data runs and 1.1 to 1.6 m/s for the reanalysis data runs. Overall, the reanalysis initialized runs generally gave better predictions for wind speed than the forecast initialized runs.

The wind direction bias ranges from -1.3 to 24 for all three cases. Mean RMSE and SDE for wind direction ranges from 48 to 93 and from 47 to 112, respectively. Moreover, it is interesting to note (figure 4.3) that runs using both input data types (forecast and reanalysis) either match, or are very close to the observations. This suggests that WRF predictions are capturing the general development of sea and land-breeze phenomena over YIC, which was described in chapter 2. For wind direction, the forecast and reanalysis runs gave similar results for cases 1 and 2, but for case 3 the forecast run gave slightly better results.

Overall for scenario#1 the forecast initialized runs better matched the observations for temperature and wind direction, although the wind direction differences were quite small compared to the temperature differences. The reanalysis runs better matched the observations for wind speed. Thus, these results suggest that the choice of whether to use forecast data or reanalysis data to drive WRF for this region should depend on whether the temperature or the wind speed fields are the most important for the overall goals of the simulation studies in question. The bias in temperature results compared to observation data ranged from 1% up to 10% for forecast data and from 3.7% up to 13% for reanalysis input data whereas the bias in wind speed results ranged from 30% up to 53% for forecast data and from 6.7 up to 27% for reanalysis input data. Based on these statistical results it can be noted that the temperature variation between both input data (forecast and reanalysis) is relatively small and any input data can be used but as for the wind speed the reanalysis input data produce better wind speed results and as the wind speed play important role in the air pollution dispersion therefore the reanalysis data was chosen for the next three days simulation.
**Table 4.2**: Model statistics using 24-hour forecast data as initial conditions. Mean Bias, root mean square error (RMSE), standard deviation error (SDE) and correlation coefficient (Corr) are used for the three cases for surface observations (Temperature (T), Wind Speed (WS) and Wind direction (WD)).

<table>
<thead>
<tr>
<th>Case#1</th>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>Mean(Observation)=23.8°C</td>
<td>0.03</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Case#2</td>
<td>-1.1</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Mean(Observation)=27°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#3</td>
<td>-3.1</td>
<td>3.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Mean(Observation)=30°C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.3**: Model statistics using 24-hour Reanalysis data as initial conditions.

<table>
<thead>
<tr>
<th>Case#1</th>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>Mean(Observation)=23.8°C</td>
<td>-3.1</td>
<td>3.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Case#2</td>
<td>-1.0</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Mean(Observation)=27°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#3</td>
<td>-2.3</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Mean(Observation)=30°C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Scenario#2 (78-hour simulation):** The purpose of this scenario is firstly to determine if any errors build up with time after the startup due to the model drifting away from the reanalysis (as it is only applied at the model boundary of domain 1) and secondly to provide input for running the air quality model.

78-hour WRF predictions for five different case studies, initiated with only reanalysis data, were statistically compared with surface observations at three sites (table 4.4 and figures 4.4 to 4.6). It is clear from the table that the correlation coefficient between prediction and observation is very high for temperature (0.7 to 0.9), generally fairly low for wind speed (≤0.5 except for case#7 where it is 0.9) and fairly high for wind direction (0.7 to 0.8). The high correlation coefficient for wind direction and the generally good
match between the simulated and observed wind direction demonstrated in figure 4.6 suggests that the WRF model is able to capture the general development of sea and land-breeze phenomena over YIC. The wind is westerly to north-westerly wind during the daytime (12 to 21 hour local time) and easterly to north-easterly during the nighttime (21 to 07 hour local time). There is transition period (between 08 and 11 hour local time) during which the wind changes its direction from land breeze to sea breeze.

WRF predictions underestimate the surface air temperature (Table 4.4) by up to -3.4 degrees for all five cases on average, which is similar to that of scenario#1 (24-hour simulation). The overall surface temperature bias is negative and ranges from -0.2 to -3.4°C. WRF predictions (figure 4.4) perform better in terms of the 2m air temperature during morning and evening when the temperature is minimum than during noon and afternoon hours when temperature is maximum for all cases. The RMSE and SDE for surface temperature range from 2.1 up to 4.3 degrees and from 2.2 up to 5.1°C, respectively. The magnitudes of the RMSE and SDE are similar to that of first scenario (24-hour simulation) in which negative biases of similar magnitude was also produced. Further, it is noted that the matches for temperature at site#1 were better than at site#2 because site#2 is located inside the heavy industrial area boundary which means more affected by the heat emission (such as ground flares) from the industries than site#1. This heat emission from local source was not taken into account in the model input.

For wind speed the mean biases of the WRF predictions are positive in all cases indicating that the simulation is overestimating the wind speed on average, although there are some instances of underestimation of the peak wind speeds during the afternoon, particularly for cases#4 and 5 (see Figure 4.5). In cases#6 and 7 the match between wind speed is generally quite good. The wind speed bias ranges from 0.2 to 1m/s on average for all cases. Wind speed RMSEs and SDE are very close to each other and are ranging from 1.4 to 2.5 m/s. Wind direction biases ranges from -3.4° up to 23. Mean RMSE and SDE for wind direction ranges from 60 to 78. These wind results agree broadly with first scenario.
Table 4.4: Statistics from the 78-hour model runs using reanalysis data for the initial and boundary conditions. Shown are the average bias, root mean square error (RMSE) and standard deviation error (SDE) for all three sites for each case for wind speed, temperature and wind direction. Also shown are the mean values for temperature and wind speed and the mean standard deviation for the wind direction.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>Case#4</td>
<td>-3.4</td>
<td>4.2</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=24.3°C</td>
<td>Mean(Observation)=3.5m/s</td>
<td>STD(Observation)=89°</td>
</tr>
<tr>
<td>Case#5</td>
<td>-1.6</td>
<td>2.3</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=27.1°C</td>
<td>Mean(Observation)=2.9m/s</td>
<td>STD(Observation)=90°</td>
</tr>
<tr>
<td>Case#6</td>
<td>-3.2</td>
<td>4.1</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=28.9°C</td>
<td>Mean(Observation)=3.0m/s</td>
<td>STD(Observation)=96°</td>
</tr>
<tr>
<td>Case#7</td>
<td>-1.2</td>
<td>2.1</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=23.0°C</td>
<td>Mean(Observation)=5.1m/s</td>
<td>STD(Observation)=89°</td>
</tr>
<tr>
<td>Case#8</td>
<td>-0.2</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=31.3°C</td>
<td>Mean(Observation)=3.7m/s</td>
<td>STD(Observation)=111°</td>
</tr>
</tbody>
</table>
Chapter 4 Evaluation of Predicted 3-D Meteorological field over YIC

Fig 4.4: Comparison of the observed surface temperature (pink dotted line) and the predictions from the 78-hours WRF runs (blue dotted line) that use reanalysis data as initial and boundary conditions for five different cases at three sites. (X-axis is local times in hours and Y-axis is degrees). No observations were available at site#3 for cases 5, 6, 7 and 8 and at site 2 for case 8.
Fig 4.5: As for Figure 4.4 except for wind speed, shown on the y-axis in m/s. No observations were available at site#3 for cases 5, 6, 7 and 8 and at site 1 for case 7.
Fig 4.6: As for Figure 4.4 except for wind direction. No observations were available at site#3 for cases 5, 6, 7 and 8.
Based on the results from both scenarios (eight cases) for surface simulations, the following can be noted:

- WRF predictions initialized using both forecast data and reanalysis data agreed well with observations as also shown by other previous studies (Henderson et al, 2007; Etherton and Santos, 2008). However, the 24-hour simulations showed that forecast-initialized runs gave slightly better predictions than reanalysis-initialized runs for 2-m surface temperature, but on the other hand the reanalysis gave better wind speed predictions than the forecast initial data. Wind directions were similar for both initial datasets.

- By comparing the results from both scenarios for the case of reanalysis-initialized simulations, it seems that there is no build up of error with time after startup for the next 78 hours as both scenarios produced relatively similar performance statistics for all parameters.

- Except for the forecast initialized run for case#1, WRF produced a mean negative bias for the surface temperature in all eight cases. The largest bias was -3.4°C, which was 13% of the average observation. Conversely, the mean bias for the wind speed was always positive with a maximum mean bias of 1.5m/s, which was 54% of the average observation. The mean wind speed biases for the reanalysis runs were lower than those from the forecast runs and ranged from 0.2 to 1m/s. These results broadly agree with findings by Cheng and Steenburgh (2005) who concluded that WRF tends to overestimate the wind speed with a bias of 0.5m/s over the Western United States during the summer. Wind speed RMSEs for the reanalysis runs were in the range of 1.3 to 2.5m/s for all eight cases and these results are similar to those by Henderson et al (2007) who found RMSEs of 1.75m/s in summer and 1.9m/s in winter. However, most of the RMSE results are slightly higher than the 1.4m/s for all forecast lead times as reported by Molders (2008). The wind speed SDEs were in the range of 1.1 to 2.5m/s for all cases which agrees with the results by Henderson et al (2007) who found values of 1.57m/s in summer and 1.7m/s in the winter.
The maximum mean wind direction bias was 24°. Mean RMSE and SDE for wind direction ranged from 48 to 93 and from 60 to 112, respectively, for all eight cases. The correlation coefficient for wind direction is high (0.7 or 0.8, except for case#3 for the reanalysis run where it was 0.6), which suggests that the WRF model is able to capture the general development of sea and land-breeze phenomena during day and night hours over YIC. However, the bias for wind direction during the transition period (i.e. from sea breeze to land breeze and vise versa) is often relatively higher. The biases for wind speed are also generally high during the transition periods, although the wind speed biases tend to be relatively high during other parts of the day as well. This should be borne in mind when making air pollution predictions during the transition periods. This could be investigated further to improve the model forecast during such transitions.

Emery et al (2001) proposed statistical benchmarks for evaluating meteorological model performance. The authors proposed benchmarks of ±0.5°C for the surface temperature mean bias, ±0.5m/s for the wind speed mean bias, ≤2m/s for the wind speed mean RMSE and ≤±10° for wind direction mean bias. Based on the results from all eight reanalysis cases, the predictions of wind speed performed better than these benchmarks, except for case#3 for the bias (=0.8m/s) and case#8 for the RMSE (≈2.5m/s). The wind direction predictions were better than the benchmarks in half of the cases. They did not meet the benchmarks for case#1 (bias=24°), case#5 (=−23°), case#6 (=−20°) and case#7 (=23.2°). The surface temperature bias is meeting the benchmark for site#1 (figure 4.4) but it is not for site#2. This may be because site#2 is located in the vicinity of an industrial area which is very much affected by heat emitted by local sources (industries) and these sources are not taken into account in the modeling input. The land use input files do not take into account the detailed urban features such as the size and locations of industries close to the monitoring stations.
4.5.2 Predicted temperature and wind profiles compared with Observations:

Scenario#1 (24-hour simulation): A statistical evaluation was performed for horizontal wind speed and direction profiles using the Sodar system. For temperature profiles the model profiles were compared to RASS profiles and radiosonde measurements were also utilized to evaluate the accuracy of the RASS temperature data. The overall averages of bias, root-mean square error and standard deviation error for all layers (from 100m up to 3000m in steps of 100m) was computed for each case study and is shown in tables 4.5 and 4.6.

As can be noticed (tables 4.5 and 4.6) the overall mean biases for comparisons to both the radiosonde and the RASS are negative for the upper air temperature for all cases, except for the forecast initialized simulation compared with the radiosonde data for cases#2 and 3. The bias ranges between -2.7 and -5.2 for all cases when compared to the RASS, but the average bias is much lower (between 0.3 and -2.4) when the radiosonde data is used. The average RMSEs are between 3.5 and 6.7°C when the RASS data is used compared to 0.9 to 3.9°C when the radiosonde data is used. Further, the average SDEs are between 1.2 and 4.6°C for the RASS data and 0.9 and 2.5°C for the radiosonde data. It can be noted that the forecast initialized data gives slightly better predictions for temperature profile than the reanalysis data. On the other hand, thus the model appears to perform better when compared to the radiosonde and the errors are generally quite high when WRF is evaluated using the RASS data. This might indicate problems with temperature retrieval of the RASS.

Figure (4.7) illustrates the comparison between the observations (RASS and Radiosonde) and the WRF predictions for both types of initialization data (forecast and reanalysis) for every six hours. It is interesting to note from this figure that above 1000-1500m the WRF predictions are very close to the radiosonde observations made at hours 03 and 15 local time for all three cases which indicates that WRF is relatively accurate at predicting the upper part of the temperature profile. However, it is possible that the radiosonde profiles were incorporated into the analysis and reanalysis data that was used to drive the WRF model. Below these heights the forecast initialized runs generally performed better in
cases#1 and 3, whereas the reanalysis initialized run performed better for case#2. However, for hour 03 for case#2 and for hour 15 for case#3 the forecast and reanalysis profiles were very similar with both matching the radiosonde profile well. In general, the temperature tended to be underestimated using reanalysis data and overestimated when using forecast data. The largest discrepancy between the forecast and reanalysis runs occurred for case#1 when the reanalysis run temperature was generally considerably lower than that for the forecast run in the lower parts of the profiles. This was also the case for the predicted 2m surface temperatures for the whole 24 hours of the simulations when compared to the surface station data (Figure 4.3). This might suggest that the reanalysis procedure did not improve the dataset compared to the forecast dataset for temperature for this case.

When only considering the radiosonde data the temperature biases are generally quite low in both the forecast and reanalysis runs for cases# 2 and 3. For both runs the biases are larger for case#1 and they are also negative. The RMSE is also larger for both runs for case#1. This suggests that case#1 is more problematic for the WRF simulations, perhaps due to problems with observational data to feed into the analysis models, or perhaps because the meteorological situation is complicated and difficult to simulate for this case. For this case the forecast run bias and RMSE are considerably lower than for the reanalysis run suggesting that the reanalysis procedure made the global NCEP model simulation worse for this region.

On the other hand the RASS observations are only similar to the WRF profiles at hour 15 for case#1 and hours 03 and 21 for case#3. At all other times the profiles are significantly different from the WRF predictions and from the radiosonde observations, generally being much higher. The RASS temperature profiles are also often very unrealistic, which suggests that the instrument was unreliable and that it is probably not worth considering this data any further within this study. Therefore it was decided that for the next scenario the radiosonde observations will be used instead of the RASS data.
Table 4.5: Overall average model statistics for the runs that used forecast data as initial and boundary conditions calculated using upper air observations. Mean Bias, root mean square error (RMSE), standard deviation error (SDE) and correlation coefficient are shown for the three cases. Values in brackets are statistics results using radisonde observations.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case#1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-2.7</td>
<td>3.5 (1.6)</td>
<td>1.8 (1.2)</td>
</tr>
<tr>
<td>Mean(Observation)=26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-4.0 (0.3)</td>
<td>4.8 (1.3)</td>
<td>2.5 (1.3)</td>
</tr>
<tr>
<td>Mean(Observation)=28.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-3.9 (0.1)</td>
<td>6.3 (1.2)</td>
<td>4.5 (1.1)</td>
</tr>
<tr>
<td>Mean(Observation)=32.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case#1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-5.2 (-2.4)</td>
<td>5.5 (3.9)</td>
<td>1.2 (2.5)</td>
</tr>
<tr>
<td>Mean(Observation)=26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-4.1 (-0.4)</td>
<td>6.7 (0.9)</td>
<td>2.5 (0.9)</td>
</tr>
<tr>
<td>Mean(Observation)=28.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-3.5 (-0.2)</td>
<td>6.2 (1.9)</td>
<td>4.6 (1.3)</td>
</tr>
<tr>
<td>Mean(Observation)=32.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Overall average model statistics for the runs that used reanalysis data as initial and boundary conditions calculated using upper air observations. Values in brackets are statistics results using radisonde observations.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case#1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-0.3</td>
<td>3.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Mean(Observation)=26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>0.1</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Mean(Observation)=4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Case#3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>-0.8</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Mean(Observation)=5.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure 4.7: WRF temperature profiles for simulations using forecast data (blue line with diamond markers) and reanalysis data (green line with triangles) compared with the RASS/SODAR system (red line with squares) and radiosonde observations (orange line with circles) for January 11 (case#1), Feb 13 (case#2) and March 08, 2010 (case#3).

With regard to the wind speed predictions, tables 4.5 and 4.6 show that the WRF model produced positive mean biases for the wind speed, with mean biases of up to 1.5m/s, when forecast-initialized data is used. The mean biases are negative in cases#1 and 3 for the reanalysis-initialized run, being -0.3 and -0.8m/s, and positive but small (0.1m/s) in
case#2. Root mean square errors (RMSE) range from 1.8 to 3.6m/s and standard deviation errors (SDE) range from 1.6 to 2.6m/s for both types of initialization data. The correlation coefficients between the SODAR observations and WRF predictions are less than 0.5 for all cases.

Figure 4.8: As for Figure 4.7 except for wind speed profiles.
Figure (4.8) shows the comparison between the wind speed observations from the SODAR system and the forecast and reanalysis initialized WRF predictions. It can be noticed that in all of the case studies there are some large discrepancies between the vertical profiles of wind speed for the two types of WRF run. The shape of the SODAR profiles is usually similar to those of the WRF runs and the observed values generally lie in between those of the simulations. In some cases there are quite good matches between the SODAR and WRF profiles such as hours 3, 15 and 21 for case#2 and hours 3 and 9 for case#3. This suggests that the SODAR profiles of wind speed may be more reliable than the temperature profiles from the RASS instrument.

However, it is difficult to use the data to decide whether the forecast or reanalysis WRF runs performed better due to the large degree of variability in the sign of the biases between the runs and the observations. This might indicate a high degree of natural variability. The accuracy of the SODAR instrument is probably uncertain during some hours. Generally speaking based on overall mean bias, RMSE and SDE results, the wind speed prediction using forecast-initialized data had fairly similar statistical results to those from reanalysis-initialized data. Therefore both types of input data (forecast and reanalysis) are equally acceptable in predicting wind speed. However, the reanalysis runs produced slightly lower biases (all cases) and RMSEs (except for case#1 when the two values were 3.1 and 3.3 and thus quite similar) and so might be expected to give slightly better results.
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Wind direction statistical results are also shown in table 4.5 and 4.6. Observed wind direction profiles for each layer are compared with forecast-initialized WRF predictions and reanalysis-initialized predictions in figure 4.9.
Based on the overall statistical analysis (tables 4.5 and 4.6) it can be noticed that the forecast-initialized WRF predictions have lower magnitude wind direction biases (19° for case#1, 4.5° in case#2 and -7.9° in case#3) than reanalysis-initialized predictions (27 in case#1, 21° in case#2 and -8.3° in case#3). The RMSE ranges from 57° to 67° for the forecast-initialized runs and from 66° to 75° for the reanalysis-initialized runs. The forecast-initialized runs have generally lower SDE than that of reanalysis-initialized runs. The overall correlation coefficient to the observations for both the forecast and reanalysis runs is fairly good (~0.8) for cases#1 and 2, but relatively poor for case#3 (<0.5). In general, the performance statistics for wind direction for the forecast and reanalysis runs were similar, although the forecast runs performed slightly better.

The profiles in figure 4.9 show that during some hours the WRF predictions are very close to the observed profile. Examples are: hour 3, 15 and 21 for case#1; hours 3 and 21 for case#2; hour 9 for case#3 at all levels and hours 15 and 21 for upper levels. This might again suggest that the SODAR profiles are likely to be more reliable than the RASS temperature profiles and thus might be useful in determining which WRF runs are likely to be the most accurate. There are large discrepancies between the simulations and the observations for some of the profiles shown and also large differences between the forecast and reanalysis runs, which might indicate deficiencies in the simulations.

**Scenario#2 (78-hour simulation):** A statistical evaluation was again performed for horizontal wind speed, wind direction and for temperature profiles using the Sodar system and radiosonde observations. Error statistics were computed using radiosonde data only for temperature due to the poor performance of the RASS profiling system in measuring temperature as highlighted in the last section. This was available every 12 hours. Only SODAR data is used to compute wind statistics because the radiosonde was located 310km far from YIC at Jeddah Air Port may not be valid to be applied here as the topography and the coastline of YIC are different from that of Jeddah (Radiosonde) which likely will affect the wind speed and direction profile unlike temperature. For example the nearest mountain (1000m height) to the measurement site at YIC is about 50km away whereas the nearest mountain at radiosonde site is about 120km and the
coastline tilt is about 10° from the north for Jeddah whereas 45° for YIC. SODAR profiles were available hourly. The overall averages of bias, RMSE and SDE over all layers (from 100m up to 3000m) and over all times were computed and are shown in table 4.7. The SODAR wind profiling system was not in operation for cases#7 and 8 and so there are no statistics for wind errors for these cases. Profiles of the bias, RMSE and SDE averaged over all times (78-hours) at each height level are shown in figure 4.10. Time-series of the bias, RMSE and SDE averaged over all altitudes are shown in figure 4.11.

It can be noticed from table 4.7 that WRF underestimates the air temperature in 4 out of the 5 cases shown, by up to -1.7°C. The WRF simulations initialized with re-analysis data also produced an overall negative bias in the 3 cases of scenario#1 (where upper air temperatures were compared to radiosonde data), with biases of -2.4, -0.4 and -0.2 °C, and negative biases were also produced in the comparison to surface station data for those 3 cases where biases of -3.1, -1.0 and -2.3 °C were produced. By comparing the different cases, it is clear that cases#4, 5 and 6 have the lowest mean bias (<-0.4°C), RMSE (<1.3°C) and SDE (<1.3°C) compared to cases#7 and 8. The largest bias (for case#8) is about 7% of the mean measured temperature value.

Temperature profiles for the average bias, RMSEs and SDEs over all times (figure 4.10) generally range between +2 and -2 °C for bias and up to 3 °C for RMSE and SDE, although there are some slightly higher or lower values. The model performed better in cases#4 and 5, and to a lesser extent case#6. In addition, the profiles suggest that there is more consistent negative bias in the upper parts of the profiles (above ~1250-1750 m). The bias in the lower levels tends to be both positive and negative in the different cases, which is perhaps expected because of the likely higher natural variability there as indicated by the higher time variability of error at those levels that is demonstrated by the SDE profiles.

Time-series of the bias, RMSE and SDE for temperature for only two local times a day (03 and 15) as shown in figure 4.11 are also ranging between +2 and -2°C for bias and
are less than 3°C for RMSE and SDE and these results are similar to those of the profiles. Again, cases#4 and 5 have the lowest bias, RMSE and SDE. There seems to be no significant trend in model error over time, except perhaps for case#6, suggesting that there is no sustained build-up of model errors over the 3 days of the simulations in most cases.

**Table 4.7**: Model error statistics for the five 78-hour WRF simulations that used reanalysis data as initial and boundary conditions. Statistics are calculated from radiosonde profiles taken every 12 hours for temperature and from hourly SODAR profiles for wind. Note, some radiosonde profiles were unavailable (see section 3 for details).

<table>
<thead>
<tr>
<th></th>
<th>Temperature (° C)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias</td>
<td>RMSE</td>
<td>SDE</td>
</tr>
<tr>
<td>Case#4</td>
<td>-0.4</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)= 17.8°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#5</td>
<td>-0.3</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)= 18.1°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#6</td>
<td>0.7</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)=21°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#7</td>
<td>-1.0</td>
<td>2.6</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)= 18.0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case#8</td>
<td>-1.7</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Mean(Observation)= 24.5°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.10: Profiles of the bias, RMSE and SDE averaged over all times for each height level for temperature, wind speed and wind direction for five different cases. Profiles for the wind errors for cases 7 and 8 are not plotted as the SODAR system was not in operation.
With regard to wind speed, table 4.7 shows that the WRF model has an average negative bias in all the case studies where wind data was available (cases #4, 5 and 6). However, the biases in cases #5 and 6 were quite small (-0.2 and -0.7 m/s), whereas for case #4 the bias was much larger (-1.8 m/s). The largest bias is about 30% of the mean measured value and the lowest bias is less than 4% of the mean measured value. The RMSE and SDE are in the range of 3.1 – 3.7 m/s for all cases. The average vertical bias is ranging between +2 and -2 m/s for all layers (figure 4.10) although there are relatively high
biases (more than -3 m/s) above ~1500 m for case#4. For cases#5 and 6 the RMSE profiles range from 1.9 to 3.9 m/s. However, the RMSEs and biases for case#4 are relatively high for layers above 1500m. SDE profiles range from 1.9 to 4.5 m/s for all layers in all cases.

The time-series of wind speed bias are mostly negative for all case studies and RMSE and SDE are mostly below 5m/s. Time series analysis shows that bias, RMSE and SDE for wind speed are generally lower during the afternoon (see breeze) until just after midnight (1500 to 0300 local time) than those other times. The RMSE values are a little higher near to hour 09 (transition period from land breeze to sea breeze) of day 3 compared to the same times on the other days, which might suggest a build up of model error as the simulation progresses. In contrast, for case#4 the RMSE errors are large on the first 2 days and slightly lower on the third. However, the bias changes from being generally negative on the first two days to positive on the third day. This might indicate that the RMSE values decreased because of a drift upwards in the predicted wind speeds, which may have been fortuitous.

Wind direction statistical results are also shown in table 4.7. The average wind direction bias is less than 10° for cases#4 and 6 but it is -33° for case#5. The mean wind direction RMSE is 56 and 67° for cases#4 and 6, but again the error is larger for case #5, where the RMSE is 93°. The SDE is relatively high for all cases. This may be because the mean standard deviations of the observations were quite high indicating large natural variability in the wind direction. The wind direction biases for cases#4 and 6 are generally quite small with absolute values less than 20° in all layers (figure 4.10). The bias for case#5 is generally negative and relatively high mostly being between -20 and -60° at all levels. RMSE and SDE values are very similar for cases#4 and 6 and are around 60° in all layers (figure 4.10). However, case#5 has higher RMSE and SDE than the other cases reaching 120 degrees. The timeseries of wind direction bias (figure 4.11) for cases#4 and 6 are generally positive and for case#5 are generally negative. The timeseries for RMSE and SDE range between 20 and 100° during all times. The wind direction bias time series show that there are generally positive biases and high RMSEs
and SDEs approximately between hours 03 and 09 (land breeze and transition periods) and negative biases, with lower RMSEs and SDEs, between hours 12 and 21 (sea breeze).

**Based on the overall statistical analysis results for upper air data the following can be noted for both scenarios:**

- The bias, RMSE and SDE errors for temperature are much lower when radiosonde observations are used compared to those values when RASS observations are applied for both data (forecast and reanalysis). By comparing RASS and radiosonde observations, it was found that RASS profiles were often unrealistic and thus it is likely that the RASS instrument is unreliable for temperature measurements. Therefore, it was decided that only radiosonde data would be considered for the temperature comparisons.

- The reanalysis-initialized WRF model simulations produced mean negative temperature biases when compared to the upper air (radiosonde) observations for seven out of the eight cases suggesting consistent underestimation of temperatures.

  – The forecast initialized runs produced positive biases in cases#2 and 3, but a negative bias in case#1. Both forecast and reanalysis runs performed worse for case#1 and both showed negative biases. However, the reanalysis run bias and RMSE was considerably higher, suggesting that the reanalysis procedure degraded the global simulation for the YIC region for this case.

  – In scenario 2 the model performed better in terms of temperature for cases#4, 5 and 6 than for cases# 7 and 8.

- For the scenario 1 cases the model better matched the observations above 1000-1500 m. For the scenario 2 cases there was a more consistent negative mean temperature bias between the heights of 1250-2000 m. At lower levels there was more variability in the sign of the bias probably because natural temperature variability is likely to be higher there.
- The correlation coefficient between WRF prediction and observation (radiosonde) for temperature profile is very high (>0.9) for all cases. Temperature biases are less than 2% of the mean measured value when radiosonde profiles are used. These results suggest that WRF predictions for temperature profiles are quite reliable.

- The wind speed and direction profiles from the SODAR instrument look reasonable compared to the WRF profiles, which suggests that this instrument is capable of producing reasonable wind speed measurements. However, it would be advisable to compare these observations with another form of observation, (such as radiosonde data) at the same site.

- The variability of the profiles makes it hard to distinguish between forecast and reanalysis runs for scenario 1 by eye. There were large differences between the forecast and reanalysis runs in many of the profiles, but the observed profile often fell in between the two model profiles, or the better performing run type was not consistent. However, the statistics might allow such distinctions to be made.

- The wind speed forecast runs produced positive mean biases in all three cases of scenario 1, whereas the reanalysis runs produced small or negative biases for wind speed. The reanalysis runs also gave negative biases in all three cases of scenario 2 (there was no wind data available for cases 7 and 8).

- The wind speed predictions for the runs using reanalysis data had lower biases in all 3 cases and similar or lower RMSEs than for the forecast-initialized runs. Overall, the statistics were fairly similar and so both types of input data (forecast and reanalysis) are likely to be comparable for predicting wind speed, although reanalysis data may give slightly better predictions.

- For scenario#2, case#4 produced much larger wind speed biases and RMSEs above 1500m, whereas the other two cases showed little height variation.
Chapter 4  Evaluation of Predicted 3-D Meteorological field over YIC

- The reanalysis WRF runs had mean bias magnitudes that were less than 0.8m/s in 5 out of the 6 cases and were less than 0.3m/s in 3 of those cases. The low biases suggest that the wind speed predictions for the reanalysis runs are reasonable, although the RMSE results may provide a fairer assessment. RMSE values were between 1.8 and 3.7 m/s.

- Emery et al (2001) proposed statistical benchmarks for evaluating meteorological model performance. The authors proposed benchmarks for wind speed of 0.5m/s for mean bias and 2m/s for RMSE. Our overall wind speed bias exceeds or is close to this benchmark for the bias in 5 out of the 6 cases, but the RMSE values exceed this criteria for all but one case (case#2) by 45-85% of the benchmark with a mean difference of 61% for the 5 cases in question. However, these benchmarks were not necessarily constructed to pass or fail any modeling application, rather to put its results into the proper context. Overall, the wind speed results come reasonably close to these benchmarks given the expected spread of results and the relatively small number of cases considered.

- Henderson et al (2007) evaluated WRF prediction using NCEP/NCAR reanalysis data for July and December, 2005 over Siberia. The authors found RMSE (SDE) of 2.4 (2.36) for July at 850hPa and 700hPa and 5m/s (4.7) at 850 hPa for December. Our mean wind speed RMSEs of 1.8 to 3.7m/s and SDEs of 1.6 to 2.6 for all six case studies are better results than those reported by Henderson et al (2007).

- Molders et al (2010) performed numerical experiments with WRF using two different physical package combinations and the authors noticed that the upper air wind speed bias ranged from 0.6 to 2.8m/s for first physical option and 0.1 to 2.2m/s for the second physical option. It can be noted that our wind speed bias results which range from 0.2 up to 1.8m/s for all six cases are better than those achieved by Molders et al (2010). Further, Molders et al (2010) reported RMSE values that ranged from 1.5 to 5m/s with 2.9m/s on average for first physical option and 1.2 to 4.3m/s with 2.6m/s on average for the second physical option. The authors also noted the SDEs reached up to 4.4m/s and 3.99m/s with a mean of 2.46m/s and 2.4m/s for first and second physical option respectively. Our
results for RMSE (1.8 to 3.7 m/s with 2.9 m/s on average) and SDE (1.6 and 3.4 m/s with 2.5 m/s on average) were slightly better than that achieved by Molders et al.

- For wind direction in scenario#1 there were several profiles where there were large discrepancies between the forecast and reanalysis runs and also large differences when compared to the SODAR observed profiles. This suggests considerable model deficiencies at certain times. However, at other times there were very good matches between the models and the observations.

- Wind direction biases were lower for forecast runs compared to reanalysis runs. RMSEs were generally slightly better for the forecast runs, although the statistics for this were similar for both types of run.

- The mean wind direction bias for 3 out of the 6 cases exceeds the benchmark proposed by Emery et al (2001) for wind direction of (10°). The biases for the other cases range from 20.9 to -33° and thus fail the criteria. The RMSE values were in the range 56-75° for 5 out of the 6 cases. For case#5 the performance was generally worse for both bias (-33°) and RMSE (93°).

- Profiles showed little pattern of errors with height. Timeseries suggested that the reanalysis runs generally produced positive biases and high RMSE values during the hours of 03-09 local time and the opposite was the case between 12 and 21 hours.

- Time series of wind speed and direction showed that there is little consistent error build up with time as the bias, RMSE and SDE are generally consistent over the 78-hours simulations. It is possible that there some slight increase of RMSE for wind speed, although it is hard to be conclusive with only 3 cases.
4.6 **Summary and Conclusion:**

A detailed comparison of WRF predictions over two different scenarios (eight case studies) against surface and upper air profiles were made. First scenario (three case studies) was for 24-hour simulation using two different initial conditions (forecast and reanalysis initial data) and second scenario (five case studies) was for 78-hours simulation using only reanalysis initial data.

WRF predictions for both scenarios tends to underestimate the 2-m surface temperature on average in seven cases out of eight with bias ranging from -0.2 up to -3.4 degree. The largest bias (-3.4°C) was 13% of the average observation and the possible reason for this high bias is that there are some local sources (e.g. ground flares) were not considered in the modeling input but they affect the observation data (site#2). Conversely WRF tends to overestimate the surface wind speed in all eight cases with positive bias ranging from 0.2 to 1.5m/s on average (6% to 54% of the average observation). The mean wind speed biases for the reanalysis runs were lower than those from the forecast runs and ranged from 0.2 to 1m/s. The prediction of wind direction is very close to observation with bias ranging from 1.3° to 24°.

The correlation coefficient between WRF predictions and surface observations are very high for temperature (0.7 to 0.9), moderate to high for wind speed (0.4 to 0.9) and wind direction (0.6 to 0.8). High correlation coefficient for wind direction with low bias (<24°) suggests that the WRF model is able to capture the sea and land-breeze phenomenon occurred over YIC during day and night times. Further, by comparing the overall 24-hour simulation results for scenario#1 (forecast and reanalysis) it was noticed that forecast-initialized runs gave slightly better predictions than reanalysis-initialized runs for 2-m surface temperature, but on the other hand the reanalysis gave better wind speed predictions than the forecast initial data. Wind directions were similar for both initial datasets although the forecast run gave slightly better results for one case study (case 3) out of three.
By comparing the results from both scenarios for the reanalysis-initialized simulations for the surface parameters, it seems that there is no build up of error with time after startup for the next 78 hours as both scenarios produced relatively similar performance statistics for all parameters.

WRF tends to underestimate temperature profile when reanalysis data is used and overestimate it when forecast data is applied. Further, it can be noted that the forecast initialized data give slightly better prediction for temperature profile than the reanalysis data in some cases which indicating that the reanalysis procedure made the global NCEP model simulation may not be necessary to improve the data especially for complicated flow such as sea and land breeze. For example scenario#1 profile – case#1 the forecast run bias and RMSE are considerably lower than for the reanalysis run. The overall mean biases for comparisons to both the radiosonde and the RASS are generally negative for the upper air temperature in seven cases out of eight. The bias ranges between -2.7 and -5.2 for all cases when compared to the RASS, but the average bias is much lower (between 0.3 and -2.4) when the radiosonde data is used. The model appears to perform better when compared to the radiosonde data with very high correlation coefficient (>0.9) suggesting that WRF predictions for temperature profiles are quite reliable and the errors are generally quite high when WRF is evaluated using the RASS data. This might indicate that RASS temperature profiles are often unrealistic and the instrument was unreliable especially noon and after noon hours when the wind speed is relatively high.

Time-series of the bias, RMSE and SDE for temperature profile for only two times a day (03 and 15) are ranging between +2 and -2°C for bias and are less than 3°C for RMSE and SDE and these results are similar to those of the profiles. Temperature time-series showed generally no significant trend in model error over time suggesting that there is no sustained build-up of model errors over the 3 days of the simulations in most cases.

WRF model generally overestimates the wind speed profile with forecast-initialized data but it underestimates it with reanalysis-initialized data. The wind speed prediction using forecast-initialized data had fairly similar statistical results to those from reanalysis-
initialized data although the reanalysis runs produced slightly lower biases and RMSEs and so might be expected to give slightly better results. However, both types of input data (forecast and reanalysis) are equally acceptable in predicting wind speed.

As wind speed bias in most cases (five cases out of six) are less than 1m/s, one may conclude that that the wind speed predictions for the reanalysis runs are reasonable especially in lower and mid level of boundary layer, although the RMSE results may provide a fairer assessment. RMSE values were between 1.8 and 3.7 m/s. The wind direction profile bias are generally positive and they are less than 20° in all layers although some vertical bias is relatively high (>40°) at higher layers.

The mean wind speed bias in 5 out of the 6 cases are either meeting or close to the benchmark proposed by Emery et al (2001) for wind speed of ±0.5 and the mean wind direction bias for 3 out of the 6 cases exceeds the benchmark proposed by same authors for wind direction of (10°). The wind speed and direction profiles from the SODAR instrument look reasonable compared to the WRF profiles, which suggests that this instrument is capable of producing realistic wind measurements although the accuracy of this instrument (SODAR) is probably uncertain during some hours. However, it would be advisable to compare these observations with another form of observation, (such as radiosonde data) at the same site.

Time series of the wind speed and direction showed that there might be little consistent error build up with time as the bias, RMSE and SDE are generally consistent over the 78-hours simulations. However, it is possible that there was some slight increase of RMSE for wind speed, although it is hard to be conclusive with only 3 cases.

The evaluation presented in these case studies suggests that WRF prediction can be used for air dispersion modeling to produce reasonable outputs. Further, it is suggested to use reanalysis data as initial guess and boundary condition for running CALMET model as this type of data give slightly better prediction for wind speed and similar wind direction for forecast data. Among the five reanalysis cases, some cases (such as cases# 4 and 8)
may give better air dispersion modeling results as they have lower wind speed and direction bias.

It should be mentioned that during the transition periods from sea breeze to land breeze and vice versa the bias in wind direction was often relatively higher. The biases for wind speed are also generally high during the transition periods, although the wind speed biases tend to be relatively high during other parts of the day as well. This should be borne in mind when making air pollution predictions during the transition periods. This could be investigated further to improve the WRF model forecast during such transitions.
Chapter 5: Predictions of NO\textsubscript{x} and Particulate number over YIC

5.1 Introduction:
There have been many studies addressing the dispersion of gaseous pollutants from anthropogenic sources (vehicles and industries), but fewer addressing the dispersion of particle number concentrations at small scales. Gaseous pollutants (e.g. NO\textsubscript{x}) can be predicted using either relatively simple or highly complicated air dispersion models depending on the case. Particle numbers can be predicted using highly sophisticated models such as Computerized Fluid Dynamic (CFD) models for the micro-scale (such as street canyons) or other models (e.g. MATCH) for the urban scale with some limitations for both models (Gidhagen et al., 2005 and Albriet et al., 2010). In order to make a good prediction for particle number concentrations at urban scales, dispersion models include all the necessary removal and growth processes of particles, which is challenging (Ketzel and Berkowicz, 2004). Alternatively, particle number concentrations can be estimated based on the observed correlation between some gases (mainly NO\textsubscript{x}) and the number concentrations of particles of certain sizes along with proper usage of advanced dispersion models with high quality input data.

For convenience, air dispersion models can be divided into two types: steady state Gaussian plume models (such as AERMOD) and non-steady state 'advanced' models (such as CALPUFF). A fundamental difference between the two types of model is that the advanced models require three-dimensional meteorological fields rather than measurements at a single point and an assumption of homogeneous wind field over the entire domain. Accordingly steady state models will produce a straight-line plume trajectory based on the wind direction at a single location whereas the non-steady state models are capable of changing the plume trajectory from hour to hour due to the terrain features and wind field. Further, steady state models cannot adequately simulate the complex features such as sea-land breezes, calm wind or complicated terrain. Non-steady state models can simulate the real meteorological conditions effectively beside other important features such as: simulating complex terrain or frequent low wind speed conditions (<0.5m/s); treating chemical transformations between pollutants; considering the effects of changes in contaminants over time.

In this chapter, the non-steady state CALPUFF dispersion model will be applied with meteorological data from the WRF model to predict the NO\textsubscript{x} concentrations from stationary (industries) and mobile (traffic) sources for two cases: weekday and weekend.
The particulate number concentrations for different sizes will also be predicted based on
the correlation between NO\textsubscript{x} and particle number observations as derived earlier in
chapter 2. The prediction will be evaluated using some recommended statistics of the
observed and modeled concentrations at two monitoring sites.

5.2 Observations:
All the necessary information required for running CALPUFF/CALMET model and
performance evaluation was collected. This information consists of the following: air
quality data (NO\textsubscript{x} and O\textsubscript{3}); meteorological data (wind speed and direction, temperature, etc); industrial source emission rates and stack characteristics; the traffic densities for
major roads.

*Industrial sources:*
Stack emissions rates and characteristics including stack height and diameter, exit gas
velocity and temperature were obtained from each facility. All industrial sources are
equipped with appropriate control devices (such as Low NO\textsubscript{x} burner or Ultra-Low-NO\textsubscript{x}
burner or others) to reduce NO\textsubscript{x} emission so that the sources will comply with the local
source standard. Most of the emission rates (mass per unit time) were collected through
stack tests using US-EPA Method 7E, but some data was based on calculations using the
US-EPA method AP-42 and some given information such as source type, quantity of fuel,
type of fuel etc.

*Traffic sources:*
Traffic counts were conducted at major traffic roads for two cases: Case-A (Saturday,
Sunday and Monday) and Case-B (Wednesday, Thursday and Friday). In Saudi Arabia,
the weekdays are Saturday to Wednesday and the weekends are Thursday and Friday. The
traffic counts were performed for all major roads and streets for both cases. As an
example, the traffic density for the main highway in YIC (King AbdulAziz road) is
shown in figure 5.1. It is clear that the maximum traffic density is observed between
07:00 and 08:00 hr with another peak at 17:00hr during weekdays, but during the
weekend the maximum traffic count is noted during evening times because many of the
residents travel from YIC on Wednesday afternoon and return on Friday evening.
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Fig 5.1: Diurnal variation in traffic volume near site#1 for case A (I) and Case B (II).

Air Quality Monitoring Data:
Particle number, NOₓ and ozone data were continuously monitored at site#1 and site#3 (see figure 5.2) using standard gas analysers and ELPI equipment as explained in detail in chapter 2. There was no missing data during the measurement period. The hourly ozone data were used as input for the chemical reaction calculations in the CALPUFF runs. The hourly NOₓ and particle number observations were utilized for the evaluation of the performance of CALPUFF. Figure 5.2 shows the locations of the community area, light industrial area (e.g. gypsum plant, fabrication projects, etc) and heavy industrial area.
(power plant, refinery, petrochemical plant, etc). Further, the main road (King AbdulAziz Road) in the YIC is marked with the blue color (volume sources). Area sources are marked by green color and these will be discussed further in the next sections.

Figure 5.2: YIC map showing locations of the heavy industrial area; light industrial area; community area; main roads and streets; and sites#1 and 3.

5.3 Model description and setup:
The CALMET/CALPUFF modeling system was selected to predict the NO$_x$ ground level concentration over YIC. This modeling system comprises of three main components: CALMET (Scire et al., 1997), CALPUFF (Scire et al., 2000) and CALPOST. CALMET is a diagnostic meteorological model, CALPUFF is a dispersion puff model and CALPOST is post-processing software used to generate ground level concentration files for all modeled parameters at the required domain or district receptors. In addition to these three components, there are other processors (such as Terrel, Makegeo, CALWRF) which are also used to prepare geophysical (land use and terrain) and meteorological data in the required standard format for running CALMET. The outputs from a prognostic meteorological model (WRF) were used directly as input for CALMET using the CALWRF software. In this study, the latest US.EPA-approved versions of CALPUFF
(version 6.268– level00318) and of the CALMET model (version 6.327– level090511) were used. More details on the CALMET and CALPUFF models are given shortly.

**CALMET- Meteorological model:**
The CALMET model is a meteorological preprocessor that compiles meteorological data from observations (surface, upper air, precipitation, over-water data if available), prognostic model output (WRF/MM5) and geophysical data into hourly, three-dimensional gridded datasets spread over the entire domain for input into CALPUFF. In addition, two-dimensional fields such as mixing height and other meteorological parameters are predicted.

CALMET model contains a diagnostic wind field module that uses a two step procedure for computing the final wind fields in the case where both prognostic and observations are utilized (Douglas and Kessler, 1988). For the first step, the prognostic wind field from WRF is introduced into CALMET as the initial guess parameters for each grid cell in the modeling domain. Once the initial estimate (initial guess) of wind field is created, the wind data is adjusted for the kinematic effects of terrain, slope flows, terrain blocking effects, and divergence minimization scheme to produce a first step of wind field. The second step is to introduce the observational data into the step 1 wind field through an objective analysis procedure which eventually the final wind field is produced. An inverse distance squared interpolation scheme is used to improve all wind field data within a defined radius of influence based on the observational station, while the step 1 wind field dominates the interpolated wind field in regions where no measurements are available. The resulting wind field is subject to smoothing, an adjustment of vertical velocities and divergence minimization to generate a final step 2 wind field. If there is no observational data, the first step will be considered as the final wind field.

In this study only step 1 will be applied where the prognostic meteorological data from the WRF model, as introduced in the previous chapter, was used as input to the diagnostic meteorological model (CALMET) to obtain meteorological wind fields for running the air quality model (CALPUFF). Other information, such as conditions over water and cloud cover, were estimated based on prognostic data, such as relative humidity. Upper air observations were not utilized in this study as only one station was available, the data was not available for all hours and some data (temperature profile) was not confirmed quality assured data. The reason for not using surface observations was because the surface station is very close to the coastline, which may not be representative and useful for this case except perhaps for the micro-scale conditions.
CALPUFF- Air Quality model:
CALPUFF (California Puff Model) is a multi-layer non-steady state puff dispersion model designed to predict ground level concentrations of gases and particles in terms of mass concentrations using space and time varying meteorological parameters and other processes (transport, transformation and removal). The model does not incorporate any modeling of the particle dynamics and therefore it does not calculate particle number and size distribution. Two studies (EPA, 1998; Elbir, 2003) in which gas dispersion in CALPUFF was examined showed good correlations with field data. Another study during the winter over Christchurch (Bana and Gimson, 2002) predicted hourly PM$_{10}$ concentrations and also showed good agreement (the index of agreement ranged from 0.67 to 0.87) with the measured concentration. Holmes et al (2006) made a review of dispersion modeling and concluded that generally CALPUFF showed reasonable agreement with field data in the validation studies although some discrepancies were found due to unknown reasons.

US-EPA (2003) indicates that CALPUFF is intended for use on scales of tens of meters up to hundreds of kilometers from a source. The model contains algorithms for both near-source effects (such as building downwash, transitional buoyant and momentum plume rise, partial plume penetration, subgrid scale terrain, coastal interaction effects, and others) and longer range effects (such as wet scavenging and dry deposition; chemical transformation; overwater transport; vertical wind shear; plume fumigation; and others).

CALPUFF is designed to simulate a continuous series of puffs that are released in the ambient air and allowed to move and disperse horizontally and vertically according to local meteorological conditions. As the wind flow changes with time, the path that each puff takes changes according to the new wind direction. Puff diffusion is Gaussian and the predicted concentration is based on the contribution of each puff as it passes over or near a grid point (Scire et al., 1999b). CALPUFF dispersion emissions may be configured as integrated puffs or as slugs depending on local-scale applications such as the distance between the source and the receptor. The slug option can be considered as a group of overlapping puffs having very small separation distances between each other. This option is usually chosen to better characterize local source impact and when the distance between the source and receptors are very close as in this study where site#1 is very close to the road. This technique (slug mode) is available in CALPUFF as the slug approach, and is fully described in section 2.1.2 of the CALPUFF User's Guide.
In this study the model was run with the MESOPUFF II chemical transformation options, which is preferred by the US EPA and is generally appropriate in most urban applications. The actual hourly ozone data (OZONE.DAT) necessary for chemical reactions was taken from site#1 for both cases (A and B). With regard to ammonia concentration, a constant value of 0.9ppb was assumed as the actual concentrations were not available. However, the model sensitivity to ammonia values (from 0.4 to 1ppb) is noted as negligible. The NO\textsubscript{x} loss and HNO\textsubscript{3} gain was assumed as 8.7% per hour (as concluded in chapter 3) although changes in this value will not have a significant effect on the predicted concentration of NO\textsubscript{x}.

The USGS data within the CALMET/CALPUFF domain was used to produce a gridded field of domain land use and terrain data with a 30arc-second data set at ~900m resolution. The wet deposition was not incorporated into the model as there was no rainfall during the study dates. The building downwash will have a minimal effect as the area is mainly flat. The CALPUFF model uses the same grid system as CALMET, comprising of 10 layers over 30\times30 horizontal grid cells. The vertical layers were specified with variable spacings at heights of 20, 40, 80, 160, 320, 700, 1300, 1700, 2300, 3000m.

In summary the CALPUFF simulations were conducted using the following model options:

- Plume modeled as Slug
- Transitional Plume rise
- Stack tip downwash
- PG dispersion coefficient
- Partial plume penetration for point and area sources
- Dry deposition and chemical transformation using MESOPUFF II scheme.

The model code and its documentation are available at no cost for download from the model developers' internet Web site: [http://www.src.com/calpuff/calpuff1.htm](http://www.src.com/calpuff/calpuff1.htm)

**Domain Size and Grid Resolution:**
Selecting the spacing between grid points in a modeling study is a compromise option between computation time and the required resolution. If the number of receptors is doubled the time required for each run will also be doubled. However, if the spacing is too large, the peak concentration may fall between receptor points and may not be
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captured in the final results. In this study, two types of receptors within the modeling domain were selected as shown in figure 5.3:

1- A series of nested Cartesian grid points (every 1km distance) which covers the entire domain (30km×30km).
2- Specific district receptors were also added at sensitive and important areas such as the sampling site, residential areas and markets.

The topography of the domain is not very complicated with ground elevation varying between -1 and 110m above mean sea level. The terrain in the YIC is assumed flat as the average height of the buildings is fairly low (most buildings are lower than 15-20m) and as all terrain features are lower in elevation than the top of the stack of the sources (maximum height=150m).

CALPUFF shares the same model domain as CALMET as shown in figure 5.3. The modeling domain has a uniform horizontal grid with a grid cell size of 1 km in order to properly resolve any spatial variations in the flow field and surface characteristics. The coordinates of the reference point defining the domain location are specified at the southwest corner and are 409km east and 2640km north in UTM Zone 37 (Lat: 23.875687 and Lon: 38.112153). In the vertical dimension a stretched grid is used, with the layer thickness increasing with height. Ten layers were defined to extend from the surface up to 3000m above ground level as indicated previously.

![Figure 5.3: Receptors used over study domain (30km×30km) over YIC](image-url)
5.4 Model Input Data:
The amount of required input data for running air dispersion models is proportional to the complexity of the selected model. Performing a dispersion modeling simulation using a complex model (such as CALMET/CALPUFF modeling system) requires numerous input data including such as source emissions, terrain data and meteorological data and also assumptions on physical and chemical processes in the atmosphere. The modeling results depend mainly on the accuracy of all these input data. Unfortunately, obtaining representative and reliable input data and high quality observations is not always achievable.

5.4.1 Meteorological data:
One of the challenges for conducting air quality modeling analysis is obtaining representative and reliable three dimensional meteorological data. In most cases, observation stations are usually sparsely and/or irregularly distributed. The approach of using observation data may not be always useful because of the effects of geographic/terrain features or meteorological conditions. Within areas of complex terrain or meteorology, observation from stations can be considered as representative only within a small range of the station location. This lack of representative data especially on mesoscale domain has lead to the development of pseudo meteorological data from models such as WRF/MM5 in order to better represent local conditions. In this study the output from WRF model was used as input for running CALMET model.

The meteorological data outputs from the prognostic model (WRF), which was tested in the previous chapter (Case A represents Case 8 and Case B represents Case7), was used as input for running the CALMET model. Comparisons between WRF output (used as input for CALMET), CALMET output and observations are shown in figure 5.4. It is clear that CALMET generally under-predicts the wind speed observations with a 3day average bias of -0.6m/s and -0.9m/s for Case A and B, respectively. However, for case A, CALMET is very similar to observation for first day and then over-predicts between hours 3 and 10 on the second day. WRF generally overpredicted the wind speed values with average biases of 0.5m/s for case A and 0.3m/s for Case B. However, both CALMET input (WRF results) and CALMET outputs have a similar trend to that of the observations. The wind direction prediction by both WRF and CALMET are almost identical for both cases except for two values for case A. It is interesting to note that both WRF and CALMET predictions are generally able to capture the development of sea and land-breeze phenomena over YIC as concluded in the earlier chapter. Predictions of surface temperature by WRF and CALMET are also very close to each other and have
similar trends to the observations, although the CALMET model predicts lower maximum values compared to WRF. Predictions by both models are overall under predicting the surface temperature with the WRF average bias being -0.1 and -1.4 °C for Cases A and B respectively and a CALMET average bias of -1.5 and -2 °C for Cases A and B respectively. Detailed statistics for WRF results were discussed in earlier chapter.

**Fig 5.4:** Diurnal variation of predicted wind speed and direction and surface temperature by WRF and CALMET compared with observation for cases A and B.

Surface input data into CALMET includes wind speed and direction, temperature, cloud cover, ceiling height, surface pressure, relative humidity and precipitation (type and amount). Some parameters such as cloud cover were calculated based on relative humidity. Precipitation was not required because there was no rainfall during this study period. The upper air data needed for running CALMET was wind speed and direction, temperature, and height for each layer. Table 5.1 summarizes the parameters needed for surface meteorological data, upper air data and precipitation data used as input by CALMET and the meteorological parameters in the WRF data.
Table 5.1: Meteorological data used by CALMET and generated by WRF model

<table>
<thead>
<tr>
<th>Parameters used by CALMET</th>
<th>WRF Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- Surface parameters:</td>
<td>Wind speed and direction, pressure, temperature, elevation, vertical velocity, relative humidity, vapour mixing ratio, cloud mixing ratio, rain mixing ratio, ice mixing ratio, snow mixing ratio</td>
</tr>
<tr>
<td>Wind speed, wind direction, temperature, cloud cover, ceiling height, surface pressure, and relative humidity</td>
<td>Wind speed and direction, pressure, temperature, elevation, vertical velocity, relative humidity, vapour mixing ratio, cloud mixing ratio, rain mixing ratio, ice mixing ratio, snow mixing ratio</td>
</tr>
<tr>
<td>2- Upper air Data:</td>
<td></td>
</tr>
<tr>
<td>Wind speed and direction, temperature, pressure and elevation</td>
<td></td>
</tr>
<tr>
<td>3- Precipitation Data:</td>
<td></td>
</tr>
<tr>
<td>Precipitation rate and precipitation type</td>
<td></td>
</tr>
</tbody>
</table>

5.4.2 Source emission data:
In this study NO\textsubscript{x} emissions from stationary sources (industries) and mobile sources (traffic) are considered (sources are shown in figure 5.5). Emissions from other sources such as marine traffic and ground flare are not taken into account as the data for these sources were not available. Sources of air emission can be classified as point, line and area/volume sources.

Industry emissions:
Most of the industrial sources were modeled using the design capacity (100% load) except the power plant where the actual operating conditions are used. During stack testing every facility is required to run on design load to monitor the criteria air pollutants emitted from stacks, which were used as input for running CALPUFF. However, for a few industries actual emission data (stack test) is not available and therefore US-EPA Method AP-42 was applied for estimating the emission rates of NO\textsubscript{x}. In this study there were 84 industrial stacks (point sources) for which the following parameters were considered: stack location, stack height, inside diameter (m), exit velocity (m/s), base elevation, temperature (k), emission rates (g/s). All emission rates from all stacks were assumed to be constant with time.

An example of the emission rates and stack characteristics for three of the major sources (power plant, petrochemical and refinery stacks) out of the 84 considered in this study is shown in table 5.2. The total NO\textsubscript{x} emission from all 84 sources was 92 metric ton/day.
Table 5.2: Example for emission rate and stack characteristics for three sources

<table>
<thead>
<tr>
<th>Source name</th>
<th>Emission Rate</th>
<th>Stack Height</th>
<th>Stack Diameter</th>
<th>Exit Gas Velocity</th>
<th>Exit Gas Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Plant –Steam Turbine Generator #1</td>
<td>34 g/s</td>
<td>90 m</td>
<td>6.4 m</td>
<td>14.7 m/s</td>
<td>423 K</td>
</tr>
<tr>
<td>Petrochemical Boiler</td>
<td>5.7 g/s</td>
<td>50 m</td>
<td>2.5 m</td>
<td>9.5 m/s</td>
<td>503 K</td>
</tr>
<tr>
<td>Refinery boiler</td>
<td>20 g/s</td>
<td>150m</td>
<td>5.8 m</td>
<td>10.7 m/s</td>
<td>633 K</td>
</tr>
</tbody>
</table>

Figure 5.5: Locations of point sources and volume/area sources over study the domain.

On Road Traffic emissions:
This study deals with roads and streets in a flat area unlike a street canyon in a densely built urban area where buildings line both side of the street. Continuous traffic density was measured by the RC Road Department at the following major roads and streets inside YIC: King Abdulaziz Road, King Faisal Street, King Khalid Street, King Fahad Street, and Al-Mina Street. These measurements include only total traffic count (vehicle/hr) for each road without classification during weekdays (Saturday, Sunday and Monday) and weekend (Thursday and Friday). Classification of vehicles as Light (LDV) or moderate or heavy (HDV) was carried out manually between 8am and 10am only (peak hours). It was
assumed that the classification of vehicles during all times was as follows: 60% personal cars, 10% Van, 10% Pickup and 20% Trucks and buses.

Emissions from traffic sources can be characterized in different ways with eventually the same final results. For example, a traffic roadway can be considered as a series of area or volume sources, or in some models as a line. Determining whether selecting volume or area sources depends on the distance between the sources of emission (road) and the receptor (e.g. sites#1 or 3). As the total roadways are relatively long (40km) at YIC, it is very difficult to consider all roads as volume sources or area sources with a square aspect ratio of 1:1 (width/length) since this would be too computationally intensive and it would take too long to complete each run. Therefore, it was decided that traffic sources within 1km of site#1 would be modeled as volume sources (near-field) in order to give a better prediction near site#1, despite the longer runtime required for each run. The remaining roadways (far-field) were modeled as area sources. The area source aspect ratio (road length/road width) varies from 7 up to 90 depending on source-receptor distance. If the distance between the district receptor and the road is less than 1km, the area aspect ratio is defined as a maximum of 9 (figure 5.6). For roads located greater than 1km away from the district receptors the aspect ratio for area source was set to >9, but less than 90.

The emission rates of NO\textsubscript{x} for each road were calculated based on traffic volume, distance traveled and traffic classification during every hour. However, there are other factors which are not taken into consideration, but which could be important, such as the driving cycle (e.g. acceleration and deceleration, steady speed) and the vehicle travel speed (NO\textsubscript{x} emissions increase with the vehicle travel speed, which are significantly higher at major roads).

The emission rates of NO\textsubscript{x} vary throughout the day and also depend on the day of the week. The average of emission factor (g/veh/km) for Euro I and II and US-EPA were applied for calculating emissions from traffic flows.

Volume Sources:
The general procedure suggested by US-EPA User guide for ISCST Model (US-EPA, 1995) for estimating initial lateral (\(\sigma_y\)) and vertical dimension (\(\sigma_z\)) for volume sources was applied for the road near site#1 (see figure 5.6). The following steps and assumptions were used in estimating the lateral and vertical dimensions:

- Actual Width of the road (both direction) = 10m
- Number of volume sources = 200
• Height of volume source generating emission = 2 × the height of the vehicle generating emission = 2 * 2.5m = 5m

• Initial lateral spread (\(\sigma_y\)) = 2 * road width/ 2.15 = 9.3m

• Initial vertical spread (\(\sigma_z\)) = Height of the volume source/ 4.3 = 5/4.3 = 1.17m

• Emission rate (g/s/m\(^3\)) = Total emission/number of volume sources= (g/s) / 200

**Area sources:**
The sizes of all area sources (with a maximum of 900m×10m for each source) were smaller than that of one computational grid cell of the CALPUFF runs (1km×1km) as recommended by Popovic J. (2009). The following assumptions were applied:
- The release height of each area source = 2.5m
- Road length = 70 - 900m
- Road width = 10m
- Total area for each road = Width × Length
- Area source emission for each road = total emission/total area = g/s/m\(^2\)

Emission factors (g/km) for traffic emissions in YIC were obtained from two references: DELPHI 2010 and USEPA. As per first reference (DELPHI 2010, page 52), Saudi Arabia implements Euro 2 for personal Cars and Euro 1 for Light commission Vehicles. However, the second reference (World Bank Policy Research Working Paper 4867 of 2009) indicates that Saudi Arabia follows the U.S. emission regulation (ECE 15.03 equivalent). Therefore, the emission from traffic was calculated as an average of Euro-I or II and USEPA emission standards for Saudi Arabia as shown in table 5.3.

**Table 5.3: Emission rate for traffic (g/km) applied for this study**

<table>
<thead>
<tr>
<th></th>
<th>Personal Cars</th>
<th>Light Duty Vehicle</th>
<th>Heavy Duty Vehicle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 1 / Euro 2</td>
<td>0.5g/km</td>
<td>0.97g/km</td>
<td>8g/km</td>
</tr>
<tr>
<td>US-EPA</td>
<td>0.37g/km</td>
<td>0.6g/km</td>
<td>5g/km</td>
</tr>
<tr>
<td>Average</td>
<td>0.44 g/km</td>
<td>0.79 g/km</td>
<td>6.5g/km</td>
</tr>
</tbody>
</table>
Based on traffic counts and emission factors indicated in Table 5.3, the total emission from all vehicles was about 2.1 metric ton/day. By comparing the emissions of NO$_x$ from industries and traffic, it is clear that the total emission from all traffic (2.1 ton/day) is minor compared to the emission from industries (95 ton/day).

5.5 Statistical Indices:
To assess the performance of the CALPUFF model predictions compared to observations, several statistical indices were utilized including fractional bias (FB); Normal Mean Square Error (NMSE), Index of Agreement (IA) and the fraction of prediction within a factor of two of the observation (Fa2). The definition of each of these statistical measures as indicated by many authors (e.g., Kumar et al, 1999 and Gokhale et al, 2008) is as follows:

\[
\text{Fractional Bias (FB)} = \frac{\overline{C_o} - \overline{C_p}}{0.5(\overline{C_o} + \overline{C_p})} \tag{5.1}
\]

Where $C_p$ is the model prediction, $C_o$ is the observation, $\overline{C}$ is the average over all data values. FB is a dimensionless number and varies between -2, i.e. extreme over prediction and +2, extreme under prediction, and has a value of zero for an ideal model.

The Normal Mean Square Error (NMSE) = \[
\frac{(C_o - C_p)^2}{\overline{C_o} \overline{C_p}} \tag{5.2}
\]
NMSE emphasises the scatter of the entire data set and a smaller value of NMSE indicates a better model prediction. The predictions are acceptable when \( \text{NMSE} \leq 0.5 \).

\[
\text{Index of Agreement (IA)} = 1 - \frac{\sum_{i=1}^{N} (C_{pi} - C_{oi})^2}{\sum_{i=1}^{N} [\text{ABS}(C_{pi} - \bar{C}_o) + \text{ABS}(C_{oi} - \bar{C}_o)]^2}
\]

(5.3)

The index of agreement (IA) measures the degree to which the variation in the prediction can accurately simulate the observations, or in other words it is a measure of the degree to which the model predictions are free of error. It varies between 0 and 1 with a value of 1 indicating perfect agreement between observation and predictions and 0 indicating a large degree of disagreement.

\( Fa_2 = \% \text{ of data that satisfy } 0.5 \leq C_{pi} / C_{oi} \leq 2 \)

(5.5)

\( Fa_2 \) is defined as the percentage of predictions that are within a factor of 2 of the observations. The model can be deemed acceptable if \( Fa_2 \geq 0.8 \).

Results from only one or two parameters may not give a reliable indication of the performance of the model. For example, it is possible that the prediction is completely out of phase with the observation and yet still have \( \text{FB} = 0 \) due to canceling errors. However, if the index of agreement is close to 1 and NMSE is close to 0, then the prediction is more likely to be good.

5.6 Results and Discussion:

5.6.1 \( \text{NO}_x \) predictions:

5.6.1.1 Case A (April 26-28, 2008):

The predicted hourly \( \text{NO}_x \) concentrations due to industrial, traffic and combined emissions from both sources are plotted in the form of isopleths for April, 26-28, 2008 (figure 5.7-5.9). For each day one specific hour was chosen to represent the night, morning, noon, afternoon and evening periods (table 5.4). For example, hours 1, 2 and 3 of days 1, 2 and 3 respectively represents night hours with low wind speed and low traffic volume whereas hours 6, 7 and 8 represent morning hours with moderate wind speed and high traffic volume-rush hours as clear in previous figures 5.1 and 5.4. Each isopleth graph was plotted with the appropriate meteorological parameter: traffic isopleths are presented with the surface (2m) wind speed and direction, industry isopleths are presented
with the 100m wind speed and direction, and the isopleths due to combined sources are plotted with the mixing height. Near surface sources (traffic) are distinguished from industrial sources in that the emissions are released in very close proximity to human receptors.

These three parameters (wind speed and direction, and mixing height) are the ones that are the most influential on ground level concentrations at each receptor due to emissions from these sources. The mixing height is known as the distance between the Earth's surface and the bottom of the inversion aloft. If the inversion layer extends from the surface, then the mixing height value becomes zero. Therefore, the mixing height is important in determining the volume of air available for diluting pollutants in the atmosphere. Increasing the mixing height allows more volume for pollution dilution, thus resulting in lower ground level concentrations. Decreasing wind speeds result in higher concentrations because pollutants are being removed from the local area more slowly. Of course, combinations of extreme values (lows) of both wind speed and mixing height lead to extremely high concentration.

**Table 5.4:** Hours chosen on each day for plots of cases A and B.

<table>
<thead>
<tr>
<th>Wind Speed</th>
<th>Wind Direction</th>
<th>Night Hours</th>
<th>Morning Hours</th>
<th>Transition Hours</th>
<th>Noon/After noon Hours</th>
<th>Evening Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td></td>
<td>1 2 3 4 5</td>
<td>6 7 8 9 10</td>
<td>11</td>
<td>12 13 14</td>
<td>15 16 17</td>
</tr>
<tr>
<td>Day 2</td>
<td></td>
<td>1 2 3 4 5</td>
<td>6 7 8 9 10</td>
<td>11</td>
<td>12 13 14</td>
<td>15 16 17</td>
</tr>
<tr>
<td>Day 3</td>
<td></td>
<td>1 2 3 4 5</td>
<td>6 7 8 9 10</td>
<td>11</td>
<td>12 13 14</td>
<td>15 16 17</td>
</tr>
</tbody>
</table>

**Night hours (01:00, 02:00 and 03:00 hour):**
It is clear from the graphs (figures 5.7-5.9) that during these hours of days 1, 2 and 3 the wind speed and mixing height are generally low. The wind direction is generally from the land towards the sea (land breeze) for hour 01, but had become a sea breeze by hour 02. By hour 03 it was a land breeze again. The overall contribution from traffic is generally higher than that of industries during this period and the maximum due to the former is >80% of the overall maximum, whereas it is <20% for the latter. The high contribution from traffic is due to the fact that the NO\textsubscript{x} emissions are from a very low level (<5m) compared to that of the industries (80-150m) where wind speeds are almost calm. The mixing height is also low during this period, which means that the inversion layer extends from a near surface level (probably from 50m) to aloft. Further, the likely reason why the impact from industries on ground level concentrations is very low is because the ground-level inversion layer (i.e. below the discharge point) suppresses vertical motion, which hinders the transport of the emitted NO\textsubscript{x} to ground level. Instead the plume spreads
horizontally (fanning) at a height slightly higher than that of the stack with very limited dilution in the vertical.

Maximum concentration isopleths due to both sources (traffic and industries) ranged between 40 and 300μg/m$^3$ and the emission from traffic was concentrated near road intersections. Further, it is noted that very low values (ranging from 65 to 170m) of mixing height occurred over land and sea, especially on days 1 and 2. The surface and 100-m wind speed and direction are very similar except for day#2 at hour 2 when there is a slightly different wind direction between the two layers.

**Early morning hours (06:00, 07:00 and 08:00 hours):**

During these morning hours a high traffic density is noted, but at the same time there is a gradual increase in wind speeds and mixing height, which results in more dilution horizontally and vertically for the near-surface emissions (traffic). However, the contribution from industries becomes higher (>70% of the maximum) than that from traffic (<30%) because after sunrise the ground-based inversion starts lifting, but an elevated inversion above the discharge point (stacks) might remain preventing the plume from moving upwards. Instead the plume will be brought down near to the surface leading to high ground level concentrations especially during days 1 and 2. On the other hand on day 3 the mixing height extended much higher compared to the previous days, which led to more dilution and lower concentrations.

The concentrations from traffic ranged from 20μg/m$^3$ to 60μg/m$^3$ but those from industries ranged from 40 to 170μg/m$^3$. The highest concentration (about 200μg/m$^3$) due to both sources was noted on day 2 because it seems there is more pollution brought from aloft (stacks) to ground on that day. The mixing height ranges from 200 to 600m and tends to get higher after sunrise (0700 hour). It is also noted that on day 3, hour 0800, the ground concentration is the lowest among these morning hours because of higher wind speeds and mixing height. In addition, the community/residential area is affected much more by the industrial emissions than that due to traffic especially on days 1 and 2.

**Transition period (09:00, 10:00 and 11:00 hours):**

During this time the contribution from traffic to the highest concentration (<15%) is negligible compared to that from industries (>85%) because the wind speed and mixing height have become higher compared to previous hours which dilute the emission from traffic and reduce the plume rise from stacks causing more impact from industrial sources. The ground level concentration is very much diluted due to both thermal
turbulence (caused by heating of the air at ground level) and mechanical turbulence (wind speed and surface roughness) especially during days 1 and 2. For example on day 2 there is a stronger wind speed and higher mixing height, which lead to lower ground concentrations compared to on other days. The maximum ground level concentration of NOx (about 200μg/m³) due to both sources (mainly from industries) is noted on day 3. The mixing height ranged from 300 to 1400m.

Noon and after noon hours (12:00, 13:00 and 14:00 hours): During these hours, the contribution from traffic (<15%) to the highest concentration is very low unlike that from industries (>85%), which varies from 70 to 120μg/m³. The wind speed usually is strong (>5m/s) at these times due to a sea breeze effect, i.e. the wind blowing from the sea toward the land, and the mixing height is reaching its maximum level of about 2100m over land. The emissions from both sources (traffic and industries) are more likely to be diluted during this period because of the higher wind speeds, mixing heights and increased chemical oxidation of NOx to nitric acid (HNO₃). However, the concentrations due to industrial sources are actually quite high (especially for day 3)

Evening hours (18:00, 19:00 and 20:00 hours): During this time (sunset) the wind speed and mixing height start decreasing and the sea breeze effect has started to break down as the wind direction changes to become approximately parallel with the coast. There is no dominating source although traffic impact seems slightly higher than that from industries especially during days 2 and 3. The maximum concentration from traffic is about 90μg/m³ (on day 3), from industries is about 80μg/m³ (on day 1) and the maximum from the combined effects is 110μg/m³ on the third day. It seems that inversion layer at YIC usually starts forming after sunset and disperses after sunrise.
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Figure 5.7: Predicted ground level NO\textsubscript{x} concentration from Traffic, Industries and combined sources for various hours of day 1 (April, 26, 2008). Isopleths with 2m wind (Left plots), isopleths with 100m wind (middle plots) and isopleths with mixing height (right plots).
Figure 5.8: As for figure 5.7 except for day 2 (April, 27, 2008).
Figure 5.9: As for figure 5.7 except for day 3 (April, 28, 2008).
5.6.1.2 Case B (March 25-27, 2009):
For this case simulations have been carried out for a workday (day 1: Wednesday) and a weekend (Days 2 and 3: Thursday and Friday, respectively) during the period of March 25-27, 2009. For each day, three runs were completed: run#1 only traffic emissions; run#2 only industries and run#3 the combined affect of both sources. The same number of sources considered in the previous case is taken for this case, except that the emission rates for traffic and power plants were different. As explained earlier, the traffic density at the weekend (day 2 and 3) is relatively low during morning hours and high in the afternoon and evening times because people usually returning from other places to YIC during these hours. The predicted 1-hour NO\textsubscript{x} concentrations in the form of isopleths due to the various sources are presented in figures 5.10-5.12.

Night hours (01:00, 02:00 and 03:00hour):
After midnight an inversion layer usually formed accompanied with a limited mixing height, and thus the air is relatively stagnant; i.e. characterized by calm wind conditions. The impact from automobiles on the NO\textsubscript{x} concentrations is minor compared to that of industries, unlike in the previous case, since during the weekend there is less traffic density. The contribution from traffic to the maximum concentration is less than 30% on all three days whereas that from industries exceeds 70%. The mixing height above the industrial area is very low (about 80m), which means some of the stacks with heights lower than 80m affect the ground concentrations, but higher stacks probably will not because the emitted NO\textsubscript{x} will likely be trapped aloft due to the inversion layer. Further, it can be noted from the figures that the wind speed and direction at the surface and 100m in height are similar, although the wind speed at 100m height is slightly higher. The mixing height remains shallow (ranging from 80m to 330m) over the entire domain for much of the night hours. Further, it is generally noted that a gradual increase in the mixing height occurs as one goes from the coast out into the sea during these times of the day. There is also an area of high mixing height over the land towards the east of the domain for days 1 and 2. Maximum concentration isopleths due to both sources combined (traffic and industries) range between 20 and 110μg/m\textsuperscript{3}.

Early morning hours (06:00, 07:00 and 08:00hours):
The figures show that during these morning hours there is a land breeze with fairly low wind speeds. Further, there is not much difference in the wind speed and direction between the three days both at the surface and at 100m and the mixing height remains shallow ranging from 80 to 500m. The contribution from traffic to the maximum is moderate (>40%) on day 1 (weekday) to low (<15%) on days 2 and 3 (weekends).
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compared to that from industries. The maximum concentration due to traffic is concentrated near intersections and road sides, whereas the maximum concentrations due to industries tend to be located over the sea due to the wind direction, except for day 2 when the wind speed is very low. "Hotspots" due to industrial emissions were formed on day 1 and to a lesser extent on day 3, which were probably created due to unstable conditions near the ground and stable conditions aloft. This can lead to a process called fumigating, which usually takes place after sunrise when the inversion condition is broken up bringing NO\textsubscript{x} from aloft to near the ground. Fumigation phenomenon usually occurs in coastal industrial areas during mid-morning hours when the plume is released just under an elevated inversion layer and convective boundary layer begins to grow beneath it and draws the pollution down near ground causing high air pollution concentration.

The concentrations due to traffic ranged from 20\(\mu\)g/m\(^3\) to 80\(\mu\)g/m\(^3\) and that from industries ranged from 70 to 200\(\mu\)g/m\(^3\). The highest concentration (about 220\(\mu\)g/m\(^3\)) was noted on day 1 and was due mainly to industries. The impact on the residential area is minor during these hours unlike in the previous case.

**Transition period (09:00, 10:00 and 11:00 hours):**
During this time the contribution from traffic is even lower (<10%) of the maximum value compared to that from industries (>90%) due to the relatively high wind speeds, which dilute the emission from traffic and reduce the plume rise from stacks causing more impact from industrial sources. It seems on day 1 at hour 9 there is convergence at the surface with the wind direction being northeasterly over the sea and southwesterly over the land, which probably leads to lower ground level concentrations (a maximum of 50\(\mu\)g/m\(^3\)) from both types of sources. On days 2 and 3 the impact from the industries is dominant because the inversion layer was broken down further by thermal convective and the plume probably loops downwards towards the surface. The highest ground level concentration of NO\textsubscript{x} (about 250\(\mu\)g/m\(^3\)) is noted on day 2 and is mainly due to industries. It is accompanied with a mixing height of about 350m. The concentration on day 3 was lower (180\(\mu\)g/m\(^3\)) with a higher mixing height of 700m.

**Noon and after noon hours (12:00, 13:00 and 14:00 hours):**
During these hours the wind speed is usually strong (>5m/s) and the wind speed and direction (westerly sea breeze) at the surface and at 100m aloft are similar. The mixing height is relatively shallow (<400m) over the sea and deep (>1300m) over the land. Clearly there is a stronger wind speed and higher mixing height, which leads to more
dilution from both sources (traffic and industries). The contribution from traffic (<15%) to the highest concentration is similar to that of the previous case, but the impact from industries (>85%) was high and varied from 20 to 110μg/m³. The maximum concentration during day 3 (Friday) was slightly lower than that of the previous case (Monday) because emission rates are lower especially from power plants since power consumption is less during weekend.

Evening hours (18:00, 19:00 and 20:00 hours):
Strong wind speeds continue during these hours although with relatively lower mixing heights (about 300m). The mixing height values for day 2 at hour 19 are same (50m) over the entire domain. The impact of the industries is generally higher than that of traffic for all 3 days at this time. The maximum concentration from both sources (traffic and industries) is about 60μg/m³.

It is clear from the predicted results for both cases that the maximum 1-hour values due to both sources during weekdays (340μg/m³) and weekends (220μg/m³) are much lower than the Saudi Arabia ambient air quality standard of 660μg/m³ but they are slightly higher than European ambient standard of 200μg/m³ which cannot be exceeded more than 18 times per calendar year. Further, the community area is usually affected very much by industries during mid-morning hours (07:00 – 10:00) when the wind direction shifting from land breeze to sea breeze and when the Fumigation phenomenon takes place.
Figure 5.10: As for figure 5.7 except for day 1 (March, 25, 2009)
Figure 5.11: As for figure 5.7 except for (March 26, 2009).
Figure 5.12: As for Figure 5.7 except for day 3 (March 27, 2009).
5.6.1.3 Evaluation of Model Performance for NO\textsubscript{x} prediction:
The performance of the CALPUFF predictions for NO\textsubscript{x} is evaluated using some statistical indices (explained in section 5.5) calculated from the observed and predicted timeseries at two monitoring sites during April 26-29, 2008 and March 25-27, 2009. Further, model results due to industrial emissions alone and due to combined sources (industries and traffic) are compared with observations at two sites to evaluate the predictions and to determine the contributions of each type of source to the ground level concentration of NO\textsubscript{x} (figures 5.13 and 5.14).

Hourly variations of predictions and observations of NO\textsubscript{x} concentrations:
By comparing the predictions and observations at site#1 and site#3, as shown in figures 5.13 and 5.14, the following can be noted:

- From midday on day 2 onwards there is general agreement between predictions and observations of NO\textsubscript{x} concentrations at both sites (site#1 is very close to the road and site#3 is about 1100m away from the road).
- However, for site#1 CALPUFF slightly over-predicts the maximum concentration at the end of day 1 and for day 2, but underpredicts it on day 3 and in the morning of day 1. The prediction of maximum concentration at site#3 is generally high compared to the observations, except for the afternoon peak on day 2, which is very close to that observed. Outside of the peak concentration times the predicted values are generally near zero whilst significant background concentrations or even large peaks (early on day 2) were observed by the instruments.
- The main contributor to the NO\textsubscript{x} ground level concentration at site#1 is the traffic sources, as this site is very close to the road. In contrast, at site#3 the contribution of industries is dominant compared to traffic because this site is located downwind of the industries and it is relatively far from the road (1100m away).
- It seems that the background ambient concentrations during certain hours (especially after noon hours) are negligible at site#1. Further during these hours there will be strong chemical reactions between NO\textsubscript{x} and HC in the presence of sunlight, which results in the formation of O\textsubscript{3} and the reduction of NO\textsubscript{x} levels.
- Clearly there are many low predicted values compared to the observations, which are probably due to either unidentified sources or/and emissions from sources that are not properly quantified.
- There are several maximum observed concentrations (such as site#1: day 1, hour 6 and hours 23 (day 1) to 9 (day 2); site#3: day 2, hour 1), which were not predicted by the model. One possibility is that this is caused by the simulated plume missing
the receptors due to incorrect value in wind direction. A mis-match between the observed and predicted wind direction is evident for the latter two periods, but not for the first (day 1) period when the simulated wind direction is quite close to that observed.

The results for case A (site#1) indicate that when the wind direction is blowing from the direction of the road (290 to 130° clockwise) the predicted NOx concentrations increase along with the observed values, but when the wind direction is blowing from the direction of the industries (130 to 280° clockwise) the predicted values do not increase, whereas the observed values do. This probably means that the emission rates from some industries may not be considered or quantified properly during this case.

On the other hand at site#3 when the wind is blowing from the direction of the industries and traffic (110 to 290° clockwise) the predicted concentrations of NOx increase along with the observations. However, when the wind is blowing from the desert side (300 to 100° clockwise) the predicted concentrations decrease, but the observed concentrations are usually significantly higher due to probably long-range transport of NOx. This suggests that the background levels due to some unidentified sources are not considered in the simulations.

The discrepancy between the predictions and the observations of NOx at the same time and location might be due to two main reasons. Firstly, there could be some unidentified emission sources (such as ground flaring) within the study domain, which are not considered, or it could be that the emissions rates from some industries were not well quantified. Secondly, there are some inaccurate values in the simulated wind direction input into CALPUFF as clear from figures 5.13 and 5.14 (bottom graphs). This may cause high differences, as suggested by US-EPA (2003) where it was stated that an uncertainty of 5 to 10 degrees in the wind direction can cause an error of 20 to 70% in predicted concentration for a particular time and location, depending on the stability and station location.

Further, that study indicates that even with a perfect model, there are likely to be deviations between the predictions and the observations in individual repetitions of the event, due to variations in the unknown conditions (error in the observations or error in the input data). Available evidence suggests that this source of uncertainty alone may cause a typical range of variation in concentrations of up to +/-50%. US-EPA also indicated that errors in the highest predicted ground level concentrations of +/-10 to 40% are found to be typical.
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Fig. 5.13. Hourly observed and simulated NOₓ level (top) and wind direction (bottom) at site 1 for case A (April, 26-28, 2008).

Fig. 5.14. Hourly observed and simulated NOₓ level (top) and wind direction (bottom) at site# 3 for case B (March 25-27, 2009).
Statistical analysis:
For evaluating the performance of CALPUFF in predicting NO\textsubscript{x} concentrations for the two cases several statistical parameters were computed based on the timeseries of observations and predictions at sites 1 and 3 shown in figure 5.13 and 5.14. The statistics include the maxima, means, fractional bias (FB), Normal Mean Square Error (NMSE), the index of agreement (IA) and the level of agreement within a factor of two (Fa2). Based on the statistical results shown in table 5.5, the following can be noted:

- The values of fractional bias range between 0.75 and 1.06 for site#1 and between -0.1 and 0.4 for site#3 indicating that the model tends to under-predict because negative values of FB mean a model over-prediction and positive values indicate a model under-prediction. Kumar et al. 1999 stated FB should lie within -0.5 ≤ FB ≤+0.5 for acceptable modeling results and for an ideal model FB=0.0. The majority of the results at site#1 fall outside of the required range, but the values at site#3 are meeting the criteria.

- The Normal Mean Square Error (NMSE) lies between 1.7 and 3.2 for site#1 and between 1.1 and 1.6 for site#3. Kumar et al. 1999 suggested that the NMSE should be ≤ 0.5 for acceptable modeling results and NMSE=0 for an ideal model. The NMSE results at both sites are beyond the required range indicating that the predictions and observations are not in good agreement with each other for many hours.

- The Fa2 varies between 0.2 and 0.4 for both sites, which is not meeting the acceptable criteria of Fa2 ≥ 0.8 suggested by Kumar et al. 1999.

- The IA values of the predicted and measured timeseries of NO\textsubscript{x} varies between 0.61 and 0.72 at site#1 and between 0.31 and 0.63 at site#3, which indicates fairly good correlation of the predicted and measured data for most days, especially at site#1. IA values always lie between 0 and 1, with 0 indicating absolutely no agreement between the prediction and observation and 1 denoting perfect agreement.

- The maximum predicted concentrations of NO\textsubscript{x} are over predicted at both sites, except for day 3 for site#1. The errors in the maximum predicted concentrations for all days (except day 3) for the both cases are within a range of ≈40%. US-EPA suggested that errors in the highest estimated concentrations of +/-10 to 40% are found to be typical. The daily averaged prediction values are lower than observed especially at site#1 where there are differences of more than 65%. The differences for site#3 are much lower and some values are relatively close to the observations.
Generally it seems that CALPUFF tends to under-predict the daily average values and over predict the maximum 1-hour concentrations at both sites. Predicted NO\textsubscript{x} concentrations correlate fairly acceptably with the measured values except when wind speeds are low or the wind directions are inaccurate because predicted values are very sensitive to the wind (especially direction).

Table 5.5: Statistical analysis results of model performance evaluation of NO\textsubscript{x} concentration for Case A and Case B. (Units in \textmu g/m\textsuperscript{3})

<table>
<thead>
<tr>
<th></th>
<th>Max Pred.</th>
<th>Max Cp/Co</th>
<th>Mean Pred.</th>
<th>Mean Cp/Co</th>
<th>FB</th>
<th>NMSE</th>
<th>FA2</th>
<th>IA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CASE A (Site#1)</strong></td>
<td></td>
<td></td>
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<tr>
<td>Day1</td>
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<td>50</td>
<td>0.46</td>
<td>0.75</td>
<td>1.7</td>
<td>0.3</td>
<td>0.72</td>
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<tr>
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<td>225</td>
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<td>24</td>
<td>0.32</td>
<td>1.06</td>
<td>3.2</td>
<td>0.2</td>
<td>0.63</td>
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<td>Day 3</td>
<td>66</td>
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<td>0.40</td>
<td>0.88</td>
<td>2.1</td>
<td>0.3</td>
<td>0.61</td>
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<td><strong>CASE B (Site#3)</strong></td>
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<td></td>
</tr>
<tr>
<td>Day1</td>
<td>42</td>
<td>1.4</td>
<td>11</td>
<td>0.65</td>
<td>0.4</td>
<td>1.6</td>
<td>0.3</td>
<td>0.31</td>
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<td>1.10</td>
<td>-0.1</td>
<td>1.1</td>
<td>0.4</td>
<td>0.63</td>
</tr>
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</table>
5.6.2 Towards Particulate Number Predictions:

Prediction of particle numbers using a sophisticated model such as a Computerized Fluid Dynamic (CFD) model over the micro-scale (<1km such as street canyon) could be possible. Examples of the usage of a CFD model in simulating the formation of the aerosol distribution in the exhaust plume of traffic over the micro-scale is given by Gidhagen et al., (2004) and also in Albriet et al., (2010) for a CFD code coupled to an aerosol dynamic model. This technique (CFD) requires long computational times and expensive hardware/software resources. Gidhagen et al., (2005) used a three-dimensional dispersion model (MATCH) to simulate the total particle number over the urban scale (35km×35km) and the simulation results and observations were in fairly good agreement, except for overestimated peak values, which are caused by uncertainties in the model (such as the long range transport of aerosol, the simulation of deposition losses). Further, the study by Gidhagen et al. (2005) is lacking some aspects such as particle growth due to the condensation of gases and the prediction of particles of different sizes.

Predicting the numbers of particles of different sizes over time and over the meso-scale (10s-100s km) during different weather conditions is very challenging. Various aerosol removal and formation processes, dynamic and non-dynamic processes (such as deposition, coagulation, nucleation, chemical reaction, etc) influence the particle number and complicate the process further. Therefore, it was decided in this study to derive the particle numbers of different sizes from the NO\textsubscript{x} prediction of the CALPUFF model as there is a fairly good linear relationship between both parameters. The correlation between NO\textsubscript{x} and particle number is fairly good, as established in chapter 2, because both parameters have similar sources (traffic and industries). However, the constant of proportionality (the slope of the linear relationship) may change with distance from the source because particles will undertake several processes such as deposition and coagulation that affect particle numbers and size. For example, deposition of vapour onto the particles (e.g. organics, nitric acid or sulfuric acid) can cause the particles to grow from nucleation mode size (<40nm) to larger size particle (>40nm) and this process may be dominant. Other processes such as condensation and evaporation, may also change the size of the particles (indirect removal processes), but they do not change the total number of particles. It would be expected that the number of particles at nucleation mode size (7-40nm size) might decrease with distance from a source due to the above processes (mainly coagulation and sometimes deposition) and so the slope factor might be expected to decrease (fewer particles for a given NO\textsubscript{x} concentration). This was the case for the observations shown in chapter 2 where the slope values for sites 1 and 3 were 834 and 754 respectively and the distances of these sites to road are 100m and 1100m respectively.
Zhu et al., (2002a) noted that small particles may grow by condensation and coagulation and shift towards larger diameters with increasing distance from the roads. However, this may not always be the case if there is weak coagulation process and occurrence of significant particle nucleation at downwind.

On the other hand, the total particle number of full size (7nm-10μm size) might increase with distance from the source as shown in table 2.8 of chapter 2 where the slope increase from 917 at site 1 to 1225 at site 3 due to some of the above processes (mainly nucleation) as well as the impact of other sources (industries) on the site 3.

Sometimes particle number has a different source than NOx and so the intercept in the linear regression formula is necessary. Such sources could be due to other air pollutants (such as SO2) or from dust from the unpaved road or desert. It is very difficult to apply one regression formula for the entire domain because each grid point in the domain has various sources and is located at a different distance from the sources. Therefore, there will always be some error introduced if we apply only one formula.

5.6.2.1 Sensitivity analysis:
Linear regression formulae for estimating number concentrations of particles of different sizes were derived in chapter 2 based on the actual measurements of NOx and particle number at site#1 and site#3. With these findings different options will be evaluated to determine which formula can be applied over the entire domain to give a reliable prediction of particle numbers for two sizes (7-40nm and 7nm-10μm) with the lowest possible error. This sensitivity analysis will concentrate more on the nano-particles where most of the number (>80%) exist as concluded in chapter 2 and noted by other studies (Rodriguez et al 2007 and Mejia et al 2008). One of the following options will be applied over the whole domain:

- **Option 1**: Linear regression formula derived at site#1;
- **Option 2**: Linear regression formula derived at site#3;
- **Option 3**: Average of the linear regression formulae of sites 1 and 3;
- **Option 4**: A formula based on the interpolation and extrapolation of the linear regressions formulae for site#1 and site#3 based on the distance between each site and the road.

### Site#1:
It is clear from figure 5.15 that all three formulae (site#1, site#3 and average) produce a very similar time variation of the particle number at site#1. However, when the particle number concentration at site#1 is very low the percentage differences from the site#1
numbers become high for both applied formulae (site#3 and average) although the site 3 formula gives double the percentage difference compared to that of the average formula. This would be expected since the combined formula incorporates the site#1 linear regression values. The percentage difference ranges between less than 10% up to 45% when the average formula is used, but is double these percentage values when the site#3 formula is used at site#1.

![Site#1 (Size 7-40nm)](image)

Fig. 5.15. Particle number estimated using the linear correlation derived at site#1, site#3 and an average of both (top) and the percentage differences between the Site#3 formula and the one from site#1 and between the average formula and site#1 for case A.

**Site#3**

As is clear from figure 5.16, all three formulae (site#1, site#3 and average) again produce very similar time variation of the particle number estimates. The percentage differences are low when the concentration at site#3 is high, but reach 50% when the particle number concentration is low. The differences in this case are negative for both formula (site#1 and average) because the particle number at site#3 is lower than that of site#1. This also means that the percentage differences between the different formulae are greater for this site. The error is ranges between -5 and -25% when the average formula is applied and between -10 to -50% when the site#1 formula is used.
Interpolation and extrapolation:
A formula could be developed to approximate particle numbers for locations at a known distance from a road source based on the results from sites 1 and 3. Such a formula is estimated using interpolation and extrapolation (table 5.6) of the slope of the linear formulae for site#1 (100m away from road) and site#3 (1100m away from the road). However, the intercept was calculated as an average of the site#1 and site#3 values. This interpolation/extrapolation formula could be applied for each grid point within the YIC domain if the distances to the different sources (roads, industries, etc.) were known. However, in this study such information about the domain was not available during post-run processing. Also, the accuracy of the interpolation or extrapolation results cannot be verified as there are no actual measurements in between the sites or beyond 1100m from the road. Therefore, it is difficult to justify the use of the interpolation and extrapolation formula for this case.

Fig. 5.16. Same as Figure 5.15 except for site#3 for case B.
Table 5.6: Comparison of linear regressions of aerosols sizes ranges onto NO\textsubscript{x} concentration at sites 1 and 3

<table>
<thead>
<tr>
<th></th>
<th>Size: 7nm to 40nm</th>
<th>Size : 7nm-10\textmu m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site#1</td>
<td>PM\textsubscript{no}=834×NO\textsubscript{x}+4069</td>
<td>PM\textsubscript{no}=917×NO\textsubscript{x}+9273</td>
</tr>
<tr>
<td>Site#3</td>
<td>PM\textsubscript{no}=754×NO\textsubscript{x}+7853</td>
<td>PM\textsubscript{no}=1225×NO\textsubscript{x}+9047</td>
</tr>
<tr>
<td>Average of sites 1 and 3</td>
<td>PM\textsubscript{no}=794×NO\textsubscript{x}+5961</td>
<td>PM\textsubscript{no}=1071×NO\textsubscript{x}+9160</td>
</tr>
<tr>
<td>Interpolation and extrapolation formula*</td>
<td>PM\textsubscript{no}=834×NO\textsubscript{x}×(1-(0.01×distance/100))+5961</td>
<td>PM\textsubscript{no}=917×NO\textsubscript{x}×(1+(0.037×distance/100))+9160</td>
</tr>
<tr>
<td>Max percentage difference in low concentration</td>
<td>≈ 92%</td>
<td>≈ 3%</td>
</tr>
<tr>
<td>Max percentage difference in high Concentration</td>
<td>≈ 10%</td>
<td>≈ 33%</td>
</tr>
</tbody>
</table>

*Distance means distance from the affecting source (road) to the receptor

Based on the previous arguments, it was decided that the site\#3 linear formula would be more appropriate for particle number predictions for both sizes over the entire domain as this formula is likely to represent both the industrial emissions as well as that from traffic since it is further away from the road source than site 1. As we are more interested in the high concentration episodes the percentage differences between the values calculated using the different coefficients is likely to be low: below 10% for the smaller sizes (7-40nm) and up to 33% for the entire size range (7nm-10\textmu m). When the number concentrations are large the differences in the intercept value of sites 1 and 3 make a negligible contribution to the number concentration differences. Underestimates of particle number are expected near to roadsides using the site\#3 formula since the site 1 results suggest that at distances closer to roads a given NO\textsubscript{x} value correlates with a higher particle number than that predicted by the site 3 formula. Further errors may occur since it is unknown whether number concentrations would reduce further when moving beyond a distance of 1100 m (the distance of site 3) from the road. Also, here the variation with distance of particle numbers emitted by the industrial sources has not been measured or taken into account.
In chapter 2 the linear regression formulae derived for the YIC sites was compared with other derived formulae for some UK sites and it was found that the Site#3 formula has a higher slope than that of the TORCH1 (UK site) which represents a semi-urban area and is very much affected by London anthropogenic emissions. Both formulae (YIC and TORCH1) have a relatively close intercept for both particle size ranges (7-40nm and 7nm-10μm). The slopes at site#3 of 754 and 1225 #/cm\(^3\)/ppb of NO\(_x\) for size range of 7-40nm and 7nm-10μm, respectively, were much higher than those at TORCH1 of 485 and 580, which suggests that YIC is more affected by anthropogenic sources than TORCH1. One difference is that the measurements at TORCH1 for the higher size range went up to 650nm, but those at Site#3 went up to 10μm. Gidhagen et al (2004) studied the relation between total particle number (range of 20-450nm) and NO\(_x\) during summer and winter in a street canyon in Stockholm and noted the slope and the intercept are higher during winter (slope=388 #/cm\(^3\)/ppb of NO\(_x\) and intercept=8384 particle cm\(^{-3}\)) than during summer (slope=208 #/cm\(^3\)/ppb of NO\(_x\) and intercept=5757 particle cm\(^{-3}\)). The slope and intercept at Site#3 (see table 5.6) is also much higher than these results.

5.6.2.1 Case A (April 26, 2008):
Two particle sizes (7-40nm and 7nm-10μm) were estimated for April 26, 2008 (weekday; same case study (Case A) as for chapter 5) at four different times (01, 07, 12, 18hr) based on the CALPUFF NO\(_x\) predictions and linear regression formula for site#3 as shown in figure 5.17. These four different times (01, 07, 12 and 18hr) were chosen for the following reasons: lowest and highest traffic emissions are expected at midnight (01hr) and early morning (07hr) respectively and maximum solar radiation and maximum wind speed are expected at noontime (12hr) and after noon hour (18hr) respectively. All these factors (traffic count and meteorological conditions) play major role in the ground level concentrations for particle number and NO\(_x\). As is clear from figure 5.17 the peak concentration of particle number coincided with peaks in the NO\(_x\) concentration due to emissions from both sources (traffic and industries) as shown in previous figures (5.7, 5.8), as expected due to the linear relationship formula applied.

At 01 hour, which is representative of the night hours, the highest particle numbers of both sizes (7-40nm and 7nm-10μm; 120,000 and 250,000 #/cm\(^3\), respectively) are mainly due to traffic emissions when there are very low dispersion conditions (i.e. an inversion layer with minimum mixing height). Particle numbers of 10,000 #/cm\(^3\) (slightly above the background concentration of 9047 #/cm\(^3\)) are present over most of the domain before and during sunrise.
During the early morning hour (06hr), it seems that the contribution from industries becomes relatively high in addition to the contribution of traffic sources. It is clear from the figure that high concentrations were located near the road due to traffic and a way due to industries. The particle number concentrations were 100,000#/cm³ in the lower size particle and 140,000#/cm³ for the full size.

However, around noon time the total particle number (with maximum of 100,000#/cm³) is lower than that of previous times probably due to the affect of chemical reaction (ozone formation and NOx depletion). After noon hours (1800hr) it seems there is no dominating source although traffic impact seems slightly higher than that from industries because most of high particle number are concentrated near roads. The particle number concentrations of both sizes during this time are similar to that during early morning time.

The above results indicate that during the nighttime the main contributor is the traffic because of the low mixing height, which traps the emissions from traffic near to the ground and keeps the emissions from industries aloft. During daytime the main contributor is the industries because the emissions from the stacks will be brought to the ground by higher wind speeds which reduce the plume rise accompanied with unstable conditions.
Particle Size: 7-40nm  

Particle Size: 7nm-10μm

Day 1, Hour=01

Day 1, Hour=06

Day 1, Hour=12

Day 1, Hour=18

Fig 5.17: Particle number prediction for two sizes (7-40nm and 7nm-10μm) during April 26, 2008.
5.6.2.2 Case B (March, 27, 2009):

For this case, the particle numbers of two sizes (7-40nm and 7nm-10μm) are predicted for a weekend day (Friday) at different hours (03, 08, 11, 20hours). Again these times were chosen for the same reasons indicated in previous case except the time were shifted one to two hours from the previous case to cover more time range. The particle number is much lower during the night of this case (weekend) compared to that of previous case (workday) because of less traffic density. It is clear from figure 5.18 that during night times, morning and afternoon hours the particle number is about 80,000 to 90,000#/cm$^3$ in the 7-40nm size range and about 130,000 to 140,000 #/cm$^3$ for the 7nm-10μm size range. However, the highest predicted particle number was noted before noon time (11hour) and the concentration was about 150,000#/cm$^3$ in the lower size range (size 7-40nm) and was 240,000#/cm$^3$ in the entire size range (7nm-10μm). Therefore, the contribution of the lower sizes (7-40nm) to the particle number compared to that of the complete size range (7nm-10μm) is about 63% during high concentrations. However, this contribution percentage becomes higher when the particle number gets lower because the intercept of linear regression will have more weight. When the NO$_x$ level is negligible the contribution of the lower sizes (7-40nm) compared to that of the upper sizes (7nm-10μm) becomes 86%.

The main source of particle number for this case is industries as shown in the NO$_x$ prediction scenario section 5.6.1. The impact of traffic is minor because there is generally less traffic density during the weekend and when the traffic density is highest (during the afternoon) the surface wind speed is relatively strong, which dilutes the emission from low level sources (traffic).

Comparison between these predicted particle number concentrations of both sizes with other places worldwide will be discussed in section 5.6.3.
Chapter 5

Prediction of NO$_x$ and Particle Number Over YIC

Particle Size: 7-40nm

Hour=03

Hour=08

Hour=11

Hour=20

Particle Size: 7nm-10μm

Fig 5.18: Particle number prediction for two sizes (7-40nm and 7nm-10μm) during March 27, 2009.
5.6.2.3 Evaluation of Model Performance for Particle number prediction:
Predictions as well as observations of particle number concentrations at two monitoring sites were utilized to carry out a statistical model evaluation analysis. The evaluation of particle number predictions will be based upon time-series of both the predictions and observations. The statistical parameters (including FB, NMSE, FA2, I) that will be used in this analysis were defined earlier in section 5.4.

Hourly variations of predicted and measured particle number concentrations:
By comparing the predicted particle number concentrations of two sizes with the observations at site#1 and site#3 paired in time and space (figures 5.19 and 5.20), the following can be noted:

- The predictions and observations at both sites (site#1 is very close to the road and site#3 is about 1100m away from the road) are in general agreement for the times of the highest and lowest particle number concentrations for both site#1 and at site#3, respectively. A notable exception is during the early morning of day 2 for site#3 when there is a peak in the observed concentration, yet the predicted values are very low.

- The daily peak concentrations for both sizes are usually quite close to those of the observations and the timing of the maxima is reasonably close to that of the observations too, except for day 1.

- For site#1 elevated concentrations continued to be observed for a number of hours after the daily peaks, whereas the modeled values tended to drop off more rapidly after the peak.

- The agreement is very good from the second half of day 2 until the end of day 3 for site#3. However, the match for times prior to this was generally poor.

- For site#1, CALPUFF is slightly over-predicting the maximum particle number concentrations, but the general trend is for under prediction.

- There are several maximum predicted concentrations (such as site#1 hour 6 on day 1, and site#3, hour 17 on day 1), which are not observed. It could be the case that the predicted plume occurred, but did not hit the receptor location. The most likely reason for the simulated plume being different to that observed is errors in the simulated wind direction.

- The particle number is generally higher (up to ≈162,000#/cm³) at site#1 compared to that at site#3 (up to ≈56,000#/cm³) because the former site is more affected by traffic emissions, whereas the latter site is more affected by industries.
Fig. 5.19: Comparison of predicted particle number of sizes 7-40nm (top graph) and 7nm-10μm (bottom graph) with observations at site#1 during April 26-28, 2008.

Fig. 5.20: Same as figure 5.19 except for site#3 during March 25-27, 2009.
Statistical analysis for particulate number prediction:

Statistical analysis (FB, NMSE, IA and Fa2) was performed to evaluate the particle number predictions for two size ranges (7-40nm and 7nm-10μm) as derived from CALPUFF NOx predictions using the site#3 linear regression formula for the two cases. The following points can be noted based on the statistical evaluation results shown in Table 5.7:

- The maximum particle number concentrations are generally over-predicted at site#1 (except for day 3 for both size ranges) and under-predicted at site#3 by CALPUFF (except for day 1 for 7nm-10μm). The over prediction at site#1 ranges from 2 to 46% and the under prediction at site#3 ranges from 6 to 20%.
- The daily average of particle number of both sizes are under predicted at site#1 by up to 52% and over predicted at site#3 by up to 27% for both sizes.
- All fractional bias values for both sizes are meeting the criteria suggested by Kumar et al. (1999) for acceptable modeling results \(-0.5 \leq \text{FB} \leq 0.5\), except for one value for site#1, day 2, 7-40nm. The FB ranges between -0.2 and 0.7 for both sizes at sites 1 and 3.
- The Normal Mean Square Error (NMSE) lies between 0.6 and 1.7 at site#1 and between 0.4 and 0.6 at site#3 for both sizes. These results indicate that particle number predictions at site#1 are beyond the range suggested by Kumar et al. (1999) for acceptable modeling results (NMSE \leq 0.5), but the predictions at site#3 are mostly within the acceptable range.
- The Fa2 varies between 0.3 and 0.5 at site#1 and between 0.7 and 0.8 at site#3, except for day 3 for 7-40nm when the value is 0.5. These results show that the predictions at site#1 are not meeting the required criteria of \(\text{Fa2} \geq 0.8\) but the results at site#3 are either meeting the criteria or are close to it.
- The IA values for predicted particle numbers of both sizes range between 0.6 and 0.69 for site #1, which implies that there is fairly good correlation between predictions and observations. At site #3 the values are generally lower for days 1 and 2 being in the range 0.36-0.61, although they are higher for day 3 when they are 0.67 and 0.72 for the two size ranges.
- Site #3 actually has lower IA values despite better FA2 values on days 1 for both sizes and on day 2 for lower size (7-40nm). This perhaps suggests that the correlation is not that good, but that generally the predictions and observations were quite close – so perhaps the timing of the big events is not good due to probably inaccurate simulated wind direction data, but the overall mean differences are small.
Overall, the quantitative comparison of the model prediction and observation as shown in figures 5.18 and 5.19 and the statistical analysis presented in table 5.7 suggests that using the CALPUFF model and linear regression formula for YIC may overall give a reasonable prediction of particle numbers of both sizes (7-40nm and 7nm-10μm), especially for the high concentrations of the daily peaks. This is useful as such high concentration events are likely to be the times of the greatest interest. However, there were a few occasions when model peaks were predicted that were not observed to occur and vice versa.

Further, based on the statistical analysis results for both particle numbers and NO\textsubscript{x} it seems that the prediction of particle number is better than that of NO\textsubscript{x} due mainly to adding the background term (intercept) for the particle number predictions. Almost all statistical results improved after adding the intercept values for both sizes. For example for day 1 of case A the FB improved from 0.6 to 0.3 after adding the intercept for first size (7-40nm) and from 0.3 to 0.1 for the second size (7nm-10μm). NMSE improved from 2 to 1.2 for the first size and from 1.6 to 1.2 for the second size.

Table 5.7: Statistical analysis results of the model performance evaluation for particle number concentrations for sizes 7-40nm and 7nm-10μm and for Case A and Case B.

<table>
<thead>
<tr>
<th>CASE A (Site#1)</th>
<th>Particle size: 7-40nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Pred.</td>
<td>Max Obs.</td>
</tr>
<tr>
<td>Day1 134,921</td>
<td>126,425</td>
</tr>
<tr>
<td>Day2 98,966</td>
<td>96,746</td>
</tr>
<tr>
<td>Day3 34,497</td>
<td>60,835</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size: 7nm-10μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day1 215,490</td>
</tr>
<tr>
<td>Day2 157,076</td>
</tr>
<tr>
<td>Day3 52,334</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CASE B (Site#3)</th>
<th>Particle size: 7-40nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Pred.</td>
<td>Max Obs.</td>
</tr>
<tr>
<td>Day1 24,862</td>
<td>26,543</td>
</tr>
<tr>
<td>Day2 30,056</td>
<td>35,285</td>
</tr>
<tr>
<td>Day3 30,527</td>
<td>38,119</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size: 7nm-10μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day1 36,682</td>
</tr>
<tr>
<td>Day2 45,119</td>
</tr>
<tr>
<td>Day3 45,885</td>
</tr>
</tbody>
</table>
5.6.2.4 **Comparison of predicted particle number at YIC with other studies:**

It is interesting to compare the predicted (and observed) particle number concentrations over YIC with other values observed elsewhere worldwide. Table 5.8 shows a comparison between the particle number concentrations of two sizes (7-40nm and 7nm-10um) predicted in this study with some typical values and observations conducted at other places. The main difference between this study and others is in the particle size ranges. The measurements at YIC for the higher size range went up to 10μm. The upper limit of other studies is sometimes up to only >500nm, but this difference may not affect the total particle number much because more than 90% of the total number is noted to be in the ultrafine sizes. However, the lower size range at YIC was up to 40nm, but some other studies have a lower range of up to 20nm and this may cause significant difference in particle number values between the YIC study and the others, which should be borne in mind for this comparison.

The hourly maximum and daily average concentrations at all four sites of YIC were calculated over the study period (April 26-28, 2008 and March 25-27, 2009). The locations of these four sites are shown in the figure 5.21. It is clear that site#1 is very close to the traffic road, site#2 is located inside the heavy industrial area (restricted area with less traffic density) and affected more by industries and long range transport particles while site#3 represents urban background and is located downwind of the industrial emissions and located 1100m away from traffic road. Site#4 represents the community area and is affected by both industries as well as traffic. It is clear from table 5.8 that there are observed and predicted values at site#1 and site#3 whereas at the other sites only predicted values are available. The errors in predictions at site#1 and site#3 could reach up to 46% and 21% respectively as discussed in the previous section. However, in this section the predicted values at all four sites will be used for comparison with other studies bearing in mind this percentage error range.

* a. **Full size range:**

The hourly maximum and daily average concentrations of particle number (215,490#/cm$^3$ and 27,597#/cm$^3$, respectively) at site#1 are higher than those at the other sites of YIC because this site is very close to the road and affected very much by traffic emissions. The average concentrations at all YIC sites are much higher than the typical value for rural area (1000#/cm$^3$-10,000#/cm$^3$), but they are within the range of urban typical value (>10,000#/cm$^3$). Further, the daily average concentrations of particle number at site#1 (27,597cm$^{-3}$) are about 1.5 to 2 times higher than those at other YIC sites. The daily
average value at site#1 is relatively similar to those noted in other studies for urban sites (Erfurt, Alkmaar, Copenhagen). However, the hourly maximum particle number concentration for the full size range at site#1 (215,490#/cm$^3$) was higher than those at other urban sites except at in Beijing (248,700#/cm$^3$). The average and the maximum concentrations of particle number at Beijing city (32,800#/cm$^3$ and 248,700#/cm$^3$ respectively) are higher than those at all YIC sites and the other urban sites in Table 5.8. The particle number concentration at site#4, which represents the community area, has a very similar average level (16,606#/cm$^3$) to that of Helsinki, but a slightly higher maximum (165,458#/cm$^3$ compared to 145,000#/cm$^3$).

Figure 5.21. Locations of four sites over YIC map

b. Lower size range:
The hourly maximum and daily average particle number concentrations at site#1 for this size range were the highest among the YIC sites. The daily average concentrations at YIC sites (for size of 7-40nm) ranged between 10,855 at site#2 and 19,271 at site#1 and the hourly maximum ranged between 134,921 at site#1 and 30,527 at site#3. However, the average values for other urban cities elsewhere for the lower size range (3-20nm) are less than 10,000 and the maximum is 196,000 noted at Beijing city.

As for the health effects of particle number, many studies (Delfino et al., 2005; Oberdorster et al., 2005) have demonstrated that ultrafine particles are harmful to human health and can also damage DNA (Moller et al., 2008). However, none of these studies has defined an ambient standard for particle number. It is interesting to derive a value for the full size range particle number based on the linear correlation between NO$_x$ and
particle number (PMno\(=1225\times\text{NO}_x+9047\) for 7nm-10\(\mu\)m, as discussed earlier for site#3) and the national ambient standard for NO\(_x\) (660ug/m3) or the EU standard of 200ug/m3. Thus the corresponding particle number limit for the full size range is 817,547#/cm\(^3\) if the national standard is applied and 254,047#/cm\(^3\) if the EU ambient NO\(_x\) standard is used. These values are extremely high compared to those observed at the various locations in Table 5.8 and suggest that, if particle number and NO\(_x\) concentrations do correlate as suggested, then the particulate number should be taken into account when setting NO\(_x\) limits. Further, if the correlation holds then it seems likely that the current NO\(_x\) limits would allow probably dangerously high particulate concentrations. However, there are uncertainties in how well the correlation would hold at very high NO\(_x\) levels since such values were not measured in this study.
### Table 5.8 Comparison of predicted (and measured) PM_{no} at YIC sites with other studies

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Site type</th>
<th>Concentration Range (#/cm^3)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Nucleation</td>
<td>Total number</td>
</tr>
<tr>
<td><strong>Particle number prediction over YIC</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>7-40nm</strong></td>
<td><strong>7nm-10um</strong></td>
<td></td>
</tr>
<tr>
<td>YIC, Site#1</td>
<td>Traffic road</td>
<td>Avg=19,271</td>
<td>(32,654)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max=134,921</td>
<td>(126,425)*</td>
</tr>
<tr>
<td>YIC, Site#2</td>
<td>Industrial area</td>
<td>Avg=10,855</td>
<td>13,924 Avg=</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max=48,639</td>
<td>75,311 Max=</td>
</tr>
<tr>
<td></td>
<td>Urban background</td>
<td>Avg=13,185</td>
<td>17,710 Avg=</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max=30,527</td>
<td>(38,119)*</td>
</tr>
<tr>
<td>YIC, Site#4</td>
<td>Urban Community</td>
<td>Avg=12,505</td>
<td>16,606 Avg=</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max=104,126</td>
<td>Max=165,458</td>
</tr>
<tr>
<td><strong>Particle number measurements at other sites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical value</td>
<td>Rural area</td>
<td>-</td>
<td>1,000 – 10,000</td>
</tr>
<tr>
<td>Typical value</td>
<td>Urban area</td>
<td>-</td>
<td>&gt;10,0000</td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>3-20nm</strong></td>
<td><strong>3nm-10um</strong></td>
<td></td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Road</td>
<td>Avg=9,000</td>
<td>Avg=32,800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max=196,000</td>
<td>Max=248,700</td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>3-20nm</strong></td>
<td><strong>3-800nm</strong></td>
<td></td>
</tr>
<tr>
<td>Leipzig, Germany</td>
<td>Road</td>
<td>Avg=9850</td>
<td>Max=21,377</td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>3-20nm</strong></td>
<td><strong>3-2500nm</strong></td>
<td></td>
</tr>
<tr>
<td>Pittsburgh, USA</td>
<td>Urban area</td>
<td>Avg=9700</td>
<td>Max=21,988</td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>10-700nm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copenhagen,</td>
<td>Highway</td>
<td>-</td>
<td>Avg (30min) =24,900</td>
</tr>
<tr>
<td>Denmark</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copenhagen,</td>
<td>Urban</td>
<td>-</td>
<td>Avg(30min) =27,100</td>
</tr>
<tr>
<td>Denmark</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diameter range</strong></td>
<td><strong>10-500nm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helsinki, Finland</td>
<td>Urban area</td>
<td>-</td>
<td>Avg=16,600</td>
</tr>
<tr>
<td>Erfurt, Germany</td>
<td>Urban</td>
<td></td>
<td>Avg=26,200</td>
</tr>
<tr>
<td>Alkmaar,</td>
<td>Urban</td>
<td></td>
<td>Avg=26,000</td>
</tr>
<tr>
<td>Netherlands</td>
<td></td>
<td></td>
<td>Max=118,000</td>
</tr>
</tbody>
</table>

*Note: Values in brackets are measurements*
5.7 Limitations and Uncertainties in modeling predictions:

The accuracy of modeling predictions generally depends on several factors; mainly these are the quality of the input data, accuracy of the model, boundary conditions and meteorological data used for initialization, and the methodology etc. The CALPUFF model used in this study is the USEPA preferred and recommended model for near and far field sources. The justification for choosing this specific model was discussed in Chapter 1. However the uncertainties and limitations in using it for predicting NO$_x$ and PM$_{no}$ within the context of this work will be addressed hereunder.

**NO$_x$ prediction:**

There are several sources of uncertainties in NO$_x$ prediction mainly due to the following:

- Anticipated errors in source emission rates and source parameters (industries and traffic): In this study most emission rates were obtained from the stack testing reports of the facilities, whereas the emission rates for traffic were estimated based on the emission factor and traffic density as discussed at the beginning of this chapter. However, there are some secondary industries (e.g. chemical and gypsum plants, ground flares) with relatively low environmental impacts that were not considered in the input data as their information was not available for this modeling work. These sources likely do not cause large uncertainties in NO$_x$ prediction (probably <10%). However during certain weather conditions, especially when the wind direction from these sources is toward the sampling site, their impacts may become relatively higher.

- Anticipated error in the meteorological input data from WRF: The statistical results for evaluating surface and upper air predictions showed that the WRF predictions are generally good except that the wind direction and wind speed have relatively high bias during the transition period (8-11am) for some cases, which may lead to some errors in the NO$_x$ predictions. This source of error may cause large uncertainties in the predictions compared to the observations especially when the simulated plume had missed the receptor location. Therefore, for any future work, observations of data over land and sea should be introduced alongside the WRF input to improve the meteorological inputs to CALPUFF and eventually reduce the uncertainty on the NO$_x$ prediction.

- Inappropriate dispersion model: The CALPUFF model was developed (Scire et al., 1990a, 1990b) to handle some important situations such as complex terrain and/or complex meteorological conditions (such as calm wind and coastal plume fumigation which is a characteristic of YIC). However, Holmes et al (2006) indicated that the main disadvantage of CALPUFF is that the model does not
include any modeling of particle dynamics and it is not recommended for modeling secondary particles (arising from SO$_2$ and NO$_x$ mediated reactions) within less than 10km from the source. This may cause slight overestimation for short-term predictions at receptors (such as sites#1 and 3) relatively close to the sources (<10km), although it is unlikely to affect our NO$_x$ prediction by much since our assumption for NO$_x$ loss was ~8.7%/hr.

- Error in actual measurements used as input or those used for comparison with the modeling outputs to evaluate the modeling results: this source of error is likely to be minimized here because all observations used in this study were quality assured data. In our study we used observations from two sampling sites to evaluate and assess the uncertainty in the modeling results. However, alternative techniques can be applied as described by Fuller G. and Green D. (2006). Those authors used the GUM (Guide to the Expression of Measurement Uncertainty in measurements) approach (ISO, 1995) to link the output quantities with the inputs in order to link the uncertainty in the inputs to the uncertainty in the outputs.

The overall evaluation for NO$_x$ predictions using statistical indices showed that the CALPUFF model tends to over-predict hourly NO$_x$ concentrations, but under-predict the daily average. These differences between predictions and observations could be narrowed if the above limitations were solved.

**The limitation of PM$_{no}$ prediction:**

Many studies (Harrison et al, 1997, Deacon et al, 1997; Kukkonen et al 2001; Fuller et al, 2002; Fuller G. Green D. 2006) emphasized the relationship between NO$_x$ and particulate mass concentration. Deacon et al (1997) noted that the correlation coefficient between both parameters may reach higher than 0.5 during winter but may drop during summer. Another study by Kukkonen et al (2011) concluded that the PM$_{10}$ predictions are relatively good for the annual average of PM$_{10}$ with an FB range of -0.05 to 0.09 and an IA of >0.85, but the hourly predictions were worse. However, it is worth mentioning that the prediction of particle mass is different from that of particle number because particle mass is mainly concentrated in larger particles (>1µm), but particle numbers are mainly present at lower particle sizes (<40nm), as explained in chapter 2. Further, unlike mass concentration, particle number is not conservative and may change dramatically via some processes (mainly nucleation and coagulation). In our study we develop a correlation between NO$_x$ and particle numbers for different sizes instead of particle mass concentration as detailed in previous studies. Our results showed a strong correlation between PM$_{no}$ and NO$_x$ as discussed earlier in chapter 2. However, this derived
correlation between both parameters may have some limitations, which eventually may lead to under or over prediction of the PM\textsubscript{no} concentrations. Further, the PM\textsubscript{no} prediction in this study will almost certainly be affected by any anticipated error in NO\textsubscript{x} prediction because both parameters are correlated based on the derived linear regression formula. There are several limitations in PM\textsubscript{no} prediction that are listed below:

**1:** The PM\textsubscript{no} prediction accounts mainly for NO\textsubscript{x} related emissions although the intercept in our linear regression formula may take into account the particle numbers related to some other pollutants and sources. However, the percentage error in our correlation formula compared to observations ranged from 2\% up to 46\%. However, if there is any change in fuel type used by industries and/or traffic and/or change in the emission control technology used by industries and/or traffic to reduce the NO\textsubscript{x} emissions, then this relationship between NO\textsubscript{x} and PM\textsubscript{no} may change accordingly and therefore our regression coefficient may also need re-evaluation. For example, if a facility changed its fuel from gas to diesel, the NO\textsubscript{x} emission would probably remain the same, but the particle number and size would be different and this will affect our correlation formula. On the other hand, particles which are natural in origin (such as sea-spray or wind-blown soil dust) may not affect the particle number prediction notably, but will play major role in particle mass concentration.

**2:** Our linear regression formula between NO\textsubscript{x} and PM\textsubscript{no} was based on measurements that may not have taken into account all of the changes in atmospheric processes due to relatively short periods of measurement (with a maximum of two months at each site). Our measurements did not cover the summer and winter months, which probably means that some physical and chemical processes (mainly nucleation, coagulation, chemical transformation and dry and wet deposition) are not likely to have been taken into consideration. For example, during summer months there will be higher relative humidities and ambient temperatures. Higher relative humidity may lead to an increase in the number of nano particle, but not necessarily an increase the NO\textsubscript{x} emissions. Further, higher solar radiation in summer may increase new particle formation that is linked to the formation of OH via photolysis. Also, secondary particle formation due to SO\textsubscript{2} and hydrocarbon gas emissions may contribute much to the particle number and this was not included clearly in our regression formula. However, the intercept term may take into account some such secondary particles. All these conditions (including higher summer relative humidity and solar radiation) are not included in our formula. Therefore it is recommended that in any future study, the measurements should cover all seasons.
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(3): The analysis period for NO\textsubscript{x} vs. PM\textsubscript{no} may not have been representative of all locations / periods / wind directions. Our linear regression formula may be applicable to YIC, but may not be applicable for other places. Therefore, before using it for other places, this relationship should be re-evaluated for the whole year (covering all seasons) at both urban and rural sites and should include correlation with the wind direction.

(4): Our linear regression formula between NO\textsubscript{x} and PM\textsubscript{no} measurements was derived based on the Microsoft Excel Pearson formulae, which may have some limitations that affect final results. Therefore, for any future works other advanced packages that correlate not only NO\textsubscript{x}, but also other parameters (such as wind speed, temperature, relative humidity) may be recommended to achieve likely better results.

It worth noting that the particle emissions (mainly coarse particles) from other sources (such as tyre and brake wear) likely do not play as large a role in changing the total particle number as they do for particle mass (Deacon et al, 1997; Harrison et al 1997) and therefore the contribution of these sources to particle number could be ignored and the error due to not considering these sources in our formula is likely minor. Therefore, our regression formula could be applied in areas where the emission of large particles (particle size of >2.5\textmu m) is relatively high.

It was noted earlier that the prediction of PM\textsubscript{no} was better than that of the NO\textsubscript{x} prediction due mainly to adding the PM\textsubscript{no} background term (intercept of linear regression), which represents the sources of all other particles that are not related to NO\textsubscript{x}. The overall evaluation for PM\textsubscript{no} predictions showed a fairly good correlation between predictions and observations with FB ranging between -0.1 and 0.5 and Fa2 between 0.3 and 0.8 at two sampling sites. The IA values for the predicted particle numbers of both sizes range between 0.36 and 0.72. However, particle number prediction could be improved further if the above limitations were eliminated.
5.8 Summary and Conclusion:
The non-steady state dispersion model (CALPUFF/CALMET) was applied to predicting ground level concentrations of NO\textsubscript{x} over YIC for two cases (weekdays and weekends). The emissions rates from stationary sources (industries) and from mobile sources, as well as 3-dimensional meteorological data from the WRF model, were used as inputs for running the CALPUFF/CALMET system. The particle numbers of two different sizes (7-40nm and 7nm-10um) were derived based on NO\textsubscript{x} predictions and the correlation between NO\textsubscript{x} and particle number. The CALPUFF predictions for NO\textsubscript{x} and particle numbers were evaluated using some statistical indices calculated using observations at two monitoring sites during April 26-29, 2008 and March 25-27, 2009.

The following points can be concluded for the NO\textsubscript{x} prediction modeling results:

- The highest NO\textsubscript{x} concentrations were noted close to the road side during the night and early morning hours due to low wind speeds, a low inversion layer and the presence of a significant emission source. On the other hand, high concentrations were found away from the road in the downwind direction during noon and afternoon hours.

- During the night, but before sunrise, the maximum 1-hour concentration due to both sources (traffic and industries) ranged between 40 and 300μg/m\textsuperscript{3}. The contribution from the traffic to the highest concentration during that period was about 80% on weekdays and 30% on weekends while the contribution from industries was <20% on weekdays and >70% on weekends. The contribution from traffic usually becomes high when there is a relatively high traffic density, low wind speed and the occurrence of a near-surface inversion layer. Such conditions sometimes led to extremely high concentrations.

- After sunrise the contribution from industries usually became higher (>70%) than that from traffic (<30%) on all the days because after sunrise the ground-based inversion starts dispersing, but the elevated inversion above the discharge point (chimney) possibly remains. This likely prevents the plume from rising vertically and instead the plume will be brought down near to the surface leading to extremely high ground level concentrations due to industrial sources. The highest concentration due to both sources was about 200μg/m\textsuperscript{3}.

- The community/residential area is usually affected during the morning hours when the wind is shifting from a land breeze to a sea breeze (transition period). However, all hourly predicted NO\textsubscript{x} concentrations are much lower than the
national standard of 660μg/m³ for NOx although these predicted values sometimes exceed the EU limit of 200μg/m³.

- During noon and afternoon hours on weekdays and weekends the contribution from traffic is minor (<15%) compared to that from industries (>85%) because of higher wind speeds and a higher mixing height, which dilutes the emissions from traffic and brings the emissions from the stack to near ground. Further, the NOx concentration is the lowest during this period compared to at other times for two reasons: more dispersion/diffusion due to atmospheric turbulence and more chemical transformation of O₃ and NOx, which both lead to lower NOx concentrations.

- Timeseries of predictions and observations suggested that CALPUFF tended to slightly over-predicted the peak concentrations (taken every hour) of five values out of six, but was under-predicting the NOx values at most other hours and at both sites. Some maximum predicted values were not predicted at the same time as those observed possibly because the simulated plume had missed the receptor location due to incorrect wind direction. The discrepancy between the predictions and observations of NOx at both sites is probably due to two main reasons: (1) Some unidentified emission sources (such as ground flaring) were not considered, or some sources were not reasonably quantified; (2) due to some inaccurate values in the input wind direction.

- The statistical indices for NOx predictions showed that the fractional bias ranges between -0.1 and 1.06 indicating that model tends to under-predict the NOx observations. The majority of the modeling results at site#1 fall out of the required range of -0.5 ≤ FB ≤ +0.5 FB for acceptable modeling results, but the results at site#3 are mostly meeting the criteria. The Normal Mean Square Error (NMSE) lies between 1.1 and 3.2 which is beyond the acceptable range suggested by Kumar et al. 1999 of NMSE ≤ 0.5. Further, the Fa2 varies between 0.3 and 0.4, which is also not meeting the acceptable criteria of Fa2 ≥ 0.8. However, the index of agreement between the predictions and observations varied between 0.31 and 0.72, but was 0.58 or above in 5 out of 6 cases, which indicates fairly good correlation of the predicted and measured data.

- Based on the statistical results and the timeseries of NOx predictions and observations, it seems that CALPUFF tends to under-predict the daily average
values and over predict the maximum concentrations at both sites. Predicted NO\textsubscript{x} concentrations correlate fairly acceptably with measured values, except during low wind speeds and were observed to be very sensitive to wind direction.

Predictions of particle numbers of two sizes (7-40\,nm and 7nm to 10\,\mu m) over YIC domain were derived based on the NO\textsubscript{x} predictions and using a linear regression between the measurements of NO\textsubscript{x} and the particle number. Sensitivity tests using several linear regression formulae (based on site#1 data, site#3 or combinations) suggests that the site#3 formula seemed to be more appropriate for particle number prediction for both sizes and over the entire domain, as this formula represented both the industrial emissions as well as those from traffic. The maximum approximated error was 10% for the lower sizes (7-40\,nm) and up to 33% for the entire range size (7nm-10\,\mu m).

Based on the particle number simulations of both sizes, statistical analysis results and comparisons of timeseries of predictions and observations at sites#1 and 3, the following can be noted:

- During weekdays the highest particle number concentrations of both sizes over the entire domain are predicted (\approx 120,000 for sizes of 7-40\,nm and \approx 250,000 #/cm\textsuperscript{3} for sizes of 7nm-10\,\mu m) after midnight and before sunrise when there is very little dispersion, whereas the lowest concentrations of both sizes (\approx 70,000 for sizes of 7-40\,nm and \approx 100,000#/cm\textsuperscript{3} for sizes of 7nm-10\,\mu m) over the entire domain was predicted at noon due to high dilution and probably the affect of chemical reactions (ozone/HNO\textsubscript{3} formation and NO\textsubscript{x} depletion). The main contributor during night hours was the traffic because of a low mixing height, which traps the emissions from traffic near ground and keeps the emissions from industries aloft, but during the daytime the main contributor was the industries because the emissions from stacks will be brought to the ground by high wind speeds accompanied with unstable conditions.

- On the contrary, during weekends the lowest concentrations (<70,000#/cm\textsuperscript{3} for sizes of 7-40\,nm and <130,000 #/cm\textsuperscript{3} for sizes of 7nm-10\,\mu m) over the entire domain were predicted during the night hours due to relatively less traffic density, whereas the highest particle number concentrations (150,000#/cm\textsuperscript{3} for sizes of 7-40\,nm and 240,000#/cm\textsuperscript{3} for sizes of 7nm-10\,\mu m) were predicted before noon (11:00) mainly due to industrial emissions. The main contributor of particle number during the weekend is industries with less contribution from traffic.
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- Timeseries of the predicted and observed particle number concentrations at site#1 and site#3 showed that the predictions and observations at both sites are often in general agreement. The particle number at site#1 is higher (up to \(\approx 162,000#/cm^3\)) compared to that at site#3 (up to \(\approx 56,000#/cm^3\)) because the former site is affected more by traffic emissions as it is very close to the roadside (100m away), whereas the latter site is further away from the road (1100m away), but is more affected by industrial emissions.

- The statistical evaluation results showed that the maximum particle number concentrations are generally over-predicted at site#1 (by up to 47%) and under-predicted (by up to 20%) at site#3.

- All fractional bias values for both sizes range between -0.1 and 0.5, except for one value. Thus they are meeting the required criteria for acceptable modeling results (as suggested by Kumar et al. (1999)) of \(-0.5 \leq \text{FB} \leq 0.5\), indicating a fairly good agreement between the predicted and measured concentrations. The NMSE lies between 0.6 and 1.7 at site#1 and between 0.4 and 0.6 at site#3 for both sizes indicating that the particle number predictions at site#1 are beyond the range suggested by Kumar et al. (1999), but the prediction at site#3 is mostly within the acceptable range of \(\text{NMSE} \leq 0.5\). The Fa2 varies between 0.3 and 0.5 at site#1 and between 0.5 and 0.8 at site#3, which shows that the predictions at site#1 are not meeting the required criteria of \(\text{Fa2} \geq 0.8\), but the results at site#3 are either meeting the criteria or are close to it. The IA values for predicted particle numbers of both sizes range between 0.6 and 0.69 for site #1 and lower values (between 0.36 and 0.72) for site#3. These results imply that there is fairly good correlation between predictions and observations especially for site#1.

- Comparison between the predicted particle number concentrations at YIC sites and other sites elsewhere showed that the average value at site#1 (27,597#/cm\(^3\)) is relatively similar to those noted elsewhere at urban sites (Erfurt, AlKmaar, Copenhagen). However, the maximum particle number concentration for the size range of 7nm-10\(\mu\)m at site#1 (215,490#/cm\(^3\)) was higher than those at other urban sites except at Beijing (248,700#/cm\(^3\)). Further, the particle number concentration at site#4 which represents the community area has very similar average level (16,606#/cm\(^3\)) to that of Helsinki in Finland but slightly higher maximum (165,458#/cm\(^3\)) compared to 145,000#/cm\(^3\)).
Further, it is interesting to note that the statistics of particle number predictions are generally better than those of the NO\textsubscript{x} predictions perhaps because a background term for the particle number predictions was added. Almost all statistical results improved after adding the background value for both sizes. For example, for day 1 of case A the FB improved from 0.6 to 0.3 (after adding the background) for the lowest size range (7-40nm) and from 0.3 to 0.1 for the full size range (7nm-10\mu m). The NMSE improved from 2 to 1.2 for the lowest size range and from 1.6 to 1.2 for the full size range.

Based on the above results, this study suggests that reasonable predictions of particle number can be obtained based on only NO\textsubscript{x} predictions, linear correlation between NO\textsubscript{x} and particle number and analysis wind fields for specific sites. However, to obtain better results for a whole domain required the generalized use of the linear correlation between NO\textsubscript{x} and particle numbers observed at as many as possible sites downwind of sources. Further, it would be recommended that in future studies NO\textsubscript{x} predictions could be further improved if all sources were included and carefully quantified and some actual meteorological observations over the land and sea was also introduced as input for running CALPUFF alongside the 3-dimensional diagnostic meteorological model data. The development of a complete three dimensional air quality model for simulating particle numbers of different sizes over meso-scales (~50km) is recommended. Ideally, this model should incorporate all the important dynamic and non-dynamic aerosol processes in a single framework, including processes which influence the particle number; the impact of condensation and evaporation on altering the size distribution; interactions between gases and the different particle sizes (especially ultrafine particles) and others.
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Particulate matter and gases Measurements in YIC, Saudi Arabia:
Particulate number and mass concentrations, gas pollutants and meteorological parameters were measured at three different characteristic sites in YIC, which is located on the coast of the Red Sea and is very much affected by sea and land breezes. The concentrations of particulate matter and trace gases downwind of industrial locations (Site 1 and 3) are generally higher than upwind (site 2) for all particle sizes and gases. Site #1 recorded the highest maximum, minimum and average particle number concentration among the sites because this site is very much affected by traffic emissions. The maximum 10-minute number concentration (333,971 cm$^{-3}$) at site 1 was more than 2.5 times higher than that recorded at site 2 (123,842 cm$^{-3}$) and about 1.2 times higher than the value (263,572 cm$^{-3}$) at site 3. The coarse mode at all sites accounted for about 70-80% of the total mass concentration whereas the accumulation and aitken modes accounted for 20-29% and less than 1% respectively. On the contrary, the contributions of aitken mode particles to the total particle number concentration are between 80 and 87% at sites 1 and 3 and only 57% at site 2 while the accumulation mode contributes less than 20% at sites 1 and 3 but more than 40% at site 2. The contribution of the coarse mode to the total number concentration is negligible, being less than 0.2% at all sites.

The average particulate number distributions at downwind sites (1 and 3) consist of one distinguishable mode (nucleation mode $<$20nm) due to the influence of local sources (industries as well as traffic), whereas site 2 has two modes (the first in the nucleation range and the second in the accumulation) because this site is affected either by the long range transport of particles or the recirculation of built-up polluted air back to this site from the sea. The highest average particle number distribution at all sites (site 1: 108,000; site 2: 10,000 and site 3: 42,000 cm$^{-3}$) occurred when the wind blew directly from industrial or traffic regions towards these sites while the lowest number distributions occurred when the wind blew from the desert or sea. It was noted that the peak value of the average size distribution at site 3 (42,000 cm$^{-3}$) was similar to that which occurred at site 1 when the wind was blowing in the same direction (sea breeze). From this it is inferred that the impact of traffic on site 3 is negligible. The difference in the number concentration (66,000 cm$^{-3}$) in the Aitken mode between sea and breeze conditions is probably due to the impact of the traffic at site 1.

The diurnal variation of particle numbers of all sizes increased coincidentally with NOx during early morning hours (7-9a.m.) when there is a very clear signal of traffic-
generated emission that are blown towards the downwind sites (1 and 2). Afterwards both parameters decreased remarkably because of dilution within the developing boundary layer (the mixing height is rapidly increasing after 8a.m.). Further, particle numbers and NO$_x$ concentrations increased at all sites when the wind direction was blowing from the road and/or industrial area towards the sampling locations whereas the concentrations decreased when the wind was blowing from the other direction.

The correlation coefficient between NO$_x$ and particle number for the sizes of 7-40nm; 7-200nm and 7-10,000nm at sites 1 and 2 ($r>0.7$) was generally better than that ($r<0.65$) at site 3. However, the correlation decreased for larger particle sizes (accumulation mode and coarse modes) at sites 1 and 2 due to the contribution of other sources in the area (such as sand-storms and resuspension particles from the road). Further, it was noted that as the particle size diameter increased the correlation between NO$_x$/NO and particle number concentration decreased from $r=0.7$ for diameter <200nm (the fraction of which accounted for >80% of the total number concentration) to 0.3 for 200nm-10μm (the fraction of which accounted for <20% of the total number concentration) at sites 1 and 2. On the other hand, however, the correlation coefficient at site 3 was better in the upper end of the aitken mode (40-200nm) and accumulation mode (100-1000nm) than at other sites because ultrafine particles get removed by deposition and coagulation on their way from the sources (traffic or industries) to site 3.

As for the other air pollutants, the particle number concentration generally had weak correlation with the SO$_2$ at all sites except for the accumulation mode particles at site 1 because this site was the location most affected by power plant emissions. Further, there was poor correlation between CO and PM$_{no}$ (<0.02) and between CO and NO$_x$ (-0.01) because CO has different sources (such as incomplete fuel combustion from flares) than NO$_x$ and PM$_{no}$ in industrial areas.

The linear regression formulae derived for the YIC sites was compared with other derived formulae for some UK sites and it was found that the Site#3 formula had a higher slope than that of the TORCH1 (UK site), which represented a semi-urban area and is very much affected by London anthropogenic emissions. The slopes at YIC site#3 of 754 and 1225 #/cm$^3$/ppb of NO$_x$ for the size ranges of 7-40nm and 7nm-10μm, respectively, were much higher than those at UK TORCH1 of 485 and 580, which suggests that the YIC site is more affected by anthropogenic sources than TORCH1. Both formulae (YIC site#3 and TORCH1) have a relatively close intercept for both particle size ranges (7-40nm and 7nm-10μm) ranging from 6150 #/cm$^3$ (7853 at site#3).
to 8715 #/cm$^3$ (9047 at site#3) at TORCH1. Further, by comparing all six sites in Saudi Arabia and UK it was noted that YIC sites (especially sites#1 and 2) had a much better correlation coefficient between particle number and NOx than those at the UK sites and the correlation coefficient ($r^2$) at TORCH 2 for all size ranges was very poor with a maximum of 0.05 in the range of (7-200nm). A possible reason for the poor correlation and low slope and intercept at the UK sites is that these sites are relatively far from particle number sources (such as roads) and hence they are more affected by long-range transport particles.

**Chemical Composition of Size Fractioned Atmospheric particulate:**

Particle samples of different sizes, ranging from 7nm to 10μm, taken downwind of YIC (site 3) were chemically analysed using IC for inorganic ions (Sulphate, Nitrate, Nitrite, Bromide, chloride, Oxalate, Phosphate) and ICP-MS for trace metals (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Zn, Ag, Ti, V, Hg and Sn) during spring.

The ionic analysis revealed that sulfate and ammonium concentrated on particle sizes less than 0.38μm while nitrate and chloride concentrated on particles larger than 0.38μm although sulfate and other ions are present. The concentration of sulfate ranged from a minimum of 10.5ngm$^{-3}$ in the Aitken (0.028μm) to a maximum of 705ngm$^{-3}$ in the accumulation mode (0.16-0.38μm). The next highest concentration amongst anions was nitrate (485 ngm$^{-3}$) at a particle size of 2.39μm and the lowest concentration (<1ngm$^{-3}$) was at sizes of <0.06μm. The non-sea salt sulfate is dominant in all particle sizes, but the contribution of marine sulfate is minor. The contribution of marine sulfate to total sulfate ranged from 0.2% in the Aitken mode size to 18% in coarse mode particles. The total sulfate and nitrate contributed 50.3% and 24.4% of the total ionic mass, respectively, followed by chloride (13.3%) and ammonium (10.6%).

Ammonium was also observed clearly at most sizes especially in small particles (<0.61μm). However, it was in minor concentrations in the larger particles (0.95-4μm). The highest (275 ngm$^{-3}$) and lowest (4 ngm$^{-3}$) ammonium concentration were detected at particle sizes of 0.38μm and 1.6μm, respectively. Chloride and nitrate were found at particle sizes between 0.61 and 9.9μm. Generally speaking, nitrite, bromide, phosphate and oxalate were found in very low concentrations.

The trace-metals analysis results indicated that the dominant metals in all particle sizes (7nm-10μm) were Na, Al, Ti, V, Fe, Zn, Sr and Cr. The most abundant metal was Na
which represented more than 94% of the total mass of trace metals in PM$_{10}$ and was detected in all plates (7nm-10μm) with very high concentration (796ng m$^{-3}$) compared to other metals. Further, the results showed that in the lower particle size range (7-380nm) high levels of Fe (3.7ngm$^{-3}$), V (4ngm$^{-3}$), Zn (3.6ngm$^{-3}$) and Al (2.7ng m$^{-3}$) were present. On the other hand, in the upper particle size range (>380nm) there are other metals which had higher concentrations: Al (7.5ng m$^{-3}$), Cr (2.7ng m$^{-3}$), Sr (5.2ng m$^{-3}$), Mn (1.4ng m$^{-3}$), Ba (0.6ngm$^{-3}$). The remaining metals were either in very low concentration or were negligible in both size bands. Moreover, the main contributors in total mass concentration (excluding Na) are Al (25%), Sr (13%), Zn (13%), V (10%), Cr (10%) and Fe (10%). Mn, Ti, Ni, Cu, Pb and Ba account for less than 5% of total metal mass.

The possible contributing sources present within a 10km radius of the sampling site #3 were determined using the SCREEN model and based on some actual data and other assumptions. The main possible affecting sources for nitrate could be power plants, refineries, petrochemical facilities and gas plants (main sources of NO$_2$), whereas the main possible sources for sulfate ion are power plants and refineries (main sources of SOx). The sources of other ions, chloride (Cl-) and sodium (Na+) in PM10 are mostly marine air. Power plants emit both sulfate and nitrate particulate with initial size ranges of 20-130nm and will reach site#3 with final size between 200 to 410nm. However, particles emitted from refineries will grow to a size between 68 and 198nm when it reaches the sampling point (Site#3). This means that power plants are the main contributor for sulfate and nitrate with sizes of >200nm, whereas refineries are the main sources of nitrate and sulfate at sizes of <200nm. One the other hand, gas and petrochemical plants are sources of nitrate for sizes less than 120nm.

Sources of trace metals (such as Zn, V and Fe) are mainly from local combustion sources, natural gas combustion or heavy fuel oil combustion whereas Na, Cl and Sr are attributed to marine sources. Sr, Ni, Co and Mo may originate from combustion of heavy fuel oil. Ba, Cu and Fe have been attributed to traffic and natural gas combustion (such as petrochemical facilities) and Ti and Pb were attributed to LRT.

Based on the predicted values, assumed formation rate and distance between these sources and site#3, the mass concentration at site#3 will be 82μg/m^3 for sulfate due to emission from power plants and 30.4μg/m^3 for nitrate due to power plants, gas plants and refineries emissions. However, these mass concentrations for sulfate and nitrate are much higher than what was collected in ELPI plates and analyzed by IC (3.6μg/m3 for sulfate and 1.7μg/m3 for nitrate). The large discrepancy between the two results (the
calculated and measured values) could be due to several reasons. One is that the formation rate might be much lower than what has been assumed in this study. Other possible reasons are that the efficiency of sample collecting by ELPI instruments was poor during measurements, or that the values were overpredicted by the SCREEN model as many physical processes (dry deposition and wet deposition) and chemical processes were not considered in this model.

**Evaluating three dimensional meteorological data predicted by WRF model using surface observations and upper air profiles:**

A detailed comparison of WRF predictions over two different scenarios (eight case studies) against surface and upper air profiles (RASS, SODAR and radiosonde) were made. The first scenario (three case studies) was for a 24-hour simulation using two different initial conditions (forecast and reanalysis initial data) and the second scenario (five case studies) was for 78-hours using only reanalysis initial data. The aim of the first scenario was to determine which initial data (forecast or reanalysis) would give better predictions compared with observation. The main purpose of the second scenario was to determine if any errors build up with time after the startup due to the model drifting away from the re-analysis.

WRF predictions for both scenarios tended to underestimate the 2-m surface temperature on average in seven cases out of eight with biases ranging from -0.2 up to -3.4 degrees. The largest bias (-3.4°C) was 13% of the average observation and the possible reason for this high bias is that there are some local sources (e.g. ground flares) that were not considered in the modeling input, but which affect the observation data. Conversely WRF tended to overestimate the surface wind speed in all eight cases with positive biases that ranged from 0.2 to 1.5m/s on average (6% to 54% of the average observation). The mean wind speed biases for the reanalysis runs were lower than those from the forecast runs and ranged from 0.2 to 1m/s. The prediction of wind direction was very close to the observations with biases that ranged from 1.3° to 24°. However, the bias for wind speed and direction during the transition period (i.e. from sea breeze to land breeze and vise versa) was often relatively higher. The RMSE and SDE for the surface
Chapter 6  Conclusion and Recommendations

temperature ranged from 1.6 up to 3.6°C and from 1.3 up to 2.1, respectively, for runs initialized using the forecast and reanalysis datasets. Mean RMSE and SDE for wind direction ranged from 48 to 93 degrees and from 47 to 112 degrees, respectively.

The correlation coefficient between WRF predictions and surface observations were very high for temperature (0.7 to 0.9), and moderate to high for wind speed (0.4 to 0.9) and wind direction (0.6 to 0.8). High correlation coefficients for wind direction along with low biases (<24°) suggest that the WRF model is able to capture well the sea and land-breeze phenomenon over YIC during both the day and night. Further, by comparing the overall 24-hour simulation results for scenario#1 (forecast and reanalysis) it was noticed that forecast-initialized runs gave slightly better predictions than reanalysis-initialized runs for 2-m surface temperature, but on the other hand the reanalysis runs gave better wind speed predictions. Wind directions were similar for both initial datasets although the forecast run gave slightly better results for one case study (case 3) out of three. By comparing the results from both scenarios for the case of reanalysis-initialized simulations, it seems that there is no build up of error with time after startup for the next 78 hours as both scenarios produced relatively similar performance statistics for all parameters.

WRF tends to underestimate temperature profile when reanalysis data is used and overestimate it when forecast data is applied. Further, it can be noted that the forecast initialized data give a slightly better prediction for the temperature profile than the reanalysis data in some cases, which indicates that the reanalysis procedure made by the global NCEP model simulation may not be necessary to improve the data especially for complicated flows such as sea and land breezes. For example, in the scenario#1 profile, case#1 the forecast run bias and RMSE are considerably lower than for the reanalysis run. The overall mean biases for comparisons to both the radiosonde and the RASS are generally negative for the upper air temperature in seven cases out of eight. The bias ranges between -2.7 and -5.2 for all cases when compared to the RASS, but the average bias is much lower (between 0.3 and -2.4) when the radiosonde data is used. The model appears to perform better when compared to the radiosonde data with very high
correlation coefficient (>0.9) suggesting that WRF predictions for temperature profiles are quite reliable and that the errors are generally only quite high when WRF is evaluated using the RASS data. This might indicate that RASS temperature profiles are often unrealistic and that the instrument was unreliable especially noon and after noon hours when the wind speed was relatively high.

Time-series of the bias, RMSE and SDE for temperature profiles for hours 03 and 15 ranged between ±2 and -2°C for bias and are less than 3°C for the RMSE and SDE. These results are similar to those of the profiles. Temperature time-series showed generally no significant trend in model error over time suggesting that there is no sustained build-up of model errors over the 3 days of the simulations in most cases.

The WRF model generally overestimates the wind speed profile with forecast-initialized data, but it underestimates it with reanalysis-initialized data. The wind speed prediction using forecast-initialized data had fairly similar statistical results to those from reanalysis-initialized data although the reanalysis runs produced slightly lower biases and RMSEs and so might be expected to give slightly better results. However, both types of input data (forecast and reanalysis) are equally acceptable in predicting wind speed.

As the wind speed biases in most cases (five cases out of six) are less than 1 m/s, one may conclude that the wind speed predictions for the reanalysis runs are reasonable especially in the lower and mid levels of the boundary layer, although the RMSE results may provide a fairer assessment. RMSE values were between 1.8 and 3.7 m/s. The wind direction profile biases were generally positive and were less than 20° in all layers although the bias was relatively high (>40°) at higher altitudes.

The mean wind speed bias in 5 out of the 6 cases were either meeting or were close to the benchmark of ±0.5 m/s proposed by Emery et al (2001). The mean wind direction biases exceeded the benchmark proposed by same authors of 10° in 3 out of the 6 cases. The wind speed and direction profiles from the SODAR instrument look reasonable compared to the WRF profiles, which suggests that this instrument is capable of
producing realistic wind measurements although the accuracy of this instrument (SODAR) is probably uncertain during some hours. However, it would be advisable to compare these observations with another form of observation, (such as radiosonde data) at the same site.

Time series of the wind speed and direction showed that there might be little consistent error build up with time as the bias, RMSE and SDE are generally consistent over the 78-hours simulations. However, it is possible that there was some slight increase of RMSE for wind speed, although it is hard to be conclusive with only 3 cases.

It was concluded that WRF predictions can be used for air dispersion modeling to produce reasonable outputs. Further, it is suggested that reanalysis data is used as initial and boundary conditions for running the CALMET model as this type of data gave slightly better predictions for wind speeds than for forecast initialization data with similar wind direction predictions. Among the five reanalysis cases, some cases (such as cases# 4 and 8) may give better air dispersion modeling results as they have lower wind speed and direction biases.

**Predictions of NOx and Particulate number over YIC**

The CALPUFF/CALMET system was applied to predicting ground level NOx and particle number concentrations over YIC for two cases (weekdays and weekends). The emission rates from industries and traffic, as well as 3-dimensional meteorological data from the WRF model, were used as inputs for running the CALPUFF/CALMET system.

The NOx prediction modeling results can be summarized by the following:
- The highest NOx concentrations were noted close to the road side during the night and early morning hours due to low wind speeds, a low inversion layer and the presence of a significant emission source. On the other hand, high concentrations were found away from the road in the downwind direction during noon and afternoon hours.
- During the night, but before sunrise, the maximum 1-hour concentration due to both sources (traffic and industries) ranged between 40 and 300μg/m3. The contribution from the traffic to the highest concentration during that period was
about 80% on weekdays and 30% on weekends while the contribution from industries was <20% on weekdays and >70% on weekends. After sunrise the contribution from industries usually became higher (>70%) than that from traffic (<30%) on all the days because after sunrise the ground-based inversion starts dispersing, but the elevated inversion above the discharge point (chimney) possibly remains. This likely prevents the plume from rising vertically and instead the plume will be brought down near to the surface leading to extremely high ground level concentrations due to industrial sources. The highest concentration due to both sources was about 200μg/m³. During noon and afternoon hours on weekdays and weekends the contribution from traffic is minor (<15%) compared to that from industries (>85%) because of higher wind speeds and a higher mixing height, which dilutes the emissions from traffic and brings the emissions from the stack near to the ground. Further, the NOₓ concentration is the lowest during this period compared to at other times for two reasons: more dispersion/diffusion due to atmospheric turbulence and more chemical transformation of O₃ and NOₓ, which both lead to lower NOₓ concentrations.

- The community/residential area is usually affected during the morning hours when the wind is shifting from a land breeze to a sea breeze (transition period). However, all hourly predicted NOₓ concentrations are much lower than the national standard of 660µg/m³ for NOₓ although these predicted values sometimes exceed the EU limit of 200µg/m³.

- The statistical indices for NOₓ predictions showed that the fractional bias ranges between -0.1 and 1.06 indicating that model tends to under-predict the NOₓ observations. The majority of the modeling results at site#1 fall out of the required range of -0.5 ≤ FB ≤ +0.5 FB for acceptable modeling results, but the results at site#3 are mostly meeting the criteria. The Normal Mean Square Error (NMSE) lies between 1.1 and 3.2, which is beyond the acceptable range suggested by Kumar et al. (1999) of NMSE ≤ 0.5. Further, the Fa² varies between 0.3 and 0.4, which is also not meeting the acceptable criteria of Fa² ≥ 0.8. However, the index of agreement between the predictions and observations varied between 0.31 and 0.72, but was 0.58 or above in 5 out of 6 cases, which indicates fairly good correlation of the predicted and measured data.

- Based on the statistical results and the timeseries of NOₓ predictions and observations, it seems that CALPUFF tends to under-predict the daily average values and over predict the maximum concentrations at both sites. Predicted NOₓ
concentrations correlate fairly acceptably with measured values, except during low wind speeds and were observed to be very sensitive to wind direction. The discrepancy between the predictions and observations of NO$_x$ at both sites is probably due to two main reasons: (1) Some unidentified emission sources (such as ground flaring and some secondary industries) were not considered, or some sources were not reasonably quantified; (2) due to some inaccurate values in the input wind direction. The differences between prediction and observation could be narrowed if the above limitations were solved.

Predictions of particle numbers of two sizes (7-40nm and 7nm to 10μm) over YIC domain were derived based on NO$_x$ predictions and the correlation between NO$_x$ and particle number. Sensitivity tests using several linear regression formulae (based on site#1 data, site#3 or combinations) suggests that the site#3 formula seemed to be more appropriate for particle number prediction for both sizes and over the entire domain, as this formula represented both the industrial emissions as well as those from traffic. The maximum approximated error was 10% for the lower sizes (7-40nm) and up to 33% for the entire range size (7nm-10μm).

Based on the particle number simulations of both sizes, statistical analysis results and comparisons of timeseries of predictions and observations at sites#1 and 3, the following can be noted:

- During weekdays the highest particle number concentrations of both sizes over the entire domain (~120,000 for sizes of 7-40nm and ~250,000 #/cm$^3$ for sizes of 7nm-10μm) were predicted after midnight and before sunrise when there is very little dispersion, whereas the lowest concentrations of both sizes (~70,000 for sizes of 7-40nm and ~100,000#/cm$^3$ for sizes of 7nm-10μm) over the entire domain were noted at noon due to high dilution and probably the affect of chemical reactions (ozone formation and NO$_x$ depletion). On the contrary, during weekends the lowest concentrations (<70,000#/cm$^3$ for sizes of 7-40nm and <130,000 #/cm$^3$ for sizes of 7nm-10μm) were predicted during the night hours due to relatively lower traffic density, whereas the highest particle number concentrations (150,000#/cm$^3$ for sizes of 7-40nm and 240,000#/cm$^3$ for sizes of 7nm-10μm) were predicted before noon (11:00) mainly due to industrial emissions. The main contributor during night hours was the traffic, but during the daytime the main contributor was the industries.
Timeseries of the predicted and observed particle number concentrations at site#1 and site#3 showed that the predictions and observations are often in general agreement. The particle number at site#1 is higher (up to \( \approx 162,000#/cm^3 \)) compared to that at site#3 (up to \( \approx 56,000#/cm^3 \)) because the former site is affected more by traffic emissions as it is very close to the roadside (~100m away), whereas the latter site is further away from the road (~1100m away), but is more affected by industrial emissions.

The statistical evaluation results showed that the maximum particle number concentrations are generally over-predicted at site#1 (by up to 47%) and under-predicted (by up to 20%) at site#3. All fractional bias values for both sizes range between -0.1 and 0.5, except for one value. Thus they are meeting the required criteria for acceptable modeling results (as suggested by Kumar et al, 1999) of -0.5 \( \leq FB \leq 0.5 \), indicating a fairly good agreement between the predicted and measured concentrations. The NMSE lies between 0.6 and 1.7 at site#1 and between 0.4 and 0.6 at site#3 for both sizes indicating that the particle number predictions at site#1 are beyond the range suggested by Kumar et al. (1999), but the prediction at site#3 is mostly within the acceptable range of NMSE \( \leq 0.5 \). The Fa2 varies between 0.3 and 0.5 at site#1 and between 0.5 and 0.8 at site#3, which shows that the predictions at site#1 are not meeting the required criteria of Fa2 \( \geq 0.8 \), but the results at site#3 are either meeting the criteria or are close to it. The IA values for predicted particle numbers of both sizes range between 0.6 and 0.69 for site #1 and lower values (between 0.36 and 0.72) for site#3. These results imply that there is fairly good correlation between predictions and observations especially for site#1.

Comparison between the predicted particle number concentrations at YIC sites and other sites elsewhere showed that the average value at site#1 (27,597#/cm\(^3\)) is relatively similar to those noted elsewhere at urban sites (Erfurt, AlKmaar, Copenhagen). However, the maximum particle number concentration for the size range of 7nm-10µm at site#1 (215,490cm\(^3\)) was higher than those at other urban sites except at in Beijing (248,700cm\(^3\)). Further, the particle number concentration at site#4 which represents the community area has very similar average level (16,606#/cm\(^3\)) to that of Helsinki in Finland but slightly higher maximum (165,458#/cm\(^3\) compared to 145,000#/cm\(^3\)).
Further, it is interesting to note that the statistics of particle number predictions are generally better than those of the NO\textsubscript{x} predictions perhaps because a background term for the particle number predictions was added. Almost all statistical results improved after adding the background value for both sizes. For example, for day 1 of case A the FB improved from 0.6 to 0.3 (after adding the background) for the lowest size range (7-40nm) and from 0.3 to 0.1 for the full size range (7nm-10\(\mu\text{m}\)). The NMSE improved from 2 to 1.2 for the lowest size range and from 1.6 to 1.2 for the full size range.

However, we should emphasis that our linear regression formula between NO\textsubscript{x} and PM\textsubscript{no} may not have taken into account all physical and chemical processes (mainly nucleation, coagulation, chemical transformation) undertaken in atmosphere due to relatively short period of measurements (with a maximum of two months at each site). Further, this linear regression formula may applicable to YIC, but may not be applicable for other places.
**Recommendations:**
Based on this study, it is noted that there are several areas of research which require more investigation to fill in the gaps in our knowledge and improve areas of deficiency. These areas of research include the following:

- The health effects of particle matter depend on mainly the particle size and the chemical composition. The lower the particle size, the greater the health effect on humans. Many studies (such as Dockery et al., (1993), Pope et al., (1995a); Yeh et al., (1997); Lingard et al (2005)) have shown that the correlation between particle concentration and health effects increases as particle diameter decreases. However none of these studies has addressed the importance of chemical composition of different particle sizes on human health and this area of research needs more investigation. Therefore, comprehensive studies that include chemical composition, particle number size distribution and health impact are highly recommended.

- In a future study, it is recommended to collect particle samples at background site, which is not affected by any anthropogenic emissions, and compare the chemical composition results at that site with the findings at YIC in order to explore better the contribution of industries on the inorganic ions and trace metals at different particle sizes.

- Current ambient air quality standards for particle matter (PM$_{10}$ and PM$_{2.5}$) are based on mass concentration at national and international levels. Toxicological and epidemiological studies have demonstrated that ultrafine particles are more harmful to health than large particle because ultrafine particles are able to enter into the blood stream, whereas most of the PM$_{10}$ and PM$_{2.5}$ mass may be retained in the respiratory tract. The ultrafine particles (<100nm), which dominate the total particle number concentration (>80%), have negligible impact on the total particle mass; high particle number concentrations of this size (<100nm) do not necessarily mean high particle mass concentrations and vice versa. Therefore, current ambient air quality standards may not be sufficient to conclude the
relationship between particle number and the observed health effects. Thus, it is recommended that ambient air quality standards for particle number are introduced, as it is necessary to protect human health more efficiently.

- Particle removal processes (e.g. deposition and coagulation) and condensational growth are likely the most important mechanisms for the loss of particle number and the shift in particle size from nucleation mode to larger sizes. A detailed study on particle processes at sites (such as Yanbu, Saudi Arabia), which are very much affected by sea and land breeze phenomenon and emissions from different sources (industries and traffic), is recommended to understand better the relationship between particle number loss and particle growth on one hand and the sources and environment on the other hand.

- The correlation coefficient for wind direction from WRF predictions and observations is generally high (>0.7) and the mean wind direction bias ranged between less than 2° and 24°, which suggests that the WRF model is able to capture the general development of sea and land-breeze phenomena during day and night hours over YIC. However, the bias for wind direction during the transition period (i.e. from sea breeze to land breeze and vise versa) is often relatively higher. The biases for wind speed are also generally high during the transition periods, although the wind speed biases tend to be relatively high during other parts of the day as well. Therefore it is recommended to investigate further this possible drawback of the WRF model and if necessary to improve the WRF model forecast for coastal areas especially during such transition periods.

- The wind speed and direction profiles from the SODAR instrument look reasonable compared to the WRF profiles, which suggests that this instrument is capable of producing reasonable wind speed measurements. However, it would be advisable to compare these observations from SODAR with another form of observation, (such as radiosonde data) at the same site. On the other hand, it was found in this study that the overall mean biases for comparisons to both the
radiosonde and the RASS were negative for the upper air temperature for all cases. The bias was up to -5.2 when WRF predictions were compared to the RASS, but the average bias is much lower (<-2.4) when the radiosonde data is used. Therefore, the model appears to perform better when compared to the radiosonde and the errors are generally quite high when WRF is evaluated using the RASS data. It was concluded that the RASS temperature profiles are often very unrealistic and therefore the instrument was unreliable. It is recommended to conduct more research and investigation to improve the performance and the accuracy of the RASS instrument especially for high altitudes.

- It was noted in this study that the forecast initialized data gave slightly better predictions for temperature profiles than the reanalysis data in some cases, which indicates that the reanalysis procedure made by the global NCEP model simulation may not be necessary to improve the data especially for complicated flow such as sea and land breezes. Therefore, it is suggested to overcome this drawback of (National Center for Environmental Prediction) Global Forecast System (GFS), although further investigation is needed to confirm the robustness of this result for this region.

- It is suggested in this study that reasonable predictions of particle number can be obtained based mainly on only NO\textsubscript{x} predictions and a linear correlation between NO\textsubscript{x} and particle number. However, to obtain better results for a mesoscale domain requires the generalized use of the linear correlation between NO\textsubscript{x} and particle numbers observed at as many sites as possible downwind of sources. Further, it is recommended that in future studies linear regression formulae shall be based on measurements that cover all seasons and shall be tested in other places (urban, semi-urban and rural). The NO\textsubscript{x} predictions could be further improved if all sources were included and carefully quantified and some actual meteorological observations over the land and sea were also introduced as input for running CALPUFF/CALMET system alongside the 3-dimensional diagnostic meteorological model data.
- Our linear regression formula between NO\textsubscript{x} and PM\textsubscript{10} measurements was derived based on the Microsoft Excel Pearson formulae, which may have some limitations that affect final results. Therefore, for any future works other advanced packages that correlate not only NO\textsubscript{x}, but also other important parameters (such as wind speed, temperature, relative humidity) may be recommended to achieve likely better results.

- Development of a complete three dimensional air quality model for simulating particle numbers of different sizes over meso-scales (~50km) is recommended. Ideally, this model should incorporate all the important dynamic and non-dynamic aerosol processes in a single framework, including processes which influence the particle number; the impact of condensation and evaporation on altering the size distribution; interactions between gases and the different particle sizes (especially ultrafine particles) and others.
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