# Assessment of Atmospheric Emissions Due to Anthropogenic Activities In The State Of Qatar

# A Thesis submitted for the degree of PhD

# By

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# Abstract

Atmospheric pollutants in the state of Qatar are derived from flaring and fugitive emissions due to a combination of new energy projects, operational conditions and plant operational problems. This research is the first attempt to quantitatively assess key atmospheric pollutants in Qatar, in accordance with the Kyoto agreements to reduce greenhouse gas production. Two datasets were analysed:

- Between 2000 and 2002, data collected by industrial plants, as part of their own procedures, were assembled using a proforma questionnaire, to compile data on fuel consumption, fuel type, chemical characteristics, heat value, specific gravity etc, from industries in Qatar. The survey involved the oil & gas industry, petrochemical factories, power & desalination plants. Fuel data includes sulfur & nitrogen contents, chemical composition of flared gas and C content, some data compiled on road transport and fuel consumption. Analysis revealed significant atmospheric pollution.
- 2. Independent air-quality monitoring stations collected data between 2003 and 2005 to compare with data provided by industry. Three locations were chosen because of proximity to industrial plants: Mesaieed on the southeast coast, Dukhan on the west coast, and Halul Island, an offshore installation 30 km east of Qatar in the Arabian Gulf. Five key tropospheric pollutants (NO<sub>2</sub>, SO<sub>2</sub>, CO, O<sub>3</sub> and PM10), wind speed and wind direction, were monitored hourly from three stations located near gas installations across Qatar. Registered levels of CO, NO<sub>2</sub> and SO<sub>2</sub> were within Qatari and European Standards. PM10, however, was higher than the standards in all three stations and measured daily O<sub>3</sub> levels were sometimes higher than the reference for Halul Island.

Therefore, in contrast to industry data, the monitoring sites showed much pollution is below (better than) accepted thresholds, the difference between the two datasets illustrating the complexity involved in correctly monitoring pollution, and the effect of wind direction and dispersal of pollutants. Therefore these results have stimulated a comprehensive response to pollution monitoring in Qatar between 2005 and the present day, leading to reduction in flaring and fugitive emissions over the last few years, by as much as 50% in some operations, as a result of more careful operational planning, upgrading and better controls applied to new and existing projects. This research therefore provided much of the stimulus for emission reduction in Qatar, currently being investigated under the Clean Development Mechanism and Technology Transfer. Climate

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#### **Presentation**

I present this achievement to his highness the Emir of the State of Qatar, Sheikh Hamad Bin Khalifa Al-Thani, Sheikh Tamim Bin Hamad Al-Thani, The Heir Apparent, Chairman of the Supreme Council For Environment and Natural Reserves and Sheikh, Jasim Bin Hamad Al-Thani, for their genuine concern and demonstrated commitment to preserve the local, regional and global environment while sustaining such remarkable and historic development of the State of Qatar.

#### إهداء

يسعدني ويشرفني أن أهدي هذا العمل إلى مقام حضرة صاحب السمو أمير البلاد المفدى الشيخ /حمد بن خليفة آل ثاني وإلى سمو الشيخ تميم بن حمد آل ثاني ولي العهد الأمين رئيس المجلس الأعلى للبيئة والمحميات الطبيعية و إلى الشيخ / جاسم بن حمد آل ثــاني وذلك على جل اهتمامهم الخالص ودعمهم الدءوب الهادف لحماية البيئة القطرية والإقليمية والمحافظة عليها مع الالتزام بالتفوق في النهوض بالتنمية المستدامة والشاملة في دولة قطر الحديثة.

#### Chapter 1

#### **1.1 Introduction**

The State of Qatar has witnessed phenomenal economic development and growth during the past three decades as a result of the Oil boom of the 1970s. Domestic demand for energy has increased significantly during this period, reaching approximately 756 peta joules in 2005 compared to 350 peta Joules (PJ), in 1995, 240 PJ in 1986 and 100 PJ in 1975 [1]. This substantial increase in energy demand is largely attributed to the growth of economic activities in the upstream and downstream oil and gas operations, steel, chemical and petrochemical manufacturing, power generation, water desalination, transportation, and other anthropogenic activities.

This economic prosperity of the past few decades has come with environmental impacts, however. The substantial increase in fuel consumption, for energy, must have caused an associated increase in air pollution concentration, and may have resulted in an adverse impact on ambient air quality. [2] Assessment of these possible impacts is one of the main objectives of this thesis.

This phenomenon of hampering in air quality has been of real concern to various responsible sectors in Qatar, namely the Supreme Council for Environment, the Ministry of Energy & Industry and medical institutions. [3] Force field analyses of the factors impacting air quality, both pushing and pulling type, suggest that the pull [negative] type factors include:

- a) Qatar is virtually an arid country with an average annual rainfall of less than 12 cm.
- b) Forests and fresh surface water are virtually nonexistent.

The push [positive] type factors include:

- a) The buffering capacity that the surrounding seawater provides, particularly for acid type emissions from industry.
- b) The generally calcareous nature of soils in Qatar, which draws down some pollutants by reaction with surface calcium carbonate.
- c) While the rainfall is low some pollutants are still hydrolyzed or partially hydrolyzed because of the prevailing relatively high humidity.

# **1.2 AIMS AND OVERVIEW OF THIS PROJECT**

# Aims

The overall aim of this thesis is to evaluate air pollution in Qatar, in order to facilitate mitigation of the air pollution problem.

Prior to the development of this research project, data were scarce on:

A) What and how much air pollutants are emitted by various industrial sites, particularly energy based operations; and

B) On what, where and how often air pollutants are monitored in the State of Qatar.

Therefore an assessment of the various industrial emission sites, particularly Oil and Gas operations, and surveying the types and levels of the emitted pollutants, in the State of Qatar is needed. Such information would be of value for environmental, meteorology, climate change, and medical purposes, and for mitigation and planning purposes. This thesis is the first attempt to develop a comprehensive approach to air-quality monitoring, in order to promote informed decisions about mitigation of pollution problems.

# Overview

The chronology of this work is briefly described here to place the work into perspective of pollution control in Qatar. The work began in 2000-2002 with a survey of industrial activities in order to obtain an overview of the nature and composition of atmospheric pollutants in Qatar.

The results (described in Chapter 3) indicated that there is a major source of pollution arising largely from burning of fossil fuels, especially gas flaring, uncontrolled gas combustion, and use of sour gas for power generation and plant operations. Fugitive and stack emissions, primarily air pollutants, from various point sources were quantified. These data were then independently tested by three newly-installed air monitoring stations in Qatar (described in Chapter 4), which collected data from 2003-2005.

The results of this monitoring showed lower pollution levels than those indicated by the industrial activities survey, showing a discrepancy between the two sets of information. Therefore, the results show that air monitoring in Qatar requires development into a comprehensive network and better regulation of the industry. As a result of this monitoring, the author of this thesis has been involved in developing mitigation procedures in the State of Qatar, with particular effect of strong reduction of gas flaring. Thus the research presented in this thesis has had a major positive benefit for atmospheric quality in Qatar.

Therefore the impact of industrial emissions on air quality is and the "status quo" of the air quality in various parts of the state is determined and benchmarked. In arriving at this hypothesis, the Qatar environment and the local industry were examined.

Qatar air quality data on air pollution measurements were collected over the years 2003 – 2005 from three monitoring stations [Mesaieed and Dukhan, which are located onshore, and Halul Island - offshore].

The location of the onshore monitoring stations is shown in figure 1-2. These data were analyzed and the results were benchmarked against the European and Qatari Standards on air pollutants. This is all documented and explained at appropriate sections of this text.

In this chapter, elements of the Qatar environment, including location, topography, soil, rain fall, temperature, etc, along with the operating industries are described. It is hoped that this would provide a feel for how receptive / tolerable Qatar environment could be to industrial pollution.

#### 1.3 Location of Qatar on the Arabian Gulf

Qatar is a small country that is located approximately halfway along the west side of the Arabian Gulf, east of the Arabian Landmass between

latitudes 24°27′, 26°10′ north and longitudes 50°45′, 51°40′ east figure 1-1. Its shape is that of an oval peninsula that extends out in a northerly direction into the Gulf and it is surrounded by the Gulf waters on all sides apart from the southern end, where it forms a land boundary with Saudi Arabia. It has a land area of 11,427 square kilometers, with a maximum north to south length of approximately 180 km and maximum east to west width of approximately 85 kilometers. It includes a number of islands off the north and west coast and, together with these islands, has a relatively long coastline of almost 700 km, which constitutes almost 25% of the total Arabian Gulf coastline.

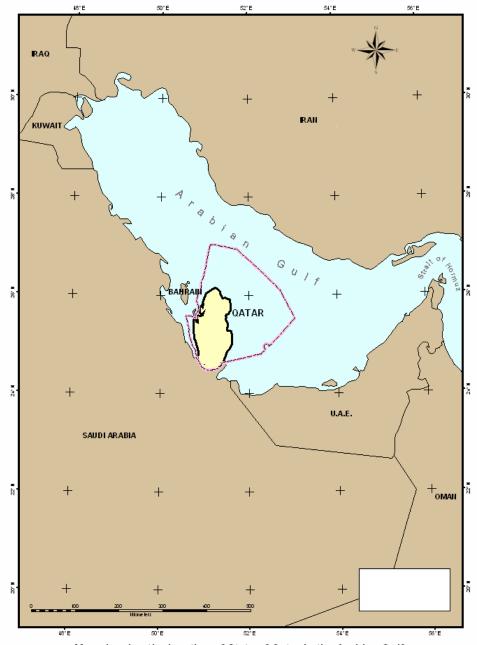


Figure (1-1): Location of Qatar in the Arabian Gulf [4]



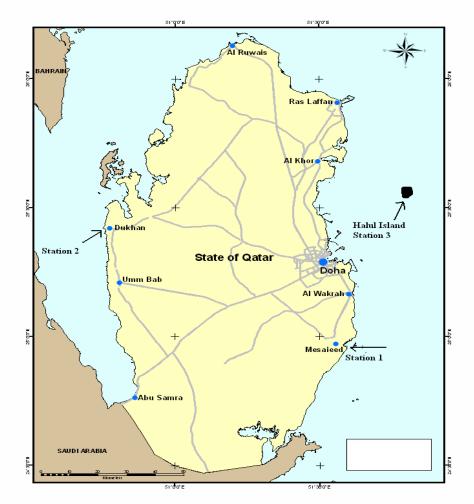


Figure (1-2): Location of onshore & offshore monitoring stations [Dukhan - northwest and Mesaieed – southeast & Halul –North] with Halul aerial view [4]



# 1.4 Topography of the Land

The topography consists essentially of flat eroded rocky low relief land with an elevation generally between sea level and 50 meters above sea level, although there are a few higher elevation areas near the center and south of the country.

There are no high peaks or large hills and the highest land elevation within the landmass is only 103 meters. The main geological elements are as follows:

1. A) Dolomite - limestone marl deposits. These hard rocky deposits cover the majority of the hinterland of the landmass but have suffered various degrees of erosion. In some areas, especially on the west side of Qatar, variable atmospheric weathering has resulted in the formation of low jagged mesa-type hill formations that are known locally as jebels, and sea weathering has resulted in the formation of shallow coves and inlets.

B) Coastal marshes and mud flats. These are known as sabhkas and generally consist of sandy areas between the low and high tidal range.These areas are subject to constant wetting by tides and can have a soft bog-like consistency when wet [5].

- 2. Sand dunes. These are unstable accumulated deposits of sand that are most prevalent in the south east area close to the Saudi Arabian border.
- 3. In many areas, the hard limestone and marl is covered with a thin layer of loose sand, giving the land a subdued appearance.

Information on the topography of Qatar is as follows. In figure 1-3, the areas marked in pink color have heights that extend from 70 to 90 meters while the grey areas coastal areas are below 10 meters high. In figure 1-4, the red marks denote places that are higher than 90 meters. In comparison between the sites of the monitoring stations as two are located onshore and one offshore full climate change are highly important to understand the local environment. [6]

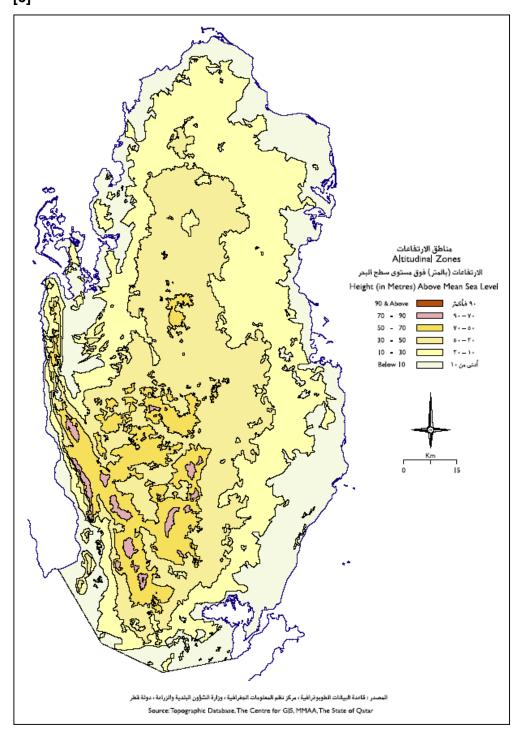
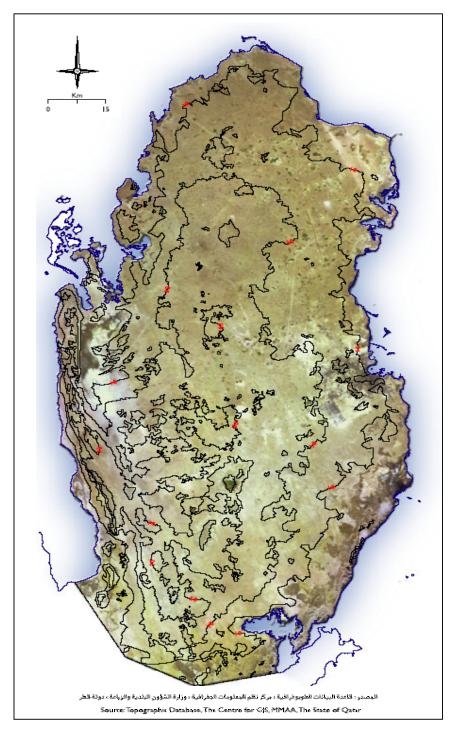


Figure (1-3): Topography of Qatar map showing places at varying heights [6]

Figure (1-4): Topography of Qatar map showing heights in excess of 90 meters, marked in red. [6]



#### 1.5 Depth, Current and Tides

The Arabian Gulf is in reality like a drowned estuary. It is a relatively shallow, enclosed sea with an average depth in the area immediately around Qatar of approximately 30 meters and a maximum depth generally around 35 meters. It becomes deeper moving out towards the Qatar-Iran water boundary but even in this area the depth rarely exceeds 50 meters. Being almost fully enclosed, the currents in the Arabian Gulf are generally not very strong and the tidal range is only around 1.5 meters [7]. The relatively stagnant condition of the Gulf waters render them highly susceptible to localized pollution by industrial and domestic effluents, which can easily cause severe harm to the delicate ecosystem contained within them.

#### 1.6 Water Salinity

Being hot and relatively stagnant, the salinity of the water in the Gulf is high, with a salt content of normal sea water, around 0.375 percent. This high salinity and the high temperature make the seawater relatively corrosive to a range of constructional materials, including carbon and stainless steels.

#### 1.7 Population

The population of Qatar was relatively small at less than 100,000 up until 1948. It then rose up to about 1970, when it was still under 200,000. Since 1970, it has risen rapidly at an average annual rate of 4%, primarily as a result of the large influx of expatriate workers, and the current 2005 estimated population is 600,000, and it is expected to rise a million by 2010 and whom only around 25% are estimated to be Qataris. [8] Approximately 60% of the population are estimated to live in and around the capital city of Doha, with the majority of the reminder living in the other main population centers of Mesaieed and Al-Wakra in the south, Dukhan in the West, Madinat Al Shamal in the north and Al Khor in he north east. With the present major expansion of Ras Laffan Industrial City, there has been a significant shift of the population to Al Khor and the other areas adjacent to Ras Laffan. Figure 1-2 shows the locations of the above towns in the country.

#### 1.8 Flora

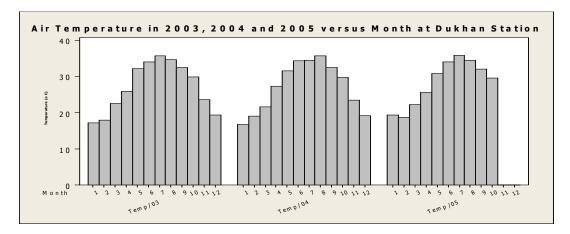
Being essentially hot and dry, the natural vegetation on the Qatari landmass is relatively open and sparse. In most areas, there is some vegetation in the form of scrub. There are, however, a number of areas, known as oases, where the ground water rises to near surface level. Denser and more luxuriant growth of bushes and trees, especially palm trees, are evident in these areas.

#### 1.9 Climate

Qatar is located in a dry desert zone with an annual average precipitation of less than 12 cm. This usually falls during the period November to March, and there is very little to no rainfall between April and October. The temperature is warm during the winter months between October and April, with an average daytime temperature of between 25°C (in January) and 35°C (in April and October). However, it is hot during the summer months of June to September, with the average daytime maximum temperatures in the range 37-45°C. The temperature of the Gulf waters surrounding Qatar generally varies between around 20°C in winter and 35°C in summer. Being a peninsula, the humidity of the air also varies greatly between summer and winter months. In winter months, it is generally low, with a value below 60%. In the hot summer months, it rises to between 70 and 90%, as evaporation of the seawater occurs.

As is shown by the bar graph of figure 1-5, the highest temperatures are recorded during June – September. Minitab Statistical Software was used to plot some of this data of interest that no noticeable rise in the average temperatures recorded for the year 2005 compared with 2003 and 2004. [9]

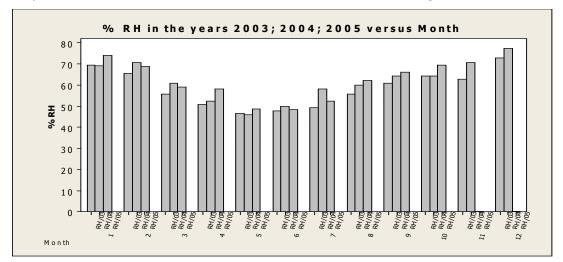
**Figure (1-5):** Average monthly air temperatures for the years 2003, 2004 and 2005 recorded at Dukhan station. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.



Data on Temperature (T), Relative Humidity (RH) and Wind (W) were tabulated, for the years 2003, 2004 and part of 2005, from the Dukhan station, and the monthly averages were calculated.

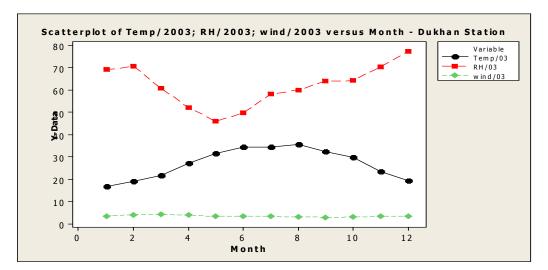
The data of figure 1-6 show monthly average relative humidity readings for the years 2003, 2004 and 2005 registered at Dukhan station. The highest relative humidity was recorded for the winter months October – February. Note that these values are the calculated averages of monthly readings.

**Figure (1-6):** Comparison of monthly average Relative Humidity [RH] for the years 2003, 2004 and 2005 registered at Dukhan. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station

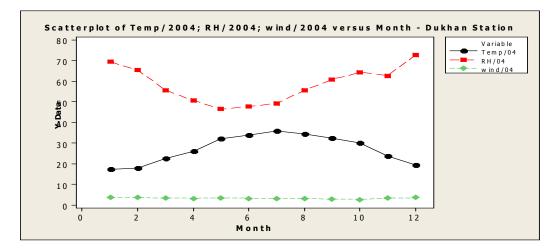


As is shown in the figure 1-7, as the temperature starts rising in March – April, the relative humidity falls then to level off between May and July after which it starts going up in August reaching nearly 80% in December.

**Figure (1-7):** Variation of temperature, RH and wind speed vs. month for 2003 at Dukhan. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station



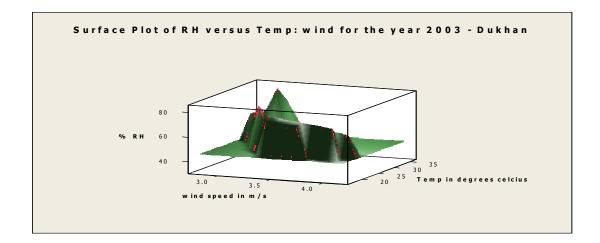
**Figure (1-8)**: Correlates the Temperature readings in <sup>o</sup>C with the relative humidity as well as the wind speed in meters/sec for the year 2004. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.



The values are again monthly averages every hour - day and night.

Figure 1-9 shows a 3 dimensional plot for the data % Relative Humidity, Wind speed and Temperature for the year 2003. In essence, it shows the relationship between temperature and wind speed on relative humidity. As is shown in the figure, the highest relative humidity is when wind speed is between 3.5 - 3.6 m/s and the temperature is between 30 - 35 C<sup>0</sup>.

**Figure (1-9):** Surface plot for RH versus Temperature: Wind for the year 2003 at Dukhan. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.



#### 1.10 Winds

The winds to which Qatar is subjected are generally light. The prevailing winds across Qatar are easterly trade winds, which carry cooler moist offshore air from the Gulf waters across the Qatari landmass towards Saudi Arabia. For limited periods of time during each year, Qatar is subject to the northerly wind known as the Shemal. These bring much cooler air from the deserts of Iran and Iraq in Fig 1-2.

**Figure (1-10):** monthly average readings for wind speed during the years 2003, 2004 and 2005 registered at Dukhan. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.

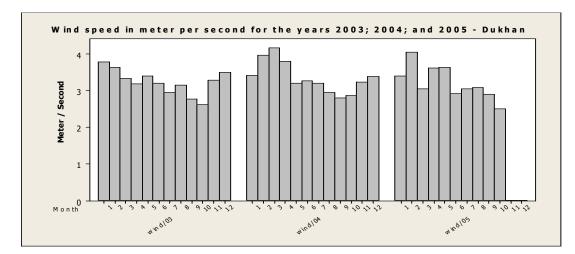
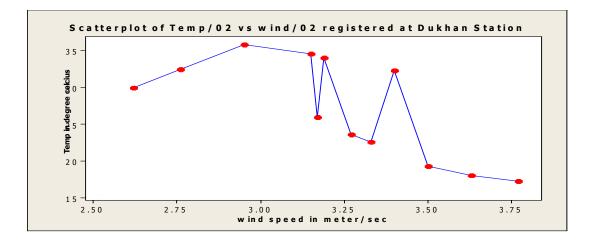


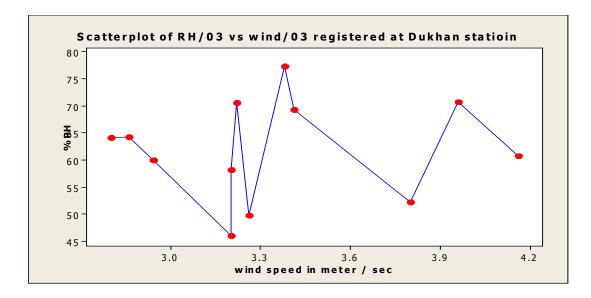
Figure 1-10 shows monthly average wind speeds registered during the last three years at Dukhan station. As is shown in the figure, wind speed is somewhat higher for the months November to March ranging between 3 and 4.2 meters per second [m/s]. The wind speeds can, however, be considered moderate throughout the year rarely exceeding 4 m/s.

Figure 1-11 shows the relationship between temperature and wind speed. Generally speaking, as wind speed picks up the temperature slowly drops. However, there does not appear to be a precise relationship between wind speed and temperature.

**Figure (1–11)**: The relationship between temperature and wind speed. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.



**Figure (1-12):** Relative Humidity (RH) versus wind speed for 2003. These data were collected as part of the dataset of this thesis, from the Dukhan monitoring station.



Figures 1-12 show the variation of wind speed with relative humidity. There is no clear linear relationship between the parameters.

# **1.11 Natural Resources**

#### a. Crude Oil

Qatar has modest oil reserves estimated at 0.6 billion barrels. Oil is produced from onshore [Dukhan fields] and offshore wells located within the territorial waters of Qatar peninsula. Onshore oil is of high quality with an API number of nearly 41 and less than 1.1% sulfur while offshore oil has an API number of 34 and a sulfur content of 1.5% [3]

#### b. Natural Gas

Qatar is blessed with an abundance of natural gas reserve estimated at 6% of the world's natural gas reserves located in one single gas field. Total gas volume is estimated at 900 trillion cubic feet. Besides nearly 500 million cubic feet per day of associated gas is produced from the oil fields [10].

# c. Mineral Resources

Deposits of Limestone, gypsum, clay, shale, sand, dolomite, and magnesium salts

#### d. Agriculture

Only 0.6% of the total area of Qatar is cultivated. This is mainly due to the saline soils, scarcity of water and rather harsh weather conditions. Efforts are being made by the State to increase the size of agricultural land through irrigation or selection of appropriate land uses.

### e. Fishery Resources

Qatar has a coastal line of nearly 700 km providing for rich fishery resources that supply local demand.

### 6. Fresh Water Resources

Desalinated water from three major power and water desalination stations in Dukhan, Ras Laffan and Ras Abu Fontas provide the main source of fresh water supply in the country. This is supplemented by natural wells. There fossil fuels consumption 50 mm ft<sup>3</sup>/d, 450 mm ft<sup>3</sup>/d, 500 mm ft3/d is averaging of one billion ft3/d of natural gas.

Table 1-1 shows the quantities of water produced from Ras Abu Fontas and from natural wells over the years 1994 – 1999.

 Table (1-1): Quantities of water in million US gallons produced from Ras Abu

 Fontas and natural field wells. [11].

Year	Ras Abu Fontas	Field Wells
1994	18372	540
1995	19233	655
1996	20326	602
1997	21442	599
1998	27090	613
1999	27071	378

	Year			
Sector	1996	1997	1998	1999
Commercial	10999.8	11917.9	13283.5	14638.4
Industrial	7615	8250.9	9196.3	1063.8
Urban	54152.7	58672.9	65395.9	55538
Government	11845.9	12834.7	14305.4	8360.7
Loss	NA	NA	NA	54191
	(Not Available)			
Total	84613.6	91676.4	102181.1	133791.9

 Table (1-2):
 Water consumption in cubic meters by various sectors between

 1996–1999

Table 1-2 shows water consumption by the various sectors between 1996 and 1999.

# 1.12 Major Cities

#### DOHA

Doha is the capital city that has undergone remarkable developments on all fronts. New and elegant looking structures have been coming up, particularly along the western sea sides that feature both traditional Arab style and modern architecture. It houses several public and private educational institutions.

#### Mesaieed Industrial City (MIC)

Mesaieed lies about 45 km south of Doha. It is the main industrial city in Qatar where numerous major industries, including the world's largest urea manufacturer, are. It is a major tourist centre, with a fine sea line beach resort and sand dunes.

### Ras Laffan Industrial City (RLC)

RLC, some 80 kilometers north of Doha, has been developing in parallel to the expanding LNG (Liquefied Natural Gas) and other hydrocarbon related process industries. It accommodates the world's largest LNG plant and export port facility.

### Halul Island:

It is an island northeast of the state of Qatar major oil export terminal. One of the air monitoring stations is located at the north side of the island at the airport.

### Al-Khor

This tiny town is situated some 57 kilometers north of Doha with a small port for small vessels. Because of its greenery nature with mangrove trees which is common plantation on the Gulf coast, it has been a recreational site, particularly during winter months.

# Al-Wakrah

This fishing town lies some 15 kilometers south of Doha on the way to Mesaieed. It has a port for small crafts and an anchorage for fishing boats.

# Dukhan

This is an oil town where most of the on-shore production facilities are located. It is nearly 85 kilometers northwest of Doha with fine sandy beaches. Figure1-1 presented earlier in the chapter shows location of the above towns. Table1-4 has the available population figures for Qatari municipalities published in March, 2004.

Municipality	Males	Females	Total
Doha	219676	120171	339847
Mesaieed	11219	1455	12674
Al Wakra	18155	13286	31441
Al Khor	25319	6228	31547

Table (1-3): Available population figures, March 2004. [11]

# 1.13 Environmental Bodies in the Country

- 1. The Supreme Council for the Environment and Natural Reserves-Governmental Organization (GO) [2].
- Ministry of Energy and Industry (GO), Qatar Petroleum Department of Environment and Sustainable Development – Semi Governmental Organization (SGO).
- The Department of Youth (GO), Center for the Friends of Environment – Non Governmental Organization (NGO).
- 4. Representatives of:
  - a) Council of Arab Ministries Responsible for Environment (CAMRE) assisted by UN's Regional Office for West Asia [ROWA].
  - b) Regional Organization for the Protection of the Marine Environment [Kuwait].
  - c) The Center for the affairs of Man and the Environment [Riyadh].

#### 1.14 HISTORICAL INDUSTRIAL DEVELOPMENT

#### Period Up Until 1949

Although there has been evidence of human habitation in Qatar for as long as 8,000 years, through most of this period, the low rainfall has made it a relatively inhospitable place for extensive human settlement. Up until the last 50 to 60 years, the hinterland was largely inaccessible and was populated only by a small number of nomadic pastoralists, who made a living from herding sheep, goats and camels. The majority of the population was located in a number of coastal towns and villages and most Qataris were fishermen or pearl divers.

These in turn supported the local industries of boat building, fishing net construction and clothing manufacture. There was also regular trading between other seafaring nations in the Gulf Region; so many people were traders of local crafts and goods. This already limited economy was dealt a severe blow in the early 1930's, when the Gulf pearl industry was badly affected by the Japanese development of the cultured pearl [12].

The industry never recovered from this setback and as a result many Qatari left to find work elsewhere, resulting in a marked decline in the population at that time. At this low point in Qatari economic fortunes, an agreement was reached with the Anglo Persian Oil Company for oil excavations to be carried out in Qatar. Oil was discovered at Dukhan on the west side of Qatar in 1939 but production was delayed by the Second World War. Following this, extensive development took place.

#### Period 1949 to the Early 1970's

The first shipment of oil left Qatar in 1949 and this marked an increase in both the economic prosperity of the country and the start of its industrialization. Within four years of oil being produced, an oil refinery was constructed at Mesaieed in the east of Qatar in 1953. Subsequent exploration in the waters surrounding Qatar led to the discovery of offshore oil fields.

The first of these offshore fields, Maydan Mahzam, was discovered in 1960 and oil production from it commenced in 1965. Subsequently, oil production commenced from the Idd Al-Sharqi field in 1968 and the Bul Hanine field in 1973. As the level of oil production increased the refining and processing capacity requirement grew and a larger and more modern refining facility was constructed at Mesaieed in 1974.

In 1978, the National Oil Distribution Company (NODCO) was formed as the sole agency responsible for the storage, distribution and retailing of oil and oil-related products in Qatar.

This company operates the pipelines that transport oil and gas around the country and to export terminals and the operation of the refinery at Mesaieed. Even more importantly, a large gas field, known as the North Gas Field, was discovered 1971. This was subsequently found to be the largest non-associated gas reserve in the world, with present proven reserves of 12 trillion standard cubic feet of Liquefied Natural Gas LNG. It extends from beneath the north east side of the Qatari landmass and out beneath the Gulf to the Qatar-Iran boundary. However, development of, and production from, this gas field did not commence until the end 1980's because the economic conditions were not considered to be viable for the large investment required up until that time .[4]

#### Early 1970's to Present

By the late 1960's, it was clear that Qatar, with its rapidly expanding oil production and processing facilities, was developing as an essentially oilbased economy and that the income from oil product sales would be the financial basis for the social development of the country. Whilst the marked increase in the price of oil that occurred in the early 1970's greatly increased the income and hence the prosperity of Qatar, there was a growing realization that the country's future financial well-being was dependent upon the price of oil remaining high. [13]

In an effort to widen the basis of the economy, and hence reduce the risk of economic problems associated with fluctuations in the price of oil, and to partly satisfy local needs and hence reduce import requirements, a number of other manufacturing industries were set up in the late 1960's and early 1970's. These industries were generally developed as joint ventures between foreign specialist companies and the Qatari government, with the latter having the majority shareholding [i.e., Qatar Fertiliser Company QAFCO is 25% Norsk Hydro of Norway and 75% government, the Qatar Steel Company QASCO was shared between CobeSteel of Japan and the government. The manufacturing facilities have in all cases been subsequently expanded to meet increasing production requirements and targets.

In 1985, the Qatar National Cement Company was established, to manufacture of the chloride-resistant cement required for industrial and urban construction and in 1969, the Qatar Flour Mills Company was set up to produce the wheat flour and derivatives required for local consumption.

Qatar Fertilizer Company (QAFCO) was set up in 1969 to manufacture ammonia and urea for both local use and export and the Qatar Petrochemical Company (QAPCO) was established in 1973 to manufacture ethylene, low density polyethylene and ethane. In 1974, the Qatar Iron and Steel Company (QASCO) was set up to produce large quantities of steel billets, steel reinforcing bars for concrete and sponge iron for both local use and export. An organic fertilizer plant designed to process refuse into organic fertilizer and recover scrap iron was commissioned in 1977 and a large number of private and semi-private light industrial engineering and specialist product manufacturing companies have also been set up in designated industrial areas.

Most of the large manufacturing facilities were set up in the Mesaieed Industrial Area, although the cement works was located in Umm Bab, close to Dukhan, due to its proximity to the raw materials required for cement manufacture.

In July 1974, by Emiri Decree, Qatar General Petroleum Company was formed as the umbrella company for all oil and gas activity in the Emirate of Qatar. The company is responsible for all oil and gas exploration, drilling, production, maintenance, transportation, distribution and retail activities and the production of derivative products .[4]

It incorporated NODCO as a wholly-owned subsidiary and gained effective control over all relevant subsidiaries and joint venture organizations. In 1993, the Qatar Fuel Additives Company (QAFAC) and Qatar Clean Energy Company (QACENCO) were set up to manufacture and export fuel additive chemicals, such as methanol and MTBE (Methyl Tertiary Butyl Ether).

In the 1990's, further offshore oil exploration took place in conjunction with foreign partners under production sharing agreements. As a result, the further offshore oil fields of Al-Rayyan, Al-Shaheen, Al-Khalij and Al-Karkara were discovered, increasing the proven recoverable Qatari oil reserves to at least 4.4 billion barrels. The bulk of these reserves, 2.2 billion barrels, still lie in the huge onshore Dukahn oil field. Development work on existing fields, especially the Idd Al-Sharqi field, has enabled production to be increased to the point where it currently has a sustainable production capacity of 850,000 barrels per day.

In spite of the continuing oil exploration and production development, the major project of the mid 1980's to the mid- 1990's has been the development of the North Gas Field and the production and shipment of LNG from it. This has required a specially designed port and industrial city to be constructed at Ras Laffan, on the north east side of the Qatar peninsula. Qatar Liquefied National Gas Company (Qatar Gas) was set up in 1984 as a joint venture to produce and export a specified minimum quantity of liquefied LNG and Ras Laffan Liquified Natural Gas Company (Ras Gas) was similarly set up in 1993 to produce and export a further specified minimum quantity of liquefied LNG. Having developed the production of LNG from the North Gas Field, the focus of the late 1990's and early 2000's has been the development of companies and facilities for converting the gas into higher value products for export. As a result, Qatar is set to become the largest LNG exporter in the world and a world leader in "gas-to-liquids" production. [14]

The refinery at Mesaieed was expanded again in 1999 and its capacity was increased from below 57,000 barrels per day to around 83,000 barrels per day. One condensate refining unit was constructed and a further unit is planned. This case increases the refinery capacity to around 137,000 barrels per day by the year 2004.

Although the existence of natural gas beneath the Qatari territorial waters had been known for some time, it wasn't until 1971 that the North Field natural gas field was discovered. Commercial exploitation of the natural gas reserves did not start until the 1980's, primarily because the economic situation up to that time did not justify the considerable investment involved in its development. Figures 1 - 14 shows the major seaside industries in MIC. [15]

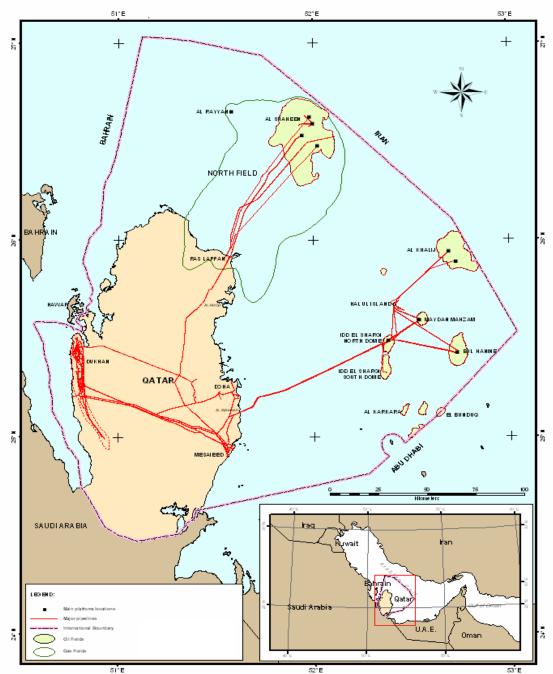


Figure (1-13): Major oil and gas fields in Qatar. [4]



# 1.15 Major Operating Industries

# 1. Qatar Petroleum (QP)

QP was established in 1974 as a national corporation completely owned by the state. The principal activities of QP, its subsidiaries and joint ventures, are hydrocarbon, both oil and gas, exploration, production, processing and sales.

# 2. Qatar Fertilizer Company

Established in 1969, with ammonia and urea process plants in Mesaieed.

# 3. Qatar Petrochemical Company

Established in 1974. A manufacturer of Ethylene and low density polyethylene. Process plants in Mesaieed.

# 4. Qatar Fuel Additives

Established in 1990 and involved in the production of methanol and methyl tertiary butyl ether plant in Mesaieed.

# 5. Qatar vinyl Company

Established in 1997. Produces Caustic Soda, Ethylene dichloride and Vinyl Chloride Monomer. Plants are in Mesaieed.

# 6. Refineries

Established in 1960. Produces Liquefied Petroleum Gas (LPG), Premium and Super gasoline, Jet fuel, Diesel and fuel oil. Plants are in Mesaieed.

# 7. Gas Processing and Liquefaction

Has four Natural Gas Liquefaction (NGL) plants producing Propane, Butane and Condensate. Plants are in Mesaieed.

# 8. Qatar Liquefied Natural Gas Company

Established in 1984 and started production in 1996. Produces Liquefied Natural Gas LNG, Natural Gas Liquid NGL Condensate and Sulfur. Plants located in Ras Laffan industrial City.

# 9. Ras Laffan Liquefied Natural Gas Company

Established in 1993, produces LNG, NGL, Condensate and Sulfur. Plants are in Ras Laffan Industrial City.

# 10. Qatar Steel Company

Established in 1974, produces Steel Bars. Plant in Mesaieed.

# 11. Qatar national Cement Company

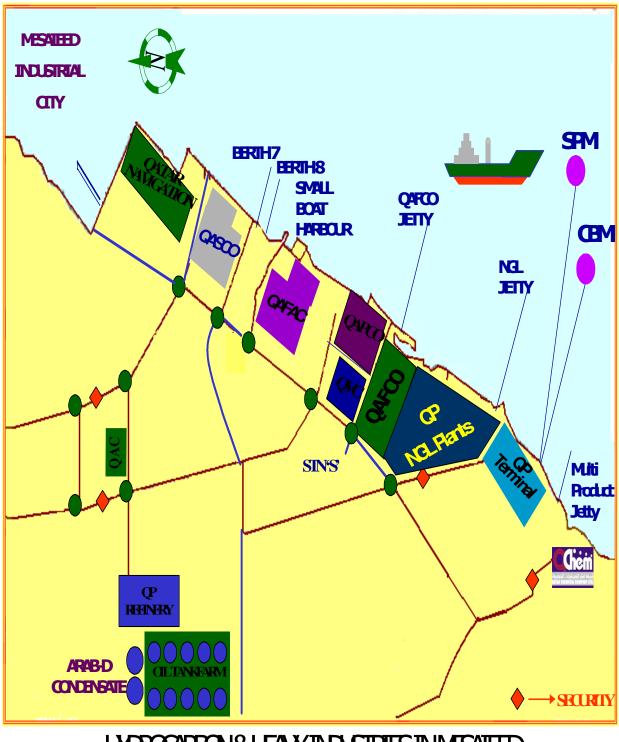
Established in 1965, produces Ordinary Portland Cement (OPCO), Sulfate Resistant Cement (SRC) and Calcined Lime. Plant is in Umm-Bab.

Several other huge industrial projects, i.e., Qatar Chemicals Company, Gas to liquid complex, Condensate refineries, etc., are under construction and numerous small and medium scale industries are in operation.

Table (1-4): List of major operating industries in Qatar [3]

Industry	Yr Established	Products	Location	Comments
QP	1974	Oil, Gas, Condensate	MIC, Dukhan, RL, Offshore	
Qatar Fertilizer	1969	Ammonia, urea, urea formaldehyde, sulfuric acid	MIC	The largest urea producer world wide
Qatar Petrochemical	1974	Ethylene, Polyethylene,	MIC	Expanding
Qatar Fuel Additives	1990	MTBE, Methanol	MIC	
Qatar Vinyl	1997	Vinyl chloride	MIC	
Refineries	1960	Typical refinery products	MIC	Expanding
Natural Gas Liquids/ NGL Complex	1968	NGL, Condensate, sulfur	MIC	
Qatargas / LNG	1984	LNG, NGL, Sulfur	RLC	Expanding
Rasgas / LNG	1993	LNG, NGL, Sulfur	RLC	Expanding
Qatar Steel	1974	Steel Bars	MIC	
Qatar National Cement	1965	OPC, SRC	Umm-Bab	
Water & Electricity	1950	Water, electricity	Doha	
Flour Mill	1993	Flour	Doha	

Figure (1-14): Major seaside industries in Mesaieed. [4]



# HDROCAREON&HEAVYINDLSTRIES INMESATED

#### Chapter 2

#### 2.1 Section A - Air Quality Monitoring

Air quality monitoring is perhaps one of the most active and diverse research areas that have recently been pursued around the world, at least in the developed countries. [16, 17] Besides the fact that information emanating from such research would provide inferences on respiratory health problems to certain interested parties, i.e., health professionals, it has been vastly linked to global warming, climate change as well as sustainable development, Human rights and economic growth issues, to name a few. [18, 19]

Since the publication of the Brundtland Report in 1987 [20], various international and national organizations have been developing sets of the measure and assess one or more aspects of sustainable development. These efforts received a major boost following the adoption of Agenda 21 at the Earth Summit in 1992, which specifically asks countries and international governmental and nongovernmental agencies and and to harmonize them at the national, regional and global levels. [21, 22]

Sustainable development is essentially about improving quality of life in a way can sustained, economically and environmentally, over the long term supported by the institutional structure of the country. For this reason, sustainable development addresses four major dimensions: social, economic, environmental and institutional. [23,24,25]

I myself have been involved in the implantation of Agenda 21 Commission on Sustainable Development CSD particularly the 2<sup>nd</sup> summit held in Johannesburg, South Africa in 2002. Furthermore, I was instrumental in developing the views of the State of Qatar in the preparation on the negations on climate change issues for more than 10 years. [26,27, 28] I also chaired on behalf of the state of Qatar many debates concerning Kyoto protocol decisions. I served as a member of the UNFCCC bureau in 2002-2003 and headed the group of 77+ China of the developing countries in 2004. During the 20<sup>th</sup> century, the Earth's average surface temperature rose by around 0.6 C and evidence is growing that most of this warming is attributable to increasing concentrations of greenhouse gases (GHGs) in the atmosphere. The amount of CO<sub>2</sub>, for example, has increased by more than 30% since pre-industrial times and is currently increasing at an unprecedented rate of about 0.4% per year, mainly due to the combustion of fossils fuels and deforestation. [29] The concentrations of CH<sub>4</sub> and NO<sub>2</sub> are increasing as well due to energy, agricultural, industrial and other activities. [30, 31, and 32]

The United Nations Framework Convention on Climate Change (UNFCCC) entered into force in March 1994. The convention included a commitment by Parties, both developed countries and economies in transition (Annex I Parties), to aim to return emissions of CO<sub>2</sub> and other GHGs not controlled by the Montreal Protocol to their 1990 levels by 2000, although relatively few parties actually met this goal [27].

The Kyoto Protocol was adopted in December 1997. It was designed to enter into force after being ratified by at least 55 Parties to the convention, including developed countries accounting for at least 55% of the total 1992  $CO_2$  emissions from this group. [33] Decision in 2004 by the Russian Federation to ratify the Protocol, it entered into force in early 2005. In any event, countries are also bound by their commitments under the convention.

In brief, the protocol is a legally binding commitment calling on industrialized countries to reduce their combined greenhouse gases gas emissions by at least 5% compared to 1990 levels in the period 2008-2012. Perhaps the most valuable part of the Kyoto Protocol is the timeframe placed on the industrialized countries to reduce these emissions. [34, 35]

The concentrations of nitrogen monoxide (NO), nitrogen oxide (NO<sub>2</sub>), Carbon monoxide (CO) and non-methane volatile organic compounds (NMVOCs) are also increasing as a result of anthropogenic activity. Although these gases are not themselves GHGs, they affect atmospheric chemistry, leading to an increase in troposhperic ozone, which is a GHG. [36, 37, 38]

The resulting effect is predicted to lead to more extreme weather events than in the past, with some areas experiencing increased storms and rainfall, and others suffering drought. How fast and where this change will happen is still uncertain, but the consequences may be serious, especially in developing countries, which are the least able to prepare for and deal with the effects of extreme weather conditions such as floods, landslides, droughts. These were confirmed as per the Intergovernmental Penal for Climate Change IPCC on their fourth assessment report in 2007. [39, 40, 41, 42, 43]

GHGs contribute in varying degrees to global warming depending in their heat absorption capacity and their lifetime in the atmosphere. The Global warming potential GWP describes the cumulative radioactive forcing effect of a gas over a time horizon (usually chosen for reporting purposes to be 100 years) compared with that Of CO<sub>2</sub>. For example, the 100 year GWP of CH<sub>4</sub> is 21, meaning that the global warming impact of I kilogram (Kg) of CH<sub>4</sub> is 21 times, higher than that of I kg of CO<sub>2</sub>. The GWP on N<sub>2</sub>O is 310.

CO<sub>2</sub> emissions from fuel combustion are calculated by multiplying the energy use for each fuel type by an associated CO<sub>2</sub> emission coefficient. Wherever possible, GHG emissions should be measured directly at the source of energy use. More commonly, however, measured data, some time are incomplete or unavailable. [44]

In the absence of measured data, emissions are calculated by multiplying some known data, such as coal production or natural gas throughout, by an associated emission factor derived from a small sample from a relevant emission source or through laboratory experiments [45, 46]. Availability of energy has a direct impact on poverty, employment opportunities, education, demographic transition, indoor pollution and health, and has gender-and age-related implications. The social dimensions: Equity and Health Social equity is one of the principal values underlying sustainable development, involving the degree of fairness and inclusiveness with which energy resources are distributed, energy systems are made accessible and pricing schemes are formulated to ensure affordability. [47, 48]

#### 2.2 Ambient concentrations of air pollutants in urban areas

An increasing percentage of the world's population lives in urban areas. High population density and the concentration of industry and traffic exert great pressures on local environments.

Air pollution from energy use in households, industry, power stations and transportation (motor vehicles) is often a major problem. As a result, the greatest potential for human exposure to ambient air pollution and subsequent health problems occurs in urban areas. Improving air quality is significant aspect of promoting sustainable human settlements. [49, 50]

It is important to monitor trends in air pollution as a basis for prioritizing policy actions; to map levels of air pollution in order to identify hotspots or areas in need of special attention; to help assess the number of people exposed to excessive levels of air pollution; to monitor levels of compliance with air quality standards; to assess the effects of air quality polices; and to help investigate associations between air pollution and health effects.

There are several international conventions that focus on controlling air emission as means of improving air quality. Concern over emissions of acidifying pollutants has led to several international agreements, including the United Nations Economic Commission of Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) Geneva, 1979) and its protocols to reduce emissions of sulfur (Helsinki, 1985; Oslo, 1994; Gothenburg, 1999) nitrogen oxides (Sofia, 1988; Gothenburg, 1999). [51] Two other protocols have also been agreed upon that aim at reducing heavy metals (Aarhus, 1998) and non-methane volatile organic compounds (Geneva), 1991. World Health Organization (WHO) air quality guidelines exist for all the pollutants. Many countries have established their own air quality standards for many of these pollutants.

Data on ambient air pollution concentrations are often routinely collected by national or local monitoring networks. Universities and research institutes often also collect data for research purposes; In addition, industry collects many data. Data on concentrations of major air pollutants are available for major cities in Organization for Economic Cooperation and Development (OECD) countries, but more work is needed to improve international comparability and to link these data to national standards [52].

#### 2.3 Air Pollutant Emission from Energy Systems

There is growing concern about higher concentrations of various air pollutants, mainly arising from energy use. The concentration of pollutants is largely influenced by energy production and consumption patterns, which in turn are affected by both energy intensity and efficiency [53]. Emissions of these pollutants are also influenced by national standards of pollution abatement and control, and the use of clean energy technologies. The level of emissions gives an indication of the impact of human activities on the environment. A country's efforts to abate air pollutant emissions are reflected in its national policies and international commitments. Concrete actions include structural changes in energy demand (efficiency improvements and fuel substitution) as well as pollution control policies and technical measures (e.g. the installation of industrial precipitators, de-nitrification and desulphurization facilities, and the use of catalytic converters on cars). [54]

Sulfur and nitrogen compounds are the source of environmental acidification. Anthropogenic nitrogen is predominantly emitted as nitrous oxides  $(NO_x)$  by transport sources, as well as by other energy uses and industrial processes. Airborne emissions of NO<sub>x</sub> contribute to both local pollution and to large-scale pollution through long-distance transport in the atmosphere. [54]

Air pollutants are associated with respiratory morbidity and mortality in humans; for example,  $NO_x$  can irritate the lungs and lower resistance to respiratory infections. The effects of short-term exposure still unclear, but continued or frequent exposure to concentrations higher than those normally found in the ambient air may cause increased incidence of acute respiratory disease. [55]

In the presences of sunlight,  $NO_x$  react with volatile organic compounds (VOCs) to form tropospheric ozone and other oxidizing chemicals, which are toxic to living things, including human beings.  $NO_x$  and sulfur dioxide (SO<sub>2</sub>) are also precursors to acids in rainwater and subsequently have deleterious effects on artifacts, aquatic organisms, agriculture and habitats. Atmospheric deposition of  $NO_x$  can also contribute to eutrophication. In some areas,  $NO_x$  are precursors to particulate matter concentrations. The deposition of nitrogen may be dry (in the form of gases and particles) or wet (in the form of rain or snow), or in the form of condensation (as fog and cloud droplets).

#### 2.4 Air monitoring Instrumentation

This chapter also contains Experimental and the Methodology description of the techniques and equipment used in this work for data collection. General: All measurement techniques employed in this work utilize the energy absorption phenomenon supplemented by the application of the Beer Lambert Law and using an emitting source except for Chemiluminescence's which measures the energy emitted by the reactants in the form of light.[7]

#### 2.5 Atmospheric pollutants relevant to this thesis:

Air pollution stems from gases and airborne particles that in excess are harmful to human health, artifacts and ecosystems. Emissions of air pollutants from anthropogenic activities are often directly related to the combustion of fossil fuels for energy. However, non-energy-related emission sources are also significant for some pollutants – for example, non-methane volatile organic compound [NMVOCs]. Emissions of greenhouse gases GHGs are such as (carbon dioxide [CO<sub>2</sub>], nitrous oxide [N<sub>2</sub>O] and methane [CH<sub>4</sub>].

## 2.5.1 Sulfur Dioxide (SO<sub>2</sub>):

The primary product from the combustion of sulfur is  $SO_2$ . However, other sulfur oxide compounds can also be produced; thus, when reported, these compounds are to be jointly referred to as  $SO_x$  (sulfur oxide).

On a global basis, sulfur compounds enter the atmosphere, primarily as  $SO_2$ , through anthropogenic activities-namely the combustion of fossil fuels. Non anthropogenic activities, including volcanic, biological decay of organic matter and reduction of sulfate also contribute to the sulfur cycle. The latter sources do so in the form of H<sub>2</sub>S. Virtually all H<sub>2</sub>S that gets into the atmosphere is converted rapidly to  $SO_2$  by the following overall reaction

H<sub>2</sub>S + 3/2O<sub>2</sub> → SO<sub>2</sub> + H<sub>2</sub>O

SO<sub>2</sub> can also get back to the earth as acid rain and/or salt.

SO <sub>2</sub>	+	1/2O2 +	H₂O►	H2SO4
NНз	+	H2SO4		NH4HSO4

Natural concentrations of SO<sub>2</sub> are normally below 5  $\mu$  g/m<sup>3</sup> although annual mean concentrations may exceed 25  $\mu$  g/m<sup>3</sup> in rural areas as a result of power plants emission stacks.

Photo-dissociation of SO<sub>2</sub>, in the troposphere, is not significant because of the lack of sufficiently energetic light (with wavelength below 218 nm). On otherhand, the presence of hydrocarbons and nitrogen oxides greatly increases the oxidation rate of SO<sub>2</sub>. Among those oxidants are HO<sup>\*</sup>, HOO<sup>\*</sup>, O, O<sub>3</sub>, NO<sub>3</sub>, ROO<sup>\*</sup> and RO<sup>\*</sup>. Ozone can, thermodynamically that is, very well react with SO<sub>2</sub> as is observed in this work. It is perceived to be somewhat slow in the gas phase however unless catalyzed by water droplets [56].

#### 2.5.2 Nitrogen Oxides (NO<sub>x</sub>):

The primary combustion product of nitrogen is nitrogen dioxide (NO<sub>2</sub>). However, several other nitrogen compounds are usually emitted at the same time, such as nitrogen monoxide (NO), nitrous oxide (N<sub>2</sub>O), etc., and these may or may not be distinguishable in available test data. Total NO<sub>x</sub> is to be reported on the basis of the molecular weight of NO<sub>2</sub>.

Three nitrogen oxides are present in the atmosphere, Nitrous Oxide (N<sub>2</sub>O), Nitric Oxide (NO) and Nitrogen Dioxide (NO<sub>2</sub>). It is relatively un-reactive and ultimately disintegrates into N<sub>2</sub> and NO appears, in the stratosphere, due to photochemical reactions:

 $N_2O$ Ο hv  $N_2$ + +  $N_2O$ Ο  $N_2$  $O_2$ + + N<sub>2</sub>O 0 2NO +

On the other-hand, colorless and odorless NO and red-brown NO<sub>2</sub> are referred to as "ambient air pollutants" as defined in the clean air act [57, 58]. Collectively known as NO<sub>x</sub>, these gases are created by lightning, fires (both natural and anthropogenic), all kinds of fossil fuel combustion, industrial processes and in the stratosphere from photo degradation of Nitrogen Oxide (N<sub>2</sub>O) and, of course, automobile emissions.

At high temperatures (those of internal combustion engines) the following reaction occurs,

N2 + O2 \_\_\_\_ 2NO

The equilibrium concentration of NO in a typical combustion chamber of an internal engine (mixture of 3% O<sub>2</sub> and 75% N<sub>2</sub>) is a function of temperature. At room temperature ( $27^{\circ}$ C) the equilibrium concentration of NO is only 1.1x10-10 ppm, whereas at 1500 °C it is 10 ppm [56].

Concentrations of NO<sub>2</sub> are relatively short lived in the atmosphere and spatially variable. NO<sub>2</sub> doesn't have a direct global warming effect, but rather affects terrestrial radiation absorption by influencing the formation of tropospheric and, to a lesser degree, lower stratospheric Ozone where it has positive radiative forcing effects.

NO + O<sub>3</sub>  $\longrightarrow$  NO<sub>2</sub> + O<sub>2</sub> NO<sub>2</sub> can also be formed through reaction of NO with hydroperoxyl radicals (HOO\*):

H <sub>2</sub> O	+	hv	<b></b>	HO* +	Н
Н	+	O <sub>2</sub>	$\rightarrow$	HOO*	
HOO*	+	NO	<b>→</b>	NO <sub>2</sub> +	HO*

HOO\* needed for the production of NO<sub>2</sub> can also be generated by the following RXs

 $HO^* + O_3 \longrightarrow O_2 + HOO^*$ 

Also through photochemical dissociation of molecular Oxygen into atomic Oxygen and subsequent production of HO\*(Hydroxyl radicals)

O <sub>2</sub>	+	hv	O +	0
0	+	H₂O →	HO* +	HO*
HO*	+	O <sub>3</sub>	HOO*+	O <sub>2</sub>

## 2.5.3 Ozone

A natural and anthropogenic gas, is included in the category known as "criteria pollutants" under the clean air act. It absorbs ultraviolet radiation strongly in the region 220 – 330 nm and therefore it is effective in filtering out dangerous UV radiation of the B type. It is present both in the stratosphere (natural), where it shields the earth from harmful levels of ultraviolet radiation, and in the troposphere (anthropogenic) where it is the main component of photochemical smog. In the stratosphere, it is produced, by the following two reactions:

O<sub>2</sub> hv 0+0 (wavelength <242.4nm) + 0  $O_2$ Μ  $O_3$ + M (energy absorbing  $N_2$  or  $O_2$ ) + + And it is destroyed by photo dissociation:  $O_3$  $\rightarrow 0_2$ O (wavelength < 325 nm) + hv +

 $O + O_3 \longrightarrow 2O_2$ 

Ozone concentration in the stratosphere is a steady state concentration (estimated at 10 ppm) resulting from the balance of ozone production and destruction by the above processes. If the entire atmospheric ozone was recorded under standard conditions of 273K and 1atm, it would only be 3mm thick.

Ozone absorbs ultraviolet radiation very strongly in the region 220 - 330 nm. It can filter out dangerous UV-B radiation (290 - 320 nm), UV-A radiation (320 - 400 nm) and UV-C radiation (<290 nm) which doesn't penetrate to the troposphere. If the UV-B radiation, being the most harmful, doesn't get absorbed, sever damage would result to the forms of life on earth. Ozone at 0.15 ppm causes coughing, wheezing, bronchial constriction and irritation to the respiratory system. Based upon health effects, a new 8-hr standard of 0.08-ppm ozone was set by the US Environmental Protection Agency in 1997. The level of tropospheric ozone has increased making it the third largest increase in direct radiative forcing since the pre-industrial era, behind CO<sub>2</sub> and CH<sub>4</sub>.

Tropospheric ozone is produced from complex chemical reactions of volatile organic compounds mixing with nitrogen oxides in the presence of sunlight. Over the last two decades, emissions of anthropogenic chlorine and bromine containing halocarbons, such as chlorofluorocarbons (CFC), have depleted stratospheric ozone concentrations. [59, 60]

#### 2.5.4 Particulates:

Terms commonly associated with particulate matter are particulate matter with a diameter less than 10 pm (PM10), total suspended particulate (TSP), primary particulate and secondary particulate. PM10 in the atmosphere can result from direct particulate emission (primary PM10) or from emissions of gaseous particulate precursors that are partly transformed into particles by chemical reactions in the atmosphere (secondary PM10. TSP consists of matter omitted from sources in solid, liquid and vapor forms, but existing in the ambient air as particulate solids or liquids). Chemical processes in the atmosphere convert large quantities of atmospheric gases to particulate matter. Among the chemical species involved are the organic pollutants and nitrogen oxides that cause formation of Ozone and photochemical smog in the troposphere. Therefore, control of hydrocarbon and NO<sub>x</sub> emissions will also curtail atmospheric particulate matter pollution.

Secondary PM10 precursors include  $SO_2$ ,  $NO_x$ ,  $NH_3$  and VOC's [62]. Reliable information on the relative contribution of VOC's to particulate formation is not available. Estimations of quantities of secondary particulates, aerosol formation factors could be used to assess the aggregated particulate formation potential arising from emissions of the different secondary pollutants.

The factors are as follows:

SO <sub>2</sub>	NO <sub>x</sub>	NH3
1.22	1.0	0.11

It should be noted that, as for the tropospheric ozone formation factors, these factors are only a best approximation of the relative contribution of the different pollutants and significant local variations may actually occur in both urban and rural areas. Although none of these gases is classified as one of the greenhouse gases labeled by the Kyoto protocol [33], they absorb/trap infrared radiation and thereby can have indirect and varying "Radioactive Forcing" impact on the earth's and more specifically, Qatar's climate. In some cases emissions from, for example, industrial plants can be estimated based on actual direct measurements in stacks or by material balances. However, in general, pollutant emissions are calculated with the help of an emission factor, which is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant.

These factors are usually expressed as the weight of the pollutant divided by a unit weight, volume, distance or duration of the activity emitting the pollutant (e.g. kilograms of particulate emitted per tonne of coal burned). Such factors facilitate the estimation of emissions from various sources of air pollution and ideally are known on a facility – or country – specific bases. In most cases, these factors are simply averages of all available data of acceptable quality and are generally assumed to be representative of long-term averages for all facilities in the source category (i.e. a population average).

Work to standardize sampling and analytical methods for air pollution has been completed by the International Organization for Standardization (ISO), the World Meteorological Organization (WMO), the World Health Organization (WHO), the Organization for Economic Cooperation and Development (OECD) and the Cooperative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP). Similarly, in recent years, considerable effort has been made to standardize or harmonize the calculation of national emission inventories for air pollutants in order to improve the comparability of national estimates.

There have been a number of initiatives that provide guidance to countries on the creation, compilation and reporting of pollutant release inventories. These include the OECD Pollutant Release and Transfer Register (PRTR) program guidance (OECD, 1996), and the United Nations Institute for Training and Research (UNITAR) guidance on pollutant release and transfer registers (UNITAR, 1997).

## 2.5.5 Volatile Organic Compounds (VOCs):

VOCs are defined as any compound of carbon (excluding CO,  $CO_2$ , carbonic acid, metallic carbides or carbonates, and ammonium carbonate) that participates in atmospheric chemical reactions. In some cases, the term non-methane volatile organic compound (NMVOC) is used to indicate that methane is exempt from the VOC categorization.

## 2.5.6 Carbon Monoxide (CO):

CO is formed from the incomplete combustion of fossil fuels, in most countries the transport sector is the main source of CO emissions. Emissions of  $NO_x$  VOCs, CO and  $CH_4$  contribute to the formation of ground-level (or tropospheric) ozone. These ozone precursors can be aggregated on the basis of their ozone-forming potential to assess the combined impact of the different pollutants. The relative weighting factors are as follows:

NO <sub>x</sub>	NMVOCs	СО	CH <sub>4</sub>
1.22	1.0	0.11	0.0149

This list of pollutants is routinely used by the European Environment Agency (EEA) for its reporting of ozone formation, but the use of such factors does not yet have broad international acceptance. The factors are assumed to be representative for Europe as a whole, but on the local geographical scale, the factors may vary. [61]

## 2.6 Monitoring system on site:

Data were collected at three monitoring stations using monitoring instrumentation, manufactured by "Advanced Pollution Instruments" of the US and provided by "Enviro Technology" of the UK. The stations were installed in the year 2001 started on 2002 at the three locations in the State of Qatar: Mesaieed Industrial City, Dukhan and Halul Island. Appendix 1-11

Each monitoring station has the dimensions 3.7 meter (Length) and 2.5 meter (Width) with internal headroom of 2.4 meters. The majority of the instruments are contained within a dual rack. Rack cooling is achieved through 12 fans mounted in the top surface. A 240 volt 50 Hz 32 amp electrical supply is provided to the enclosure with a 16A UPS circuit so that power will be maintained to the monitoring equipment during any mains supply failure. The inner station is fully air conditioned by two locally supplied wall mounted units to maintain an internal stable operating temperature of approximately 20-25°C.

A US Robotic Modem unit operating at 57Kb is used for data communication. An Opsis DL 256 Data logger is used for data collection and storage with a standard PC screen and keyboard attached. The data logger also controls the operation of the daily auto calibrations and monitors the operational status of the analyzers. [62]

The analyzers output analogue voltages continually to represent pollutant concentrations. The analogue outputs from the analyzers are collected by the data logger every 10 seconds and are stored as specified averages in the logger memory. Data are also stored in the non-volatile RAM memory pack of the logger for long-term back up. The logger is programmed to trigger the daily analyzer auto calibrations using control signals, which drive relays to initiate zero and span measurement cycles.

The configuration of the data logger channels is shown in Table 2-1.

Channel No	Parameter
1	SO <sub>2</sub>
4	NO <sub>2</sub>
5	CO
6	O <sub>3</sub>
10	Dust
11	Wind Speed
12	Wind Direction
13	Air temperature
14	Relative humidity
15	Pressure
16	Solar radiation

Table (2-1): Analytes and their corresponding channels

Two 10 liter gas bottles, fitted with pressure gauges and output regulators, are permanently connected to an M700 Dynamic Dilution Calibrator which switches the gases to the analyzers during daily automatic and weekly manual gas calibrations. One gas bottle contains SO<sub>2</sub>, NO and CO in nitrogen and the other contains methane and propane in air. Cylinders are replaced when the pressure in them drops from 150 to 50 bars.

A borosilicate glass manifold sampling system is used for transferring ambient air samples to the analyzers cells. The sample probe extends vertically through the roof of the housing for a meter giving 360 degrees unrestricted airflow. A simple rain hood is installed to prevent water from entering the manifold.

The dust monitor enables the unit to measure concentrations of particulates smaller than 10um diameter while rejecting larger sized particulates. The head extends 1 meter above the enclosure and the pipe within the enclosure is heated and insulated to reduce condensation. Table 2-2 lists the analytical techniques employed by the stations.

Analyte species	Analytical principle
SO <sub>2</sub>	UV Fluorescence
NO <sub>2</sub>	Chemiluminescence
СО	IR Absorption
O <sub>3</sub>	UV Absorption
Dust- PM10	Beta Absorption

Table (2-2): Automated Analytical Principles Employed

Published accuracy estimation of the above measurements, involving review of the calibration chain and of measured instrumental characteristics (both in service and in controlled laboratory situations) is shown in Table 2-3

Analyte	Accuracy (2σ)	Precision (2σ)
SO <sub>2</sub>	± 10%	± 1.2 ppb
NO <sub>2</sub>	± 10 – 11 %	± 3.5 ppb
СО	±8%	± 0.6 ppm
O <sub>3</sub>	± 11%	± 2 ppb
PM10	Unknown	$\pm$ 4 ug/m <sup>3</sup>

**Table (2-3):** Accuracy and precision of analyte measurements. The  $\sigma$  denotes standard deviation [62].

## 2.6.1 SO<sub>2</sub> Analyzer

Sulfur dioxide is formed by the oxidation of sulfur compounds [organic and inorganic] in fuels and process gases during combustion / processing activities. SO<sub>2</sub> is monitored using Advanced Pollution Instrument API M100A that measures the fluorescent signal generated by exciting SO<sub>2</sub> with UV light.

Ambient air is drawn through the system via an internal pump. Special software compensates for changes in lamp intensity and zero stability is accomplished through the use of a chopper-stabilized system. UV light excites SO<sub>2</sub> molecules present in the sample to higher unstable excited states. These excited states decay giving rise to the emission of secondary fluorescent radiation.

This fluorescent radiation is detected by a photomultiplier tube [PMT] causing an output voltage proportional to SO<sub>2</sub> concentration.

All analyzer functions are set up and controlled using the system microprocessor. The analyzer provides a continuous display of current SO<sub>2</sub> concentrations.

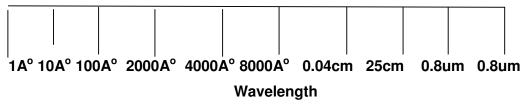
## 2.6.2 Fluorescence Spectroscopy

When molecules absorb ultra violet and/or visible radiant energy from a light source [i.e., xenon lamp, mercury lamp, etc.], this raises the energy of an electron in the ground state  $S_0$ , to an excited level  $S^*$  (e.g.,  $S_1$  or  $S_2$ ). From

this electronic excited state, relaxation to the electronic ground state occurs by emission of radiation in or near the visible spectrum. Figure 2-1 shows a schematic diagram of the electromagnetic spectrum. In general, the emitted radiation in these processes is called luminescence. Specific luminescence such as fluorescence and chemiluminescence's form the basis of rather sensitive analytical tools.

**Figure (2-1):** Schematic diagram of electromagnetic spectrum. Wavelength scale is non linear.

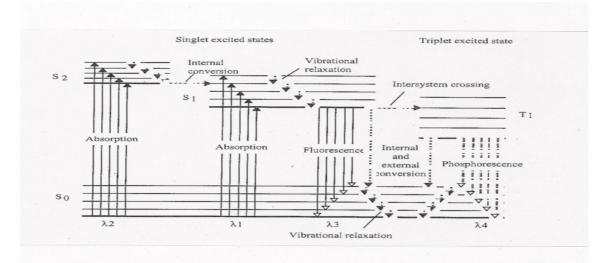
Gamma rays x-rays vacuum uv near uv visible near IR IR far IR microwave radio



#### 2.6.3 Sensitive analytical tools

Electronic and vibrational level transitions involved in luminescence phenomena can be understood with the aid of a photoluminescent energy level shown in figure 2-2

Figure (2-2): Fluorescence processes [63].



The simplified diagram above shows absorption by molecules to produce either the first  $S_1$  or second  $S_2$  excited state. Having absorbed energy and reached one of the higher vibrational levels of an excited state, the molecule rapidly loses its excess of vibrational energy by collision and falls to the lowest vibrational level of the excited state. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. This radiation can be detected by a photomultiplier tube [PMT].

In simple fluorimeters, the wavelengths of excited and emitted light are selected by filters, which allow measurements to be made at fixed wavelengths. In more sophisticated instruments, monochromators / diffraction gratings are provided for both the selection of exciting light and the analysis of sample emission. Such a fluorescence spectrometer makes full use of the analytical potential of the technique 2-3

#### 2.6.4 Instrumentation for a Fluorometer – Schematic Diagram

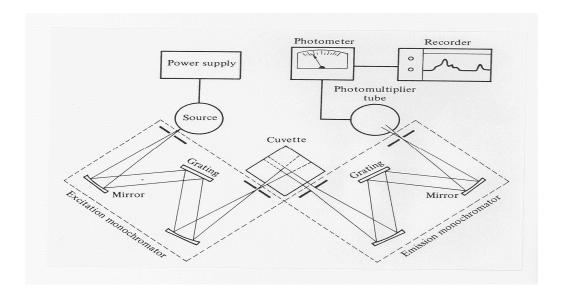
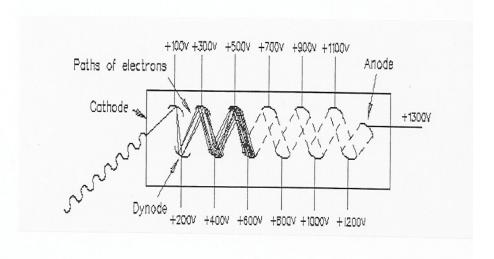


Figure (2-3): Schematic diagram of a fluorescence spectrophotometer [56]

The primary light source is a xenon arc usually 150 W which emits a Continuous spectrum from 200 to 800 angstroms (A<sup>o</sup>). The output from this excitation monochromator providing source passes into the for monochromatic radiation to excite the sample, being gas or liquid. The excited fluoresced radiation sample then becomes the source for the emission monochromator. All commercial fluorescence instruments use photomultiplier tubes [PMT] as detectors that convert photons to an electrical signal. A PMT, shown in figure 2-4, consists of a photocathode material [usually a mixture of alkali metals] and a series of electrodes, called dynodes, in an evacuated glass enclosure. The photocathode is at a high negative voltage, typically 500 - 1500 volts. When a photon of sufficient energy strikes the photocathode, it ejects a photoelectron. These photoelectrons are accelerated towards the dynodes, each maintained at successively less negative potentials, where additional electrons are generated. This cascading effect creates 10<sup>5</sup> to 10<sup>7</sup> electrons for each photoelectron ejected from the photocathode.





This amplified electrical signal is collected at an anode at ground potential, which can be measured and displayed on a readout device. Comparison of fluorescence signal readings for species and reference provides species' concentrations, in accordance to the Beer-Lambert Law.

#### 2.6.5 NO<sub>2</sub> Analyzer

NO and NO<sub>2</sub> [together called NO<sub>x</sub>] are the most abundant man-made oxides of nitrogen in air and are produced by high temperature combustion processes. Nitrogen dioxide [NO<sub>2</sub>] is formed by oxidation of nitric oxide by ozone and oxygen.

The advanced Pollution Instrument API M200A monitors the oxides of nitrogen using a chemiluminescent analyzer with a single reaction chamber and PMT detection system. A solenoid valve is used to alternatively switch between NO and NO<sub>x</sub> (NO + NO<sub>2</sub>) measurements every 15 seconds. Ambient air is drawn through the system via an externally mounted pump and drier unit. Nitric Oxide (NO) in the sample air stream reacts with ozone (O<sub>3</sub>) in the reaction chamber to produce activated nitrogen dioxide (NO<sub>2</sub>).

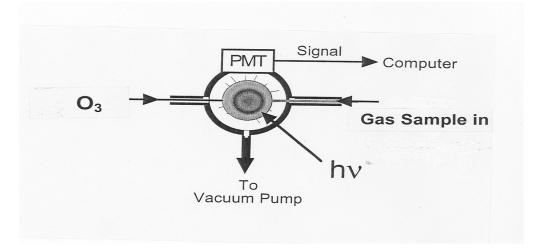
## NO + $O_3 \longrightarrow NO_2^* + O_2 + hv$

The intensity of the chemiluminescent radiation produced is measured using a photomultiplier tube. The ambient air sample is divided into two streams; in one, ambient NO<sub>2</sub> is reduced to NO using a molybdenum catalyst before reaction. This gives total NO<sub>x</sub>. A Separate measurement is then made for just NO. The ambient NO<sub>2</sub> concentration is calculated from the difference NO<sub>2</sub> = NO<sub>x</sub> - NO

All analyzer functions are set up and controlled using the system microprocessor. The analyzer displays current NO<sub>2</sub> concentrations. Daily and weekly calibrations are performed with an API M700 Calibrator.

## 2.6.6 Chemiluminescence's Spectroscopy

Like fluorescence spectroscopy, chemiluminescence's uses quantitative measurements of the optical emission from energized chemical species to determine analytic concentrations. However, unlike fluorescence, the energy necessary to excite the analytes to higher states does not come from an external light source, i.e., a laser or lamp. Instead, it is produced by a chemical reaction of the analyte and a strongly oxidizing reagent [in this case ozone] in a reaction chamber maintained at a low pressure (~1 torr) by a vacuum pump, in order to minimize the effects of collided deactivation. Again photomultiplier tubes are often used as detectors [63]. A schematic of a chemiluminescence's reaction chamber is shown in figure 2-5.



(Figure 2-5): Schematic of a chemiluminescence's reaction chamber [64]

## 2.6.7 CO Analyzer

The Advanced Pollution Instrument API M300, with an Infrared emission source, was used to analyze for carbon monoxide. CO concentration in the sample air is measured by the absorption of infrared radiation at 4.5 to 4.9 mm wavelength. A reference detection system used to alternately measure absorption due to CO in the ambient air sample and absorption by interfering species. An infrared detector and amplification system produce output voltages proportional to the CO concentration. The concentration is derived from the Beer-Lambert Law. All analyzer functions are set up and controlled using the system microprocessor. The analyzer continually displays current CO concentrations with daily and weekly automatic calibration checks through an API M700 Calibrator.

## 2.6.8 Infrared Analysis

Infrared [IR] region of the electromagnetic spectrum covers the range between 0.78 and 1000 um which is normally expressed in wave numbers that have the units cm<sup>-1</sup> (wave number = 1 / wavelength in centimeters). The most useful IR region however lies in the mid-infrared region between 4000 and 670 cm<sup>-1</sup>. Following is the range of infrared region divided into three sections; near, mid and far infrared;

<b>Region</b>	Wavelength range (um) W	ave number range (cm <sup>-1</sup> )
Near	0.78 – 2.5	12800 - 4000
Mid	2.5 - 50	4000 - 200
Far	50 - 1000	200 - 10

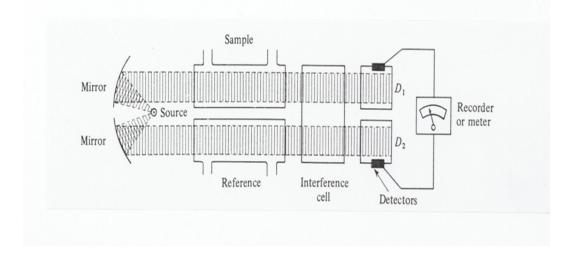
IR radiation does not have enough energy to induce electronic transitions as is in the case of UV. Absorption of radiation in this region therefore results in the excitation of bond vibrational, rotational and bending modes while the molecule itself remains in its electronic ground state.

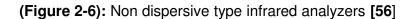
In gases, absorption of IR yields line spectra which can lead to their identification and quantification. By identifying the wavelength at which a substance demonstrates absorbance maxima, the Beer-Lambert law, which relates absorbance to concentration, can then be used to determine sample concentration. The Beer-Lambert law is:

## $\mathsf{A} = \sum \mathsf{L} \mathsf{C}$

Where A = absorbance (unit less quantity),  $\Sigma$  = absorptivity (m<sup>-1</sup>cm<sup>-1</sup>), L = length of the light path through the sample (cm), and C = concentration of the sample (mole/L).  $\Sigma$  is the absorptivity constant between the amount of light absorbed and the gas concentration. An IR instrument can be calibrated to yield this constant by measuring substances of known concentration. Knowing  $\Sigma$  and the path length (L), absorbance (A) can be measured for an unknown

sample, and the Beer-Lambert equation can be used to compute concentration. Figure 2-6 shows a non-dispersive type of an infrared analyzer.





When IR radiation is sent through a gas sample, it interacts with the molecules, causing the chemical bonds to vibrate. Each functional group of gases is characterized by the tendency to absorb IR radiation of a particular wavelength, regardless of the structure of the structure of the rest of the molecule. The only substance that can not be analyzed with IR spectroscopy are those that exist as single atoms with no chemical bonds, such as noble gases and homonuclear diatomic molecules, because they have no dipole movement. Glowers / lamps / arcs are used for IR sources and thermocouples and solid state devices for detectors.

Differences in IR absorption between the sample (ambient air) and reference gas (air with CO removed) provides CO concentration. The analyzer continually displays current CO concentrations. Daily automatic check calibrations are provided.

Contemporary advanced instrumentation utilizing Fourier transfer IR techniques has been available on the market.

#### 2.6.9 Ozone Analyzer

The Advanced Pollution Instrument API M400 in the system uses ultra violet UV absorption techniques for Ozone analysis. Ozone concentrations are calculated from the absorption of ultraviolet light at 254 nanometers wavelength. The sample passes through a cell tube of certain length (L) and the absorption is measured using a UV detector. An ozone-removing scrubber is used to provide zero reference intensity. The analyzer alternately measures the absorption (I<sub>0</sub>) of the reference sample (with no ozone present) and the absorption of the ambient air sample (I). The concentration (C) is calculated using the Beer-Lambert equation:

 $I = I_0 e^{-alc}$ 

Where I = absorption of the ambient air sample,  $I_0$  = absorption of the reference sample, a = absorption coefficient for ozone at 254 nm, L = sample cell length, C = sample concentration.

The analyzer displays current O<sub>3</sub> concentrations.

## 2.6.10 Ultra violet [UV] absorption techniques

The electromagnetic spectrum ranges from very short wavelengths; less than  $10^{-4}$  nm (including gamma and x-rays) to very long wavelengths; more than  $10^{9}$  nm (including microwaves and radio waves). The ultraviolet [UV] region approximately lies between 100-400. The analytical range however is normally between 200 – 400 nm [56].

In UV spectroscopy, a beam of light from a UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic [single beam] is split into two equal intensity beams by a half mirrored device. One beam passes through the sample container, the other passes through a reference. The intensities of these light beams are then measured by electronic detectors and compared applying the Beer-Lambert Law.

In brief, the intensity of the sample beam is defined as I and that of the reference is  $I_0$ . If the sample does not absorb light of a given wavelength, then  $I = I_0$  and one may conclude that the analyte concentration in the sample

is too low to detect. However, if the sample absorbs light then I is less than  $I_0$  and Absorbance [A] = log  $I_0$  / I. The absorbance A is a function of the analyte concentration in the sample. If no absorption has occurred, then A = 0.

#### 2.7 Calibrator

The model API M700 allows manual, automatic and remote controlled calibration of ambient air analyzers. The unit performs precision zero and span checks by applying samples from any of the four calibration gas bottles or the zero air generators to the appropriate instruments.

#### 2.8 Zero Air Source

The API M701 instrument uses regenerative heatless dryer and chemical scrubbers to produce quality air over long periods of time. The dryer removes water to provide dry air independent of inlet dew point. Other gases are also removed by the dryer thereby extending the life time of the chemical scrubbers that remove SO<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, CO and hydrocarbons. The unit feeds zero air at 30 psi directly to the M700 calibrator for use during manual and automatic calibrations of the unit. A permanent low flow supply is also fed to the Dani hydrocarbons monitor as combustion air for the flame ionization detector [FID]. In this detector, hydrogen is burnt at a small jet situated inside a cylindrical electrode. A potential of a few hundred volts is applied between the jet and the electrodes. When the carbon containing sample is burnt in the jet, the electron / ion pairs that are formed are collected, the current is amplified and fed to the data acquisition system [62].

#### 2.9 Dust Monitor

A Beta Attenuation Mass Monitor BAM 1020 automatically measures and records dust concentrations with a built-in data logging facility. The monitor uses the principle of Beta absorption to provide a simple determination of mass concentration. An energy source of beta particles, producing repeatable measurement characteristics, is coupled to a sensitive detector which counts the Beta particles. As the mass of particles increases the Beta count is reduced. Applying the Beer –Lambert Law on the ratio of the detected beta particles passing through a clean filter and those passing through the dust sampled filter [taking into consideration the sample volume] are used to calculate mass concentration. A glass fiber tape [30 mm wide and 20m long] provides lengthy monitoring periods without operator intervention. The filter tape is changed every 60 days.

## 2.10 Wind Sensor

A wind sensor Met One model 50.5 is a solid state ultrasonic instrument capable of measuring wind speeds of 0 to 50 m/s and wind direction of 0 to 360 degrees. Wind speed and direction signals are supplied to the data logger.

## 2.11 Temperature Sensor

A Met One 592 sensor is used to provide a voltage proportional to the ambient air temperature which is then supplied to the data logger.

## 2.12 Relative Humidity sensor

A Met One 593 sensor provides a voltage proportional to the ambient relative humidity which is supplied to the data logger.

## 2.13 Pressure Sensor

A Met One 594 sensor provides a voltage proportional to the ambient air pressure which is then supplied to the data logger.

# 2.14 Solar Radiation Sensor

An Opsis Sky Eye Solar Radiation Sensor incorporating a silicon short wave photocell is used to measure total solar radiation. The data from this sensor have not been analysed as part of the work.

The data collected from the monitoring stations in Qatar are analysed and discussed in the following chapters. The data from MIC encompasses diverse industrial operations including: refineries, NGL plants, petrochemicals manufacturing facilities for ethylene, polyethylene, MTBE and methanol, fertilizers (mainly ammonia and urea), steel manufacture, and other industrial operations as well as all types of gas flare.

At Dukhan station, the industrial activity giving rise to emissions is mainly oil and gas separation, again involving numerous flares and at Halul Island station, the emissions come from oil and gas separation [water removal] and crude oil storage with just two flares.

## 2.15 Section B - Thermodynamics

Table 2-4 shows the Gibbs free energy values for the individual reaction components [43]. The Gibbs free energy changes for the various reactions were calculated under standard conditions, and are shown with their respective reaction couples.

As is shown by the calculated change in free energies, all of the suspected reactions have a thermodynamic tendency to occur under ambient / atmospheric conditions. As for the kinetics involved, although such reactions are expected to be fast, as they are mainly of the oxidation-reduction type, one needs to further investigate the corresponding rates.

This might be easier said than done, under the prevailing conditions, though. However, this is outside the scope of this thesis.

Species	Phase	<b>∆G<sup>0</sup> kcal</b>
O <sub>3</sub>	gas	39.06
O <sub>2</sub>	gas	0.0
CO	gas	-32.81
NO	gas	20.72
NO <sub>2</sub>	gas	12.39
N <sub>2</sub>	gas	0.0
SO <sub>2</sub>	gas	-71.79
S <sup>0</sup>	solid	0.0
H <sub>2</sub> SO <sub>4</sub>	aqueous	-177.34
H <sub>2</sub> O	gas	-54.64
H <sub>2</sub> O	liquid	-56.69
HNO <sub>3</sub>	aqueous	-26.41
CO <sub>2</sub>	gas	-94.26

**Table (2-4):** Standard free energy of formation  $[\triangle G^{0]}$  in kcal/mole [kcal] under standard conditions [65]

#### **Observed interactions:**

1.  $O_{3g}$  and  $Co_{g}$ 

 $O_{3g} + COg \longrightarrow C O_{2g} + O_{2g} \triangle G^{0} = -100.52 \text{ Kcal}$ 

#### **Reaction favorable**

2.  $O_{3 g}$  and  $SO_{2 g}$ 

 $O_{3 g} + SO_{2 g} \longrightarrow SO_{3 g} + O_{2 g} \qquad \triangle G^{0} = -55.79 \text{ Kcal}$ 

#### **Reaction favorable**

3.  $SO_{2g}$  and  $CO_{g}$  $SO_{2g} + 2CO_{g} \longrightarrow 2CO_{2g} + S^{0} \triangle G0 = -51.13$  Kcal

#### **Reaction favorable**

4.  $NO_{2g}$  and  $Co_{g}$ 

$$NO_{2g} + Co_{g} \longrightarrow CO_{2g} + NOg \triangle G^{0} = -53.17 \text{ Kcal}$$

 $NO_{g} + CO_{g} \rightarrow CO_{2g} + \frac{1}{2}N_{2g} \triangle G^{0} = -82.18$  Kcal

#### **Overall RX.**

$$NO_{2g} + 2COg \longrightarrow 2CO_{2g} + \frac{1}{2}N_{2g} \bigtriangleup G^0 = -135.35$$
 Kcal

#### **Reaction favorable**

Or

$$NO_g + O_{3g} \longrightarrow NO_{2g} + O_{2g}$$
  $\triangle G^0 = -47.39$  Kcal

Also Favorable Rx.

Another likely reaction for  $No_X$  with  $O_3$  could be involving water vapor in the atmosphere

$$NO_{2g} + O_{3g} + 1/2H_2O_g \longrightarrow HNO_3 + 2.5/2O_2 \triangle G^0 = -50.54$$
 Kcal

Certainly there would be competing reactions to the ones mentioned above. Since they are mainly oxidation reduction type, all other reducing and oxidizing species in the atmosphere would have some sort of an impact on them. Of the most notorious oxidizers, under the circumstances, is the hydroxyl radical [66]

The hydroxyl radical is reported to react even with O<sub>3</sub>,

O <sub>2</sub>	+	hv	O +	0
O <sub>2</sub>	+	0	O <sub>3</sub>	
0	+	H₂O →	HO* +	HO*
HO*	+	$O_3 \longrightarrow$	HOO* +	O <sub>2</sub>

Of the likely reactions observed in this work, the following reactions have been reported in literature [11],

$SO_2$	+	3CO	2CO <sub>2</sub> +	COS	
$NO_2$	+	$O_3 \longrightarrow$	NO <sub>3</sub>	+	O <sub>2</sub>
$SO_2$	+	O <sub>3</sub>	SO3	+	O <sub>2</sub>

CO is reported to react with NO, over a catalyst [66]:

CO + NO → CO<sub>2</sub> + 1/2N<sub>2</sub>

The reaction of CO with Ozone was never reported in the cited literature.

#### Chapter 3

#### 3.1 Pollutant results derived from industry data in the State of Qatar

In this chapter, the volumes and types of gaseous emissions emanate from various upstream and downstream operations, through either flaring or fugitive means were identified. The work began in 2000, with a survey of industrial activities in order to obtain an overview of the nature and composition of atmospheric pollutants in Qatar (until 2002) some of the data collected used as a part of the climate change national report [67,68 and 69]

Activity data from emitting sources was collected in a number of tables with emission factors for various sources. Some examples of the input from the questionnaires of the industries responsible for emissions and calculations used to estimate emissions are in Appendix 1-1.

The questionnaires were prepared, distributed and addressed to various potential emission sources (stationary) in the State of Qatar. Data on fuel combustion by sources, chemical and physical characteristics of fuels, fugitive emissions and flares was compiled Appendixes 1-3, 1-4 and 1-5. The following tables contain adapted emission factors and computations used by the industries to estimate emissions of SO<sub>x</sub>, NO<sub>x</sub>, VOCs, CO and CO<sub>2</sub>.

Table 3-1 show the computation of emissions of Greenhouse Gases and Criteria Pollutants from the Oil & Gas Industry (Natural Gas Processing) [70, 71].

Emission Factors	Required Analysis	Computations	
	Compute the average molecular weight (MW) of flared gas	Use chemical composition data to determine MW. If e.g. gas contains 85% CH <sub>4</sub> , 14.9% C <sub>2</sub> H <sub>6</sub> and 0.1% C <sub>3</sub> H <sub>8</sub> ; MW=0.85 * 16+0.149 * 30+0.001 * 40 = 18.1	
	Compute the density of gas at (20 C & 1P)	Density (20 C, 1P = $18.1 / 24.04 = 0.75 \text{ kg} / \text{m}^3$	
<u> </u>	Compute the carbon content of flared gas	$C_{CH4} * 0.85 + CC_{2}H_{6} * 0.149 + CC_{3}H_{8} * 0.001 = 0.75 \times 0.85 + 0.8 * 0.149 + 0.82 * 0.001 = 0.75$	
CO <sub>2</sub>	$EFCO_2 (kg / m^3)$	$EFCO_2 (kg / m3) = 0.75 \times 0.75 \times 44/12$ = 0.06 EFCO <sub>2</sub> (kg/kg) = 2.06 / 0.75 = 2.75	
	Find combustion efficiency	Multiply efficiency by EF to determine net emission. In stringently regulated areas (USA), efficiency is 98%, 95% elsewhere $EFCO_2 = EF * 0.98$	
CH₄	Determine flare combustion efficiency	Total HC emission = $(1 - \text{Efficiency}) * \text{mass of flared}$ gas CH <sub>4</sub> = %CH <sub>4</sub> /THC * mass of flared gas VOC = %VOC/THC * mass of flared gas	
	Determine CH₄ and VOC concentration of flared gas	If e.g. $CH_4 = 85\%$ , VOC 15% $EF_{CH4} = 0.85 * (1 - Efficiency) * mass of flared gas$ $EF_{VOC} = 0.15 * (1 - Efficiency) * mass of flared gas$ If flared gas = 1 tonne; Efficiency = 0.98 $CO_2$ Emission = 2.70 tonne Total HC = (1 - 0.98) * 1 tonne = 20 kg	
VOC		CH <sub>4</sub> Emission = $0.85 \times 20 = 17$ kg EF <sub>CH4</sub> = 0.017 tonne/tonne VOC Emission = $0.15 \times 20$ EFVOC = 0.0035 tonne/tonne	
	Average EFCH4 USA Average EFVOC USA	0.014 (0.035 elsewhere) tonne/tonne 0.006 (0.015 elsewhere) tonne/tonne	
SOx	<ul> <li>a) Compute weight fraction of S in flared gas</li> <li>b) Total S conversion from fuel</li> <li>S → SO<sub>2</sub></li> <li>Mole Ratio = 2</li> </ul>	$EF_{SO2} = 2 * S * mass flared gas$ If e.g. S = 1% flaring of 1 tonne gas = 1/ <del>100</del> × 2 * <del>1000</del> = 20 kg SO <sub>2</sub>	
CO		$EF_{CO}$ (tonne/tonne) = 0.0087	
NOx		$EF_{NOx}$ (tonne/tonne) = 0.0015	
N2O		$EF_{_{N2O}}$ (kg/tonne) = 0.081	

# (Table 3–1): Computation of Emission Factors for combustion Flares

• Data required for computations include mass (volume) flow rate of flared gas; chemical composition, density, carbon content, sulfur content of flared gas; combustion efficiency; obtain data for (1995 - 2000).

## (Table 3-2): Emissions of Criteria Pollutants from the Oil & Gas Industry

SOURCE	DATA REQUIREMENT
Fugitive Emissions 3. Flare 4. Burn Pit	i) Volumetric flow rate, ii)Total annual flow (1995 - 2000) of flared gas; (iii) Chemical composition of flared and waste gas (CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>x</sub> H <sub>y</sub> ), H <sub>2</sub> , total sulfur content, (H <sub>2</sub> S), CO <sub>2</sub> etc., (iv) Average molecular weight; (v) Specific gravity; (vi) heat value; (vii) Flare combustion efficiency; viii) Burn pit particulars as above.
Refinery-1 Fuel combustion Equipment	<ul> <li>4) <u>Crude Distillation Unit</u> <ul> <li>(i) Number of crude charge heaters; (ii) Capacity (MW/MMBTU) of heaters; (iii) Fuel consumption rate (annual 1995 – 200) (iv) Fuel characteristics of combusted fuel (as above).</li> </ul> </li> <li>5) <u>Naphtha Hydrotreater Unit</u> <ul> <li>Number, capacity fuel consumption, fuel composition of heaters and boilers (annual 1995 - 2000).</li> </ul> </li> <li>6) <u>Platformer Unit</u> <ul> <li>Number, capacity fuel consumption, fuel composition of heaters and boilers (annual 1995 - 2000).</li> </ul> </li> </ul>
Refinery - 2	<ul> <li>(ii) Unit 5 Boilers; (ii) Crude Distillation Unit; (iii) Naphtha hydrotreater Unit;</li> <li>(iv) Platformer Unit; (v) Kerosene Hydrotreater Unit; (vi) Diesel Hydrotreater Unit;</li> <li>For all units provide:</li> <li>(ii) Number and capacity of boilers, heaters furnaces; (iii) Rate of fuel consumption (annual 1995 – 2000); (iii) Chemical composition of fuel used, specific gravity, heat value, average molecular weight etc.</li> </ul>
Emergency Generators	Number, capacity (MW/MMBTU), fuel consumption (annual 1995 – 2000) and fuel characteristics of turbines and generators.
General	Relevant information not mentioned above, including particulars for Refinery extension.

## **Questionnaire on Petroleum Refinery-Combustion and Fugitive Emissions**

(Table 3-3): Fugitive Emissions from the Oil & Gas Industry: Oil & Gas Petroleum Refining [72]

# Questionnaire on Non-Methane Volatile Organic Compound Emissions (VOC's) from Petroleum Refinery

EMISSION SOURCE	PROCESS SYSTEM TYPE	EPA – EF Rating	Required Data
Pipeline valves	Gas stream (at process condition & contains < 50% H2 by volume)	А	1) Total number of valves per process stream.
Pipeline valves	Light liquid and gas liquid streams of V.P greater than kerosene (<689 Pa@38C)	А	4) Time period in service (hr).
Pipeline valves	Heavy liquid streams with V.P equal or less than kerosene (<689 Pa@38C)	А	3) Stream composition (CH₄, NMHC, H₂O etc.)
Pipeline valves	Hydrogen streams (gas streams containing more than 50% H2)	А	
Open ended valves	All process streams	A	Total number of open ended valves, time period in service (hr) & stream composition
Flanges	All process streams	A	Total number of flanges for all process streams, time period in service (hr) & stream composition
Pump seals	Light liquid and gas liquid streams (as above)	A	Total number of pump seals, time period in service (hr) & stream composition
Pump seals	Heavy liquid and gas liquid streams (as above)	A	Total number of pump seals, time period in service (hr) & stream composition
Compressor seals	Gas stream (as above)	A	Total number of seals, time period in service (hr) & stream composition
Compressor seals	Hydrogen stream (as above)	A	Total number of seals, time period in service (hr) & stream composition
Process drains	All process streams	A	Total number of drains and stream composition.
Pressure vessel relief valves	All gas streams (leakage)	A	Total number of relief valves & time period in service (hr)
Cooling Towers	Cooling Tower	A	Total amount of cooling waters / Refinery feed ( <i>I</i> )
Oil / Water Separator	Oil / Water Separator	A	Total amount of cooling waters / Refinery feed ( <i>I</i> )

(Table 3–4): Fugitive Emissions from the Oil & Gas Industry: Oil & Gas Production Operations-[73]

Emission Source	Service <sup>(a)</sup>	Emission Factor	Required Date (c)
		(TOC) Kg yr $^{-1}$	
Valves	Gas Stream	39.4	Total number of
	Heavy Oil Stream	0.074	valves per process
	Light Oil Stream	21.9	stream and time
	Water / Oil Stream	0.861	period in service (hr)
Pump Seals	Gas Stream	21.0	Total number of
	Heavy Oil Stream	NA	seals per process
	Light Oil Stream	114	stream and time
	Water / Oil Stream	0.20	period in service (hr)
Others (b)	Gas Stream	77.1	Total number of
0	Heavy Oil Stream	0.28	others per process
	Light Oil Stream	65.7	stream and time
	Water / Oil Stream	122.6	period in service (hr)
Connectors	Gas Stream	1.75	Total number of
	Heavy Oil Stream	0.07	connectors per
	Light Oil Stream	1.84	process stream and
	Water / Oil Stream	0.96	time period in service
			(hr)
Flanges	Gas Stream	3.4	Total number of
	Heavy Oil Stream	$3.4 \times 10^{-3}$	flanges per process
	Light Oil Stream	0.96	stream and time
	Water / Oil Stream	0.025	period in service (hr)
Open-ended lines	Gas Stream	17.5	Total number of
	Heavy Oil Stream	1.23	open-ended lines per
	Light Oil Stream	12.3	process stream and
	Water / Oil Stream	2.19	time period in service
			(hr)

## Aggregate Emission Factors and Data required for computing TOC's Fugitive Emissions.

a) Water / Oil emissions apply to water streams in oil service with a water content >50%.

b) Other equipment include compressors, diaphragms, and drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief vales and vents.

c) Chemical composition of process streams in required (including conc.

of TOC's, CH<sub>4</sub> etc.)

(Table 3- 5): Fugitive Emissions of NMVOC's and CH<sub>4</sub> from the Oil & Gas Industry [74]

## Questionnaire and Emission Factors for Storage Tank Emissions: Oil Production Tank Flashing

Crude oil from production wells or oil-gas separators generally flashed when it goes into oil filed tanks. Oil production tank vents can be a significant source of  $CH_4$ , VOC,  $H_2S$  and  $CO_2$  gases. If direct measurement data is not available, emission estimates can be made on basis of API equation as follows:

## VOC (tonne/bbl) = 0.0000219 \* P<sub>sep</sub> + 0.000143 \* P<sub>RVP</sub>

## CH<sub>4</sub> (tonne/bbl) = 0.00000499 P<sub>sep</sub>

## P<sub>sep</sub> = Separator pressure in psi guage.

 $\mathbf{P}_{RVP}$  = Sale oil Reid Vapor pressure in psi absolute.

## 4) The data required for estimating emissions:

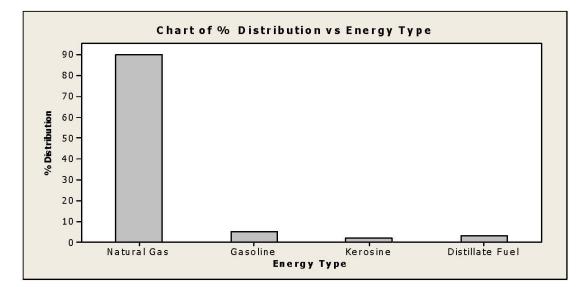
2.4 Separator pressure (psi).	(1995 - 2000)
2.5 Sale Oil Reid Vapor Pressure (psi).	(1995 - 2000)
2.6 Annual throughout of Oil in bbl.	(1995 – 2000)

#### 3.2 Qatar Energy Distribution

As per the industrial survey the data were gathered, plotted analyzed and as stated earlier Qatar has the largest single known natural gas reserves in the world. The average daily consumption of gas by the current industrial operations, including power generations and water desalination, comes to 1060 MMSCFD [million standard cubic feet per day]. Power generation accounts for nearly half the total consumption. A statistical survey showed the average power consumption per capita in 1998 was 12,475 kwh and that of water was 37,367 US gallons per year [3], Appendixes 1-9.

Figure 3-1 shows the distribution of energy consumption by type in the state of Qatar for the year 1995. This shows that natural gas accounts for 90% of the overall consumption. Gasoline, both grades premium at 90 Research Octane Number (RON) and super at 97 RON that are used primarily for car transportation, comes to nearly 5% while diesel and kerosene [jet fuel] make up the balance.

**Figure (3-1):** Distribution of Energy Consumption in the State of Qatar for 1995. These are calculated from the data provided by industries in Qatar.



Although this reflects data obtained in the mid-nineties, this distribution still holds [11]. While gasoline consumption on the road has certainly risen over the years, all incoming industrial projects use natural gas either for fuel and/or feedstock. The use of Natural Gas in the US for instance, in contrast with Qatar, accounts for only 23% of the overall energy used [75].

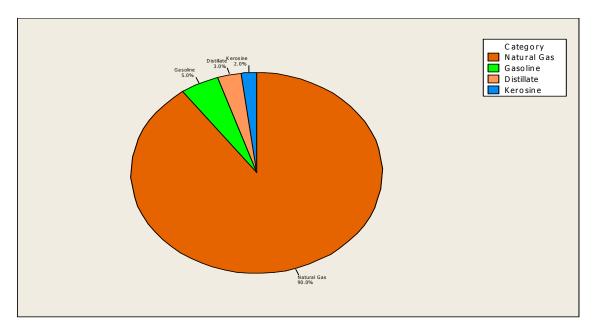


Figure (3-2): Pie chart showing Natural Gas to be the major energy consumed in Qatar

Since natural gas is a cleaner form of energy, compared to petroleum, emissions should be reduced accordingly. Natural gas produces emissions that are only about half those of diesel and less than 0.7 those of gasoline. And to portray this, data was taken from literature [73].

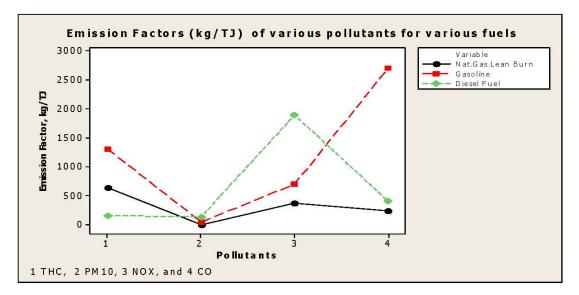
Figure 3-3 shows the emission factors for total hydrocarbon [THC], particulate matter [PM10], nitrogen oxide and dioxide  $[NO_x]$  and carbon monoxide [CO] species for natural gas, gasoline and diesel type fuels. Gasoline has the largest Emission factors for CO while diesel has the highest for NO<sub>x</sub>. This is to be expected because of the much higher compression ratio for diesel engines [19:1] compared with gasoline engines [9:1].

With a higher compression ratio, much more oxygen is available to oxidize nitrogen and carbon monoxides to their higher oxides;

$$\begin{array}{ccc} \mathsf{N}_{_2} & + \, 2\mathsf{O}_2 & \longrightarrow 2\mathsf{NO}_2 \\ \mathsf{CO} & + \, 1/2 \, \mathsf{O}_2 & \longrightarrow \mathsf{CO}_2 \end{array}$$

Diesel engines are known to emit particulate matter that consists largely of elemental carbon, hydrocarbon and hydrocarbon derivatives including organo sulfur and organo nitrogen compounds. The effects of particulate matter on visibility, air quality, the respiratory system and human health are very well documented [66, 76].

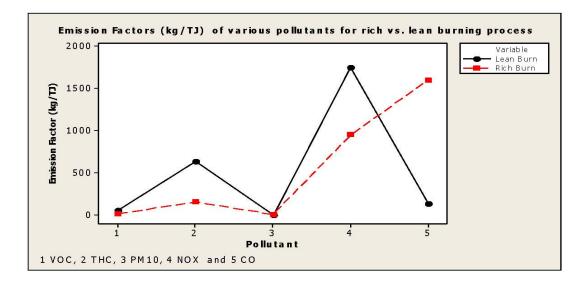
Figure (3-3): Data compiled from industrial Reports



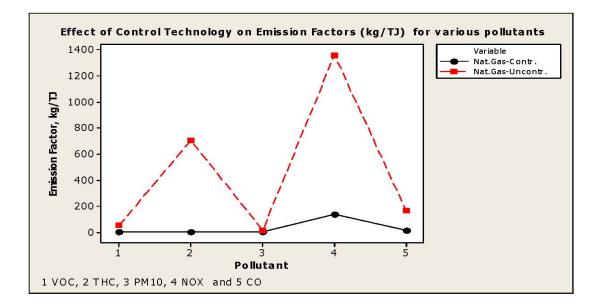
Of course there are many variables controlling exhaust emission gases but natural gas seems to generate the lowest emissions on particulate matter,  $NO_{_{\rm Y}}$  and CO.

The data in figure 3-4 show the effect of the combustion process [lean burning versus rich burning] on the emission factors for certain pollutants. The data show that lean burning [involving excess oxygen] increases the  $NO_2$  factor while reducing that of CO. This is further illustrated in figure 3-5

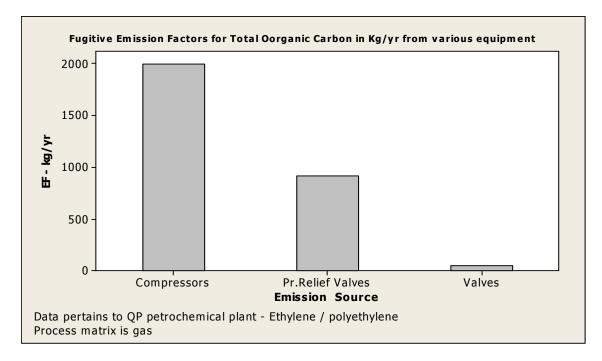
**Figure (3-4):** Effect of burning process [lean versus rich] of Nat. Gas on Pollutant Emission Factor, EF.



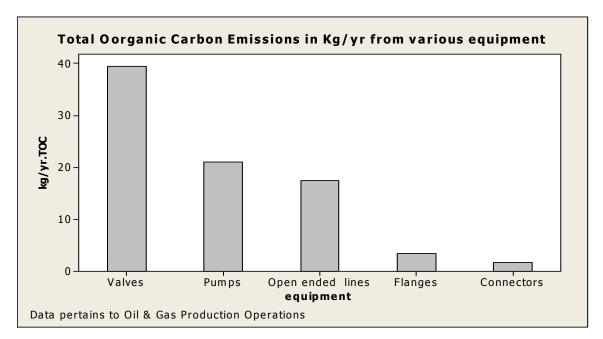
**Figure (3-5):** Effect of Control of the burning process of Nat. Gas on pollutant Emission Factor, EF where the  $NO_x$  and THC are reduced dramatically due to high efficiency of the combustion process

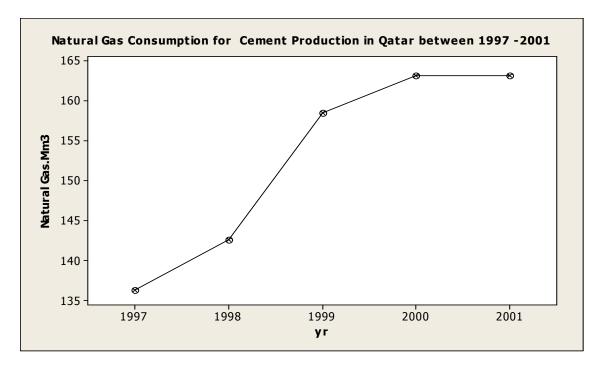


**(Fig 3–6):** Fugitive Emission Factors for Total Organic Carbon (TOC) from QP Petrochemical Plant



(Fig 3–7): Emission Factors for Total Organic Carbon (TOC) for various equipment in Oil & Gas Production Operations





(Fig 3–8): Increase in Natural Gas Consumption for the Cement Industry in Qatar.

Fugitive emissions for total organic carbon TOC from QP petrochemicals and oil and gas production operations represented in figures (3-6 & 3-7). Fig 3 - 8 shows the consumption of natural gas in the cement industry. Emission factors for combustion process are in appendix 1-7 and 1-8.

#### 3.3 Flaring in Qatar

One of the associated phenomena of the hydrocarbon industry [involving the production and/or processing of crude oil, condensate and natural gas] as well as those industries using natural gas for feed and/or power generation is flaring. The Gulf States, particularly Qatar, registered the highest CO<sub>2</sub> emissions per capita in the world [77, 78 & 79].

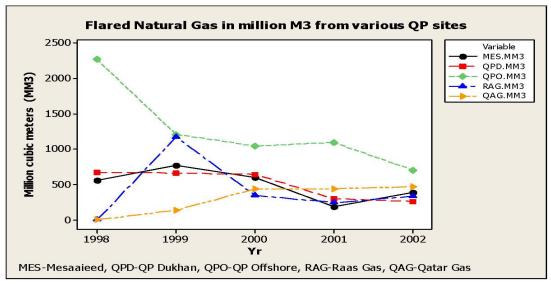
The data in Table 3-1 and Figure 3-9, quantify the amount of flared natural gas in million cubic meters (Mm<sup>3</sup>). The run chart shows quantities of flared natural gas in million cubic from various onshore and offshore Qatar petroleum production sites as well as some subsidiaries namely Qatargas and the Rasgas Liquid natural Gas complexes. Both Rasgas and Qatargas were just beginning production in 1998 and therefore had no prior emission

activities. In the meantime, Mesaieed and Dukhan operations flared well over  $500 \text{ Mm}^3$  that year. Offshore production was rather high, relatively speaking, reaching nearly 2300 Mm<sup>3</sup> [80, 81].

**Table (3-6):** Flared natural gas in million cubic meters (Mm<sup>3</sup>) per year from various sites [76]

Year / Mm <sup>3</sup>	Mesaieed	Dukhan	Offshore	Rasgas	Qatargas
1998	561	669	2268	0	0
1999	768	664	1209	1171	134
2000	603	643	1045	348	439
2001	185	300	1095	243	442
2002	384	261	704	445	469

Figure (3-9): Flared natural gas in Mm<sup>3</sup> from various QP/subsidiaries sites between 1998-2002



All flaring should be reduced over the years because of flaring mitigation activities, however. The development of the north field gas and new area of oil production i.e. Al-Shaheen, PS-1 added new stream for gas flaring [82, 83].

Flaring from offshore and Dukhan Qatar Petroleum sites was reduced due to mitigation revamp projects. For Mesaieed data, the rise in the year 2002 is attributed to more recently installed production capacities Fig 3-10. The flaring from Qatargas rose during the years 1999 –2002 and then leveled off - this can be accounted for by plant operational problems during commissioning figure 3-11. The same argument applies to Rasgas on the next chart Fig 3-12.

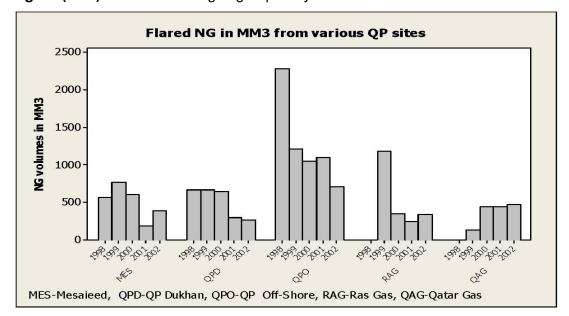
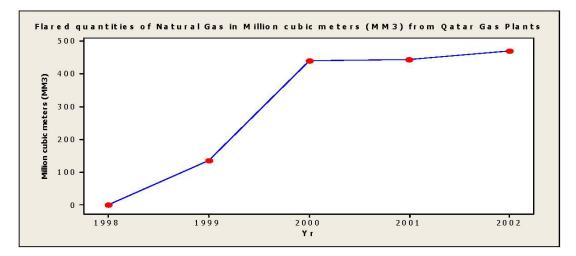
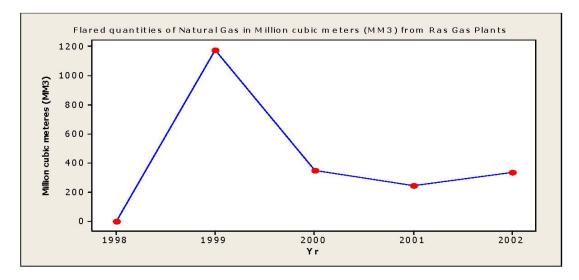


Figure (3-10): Flared natural gas grouped by site.

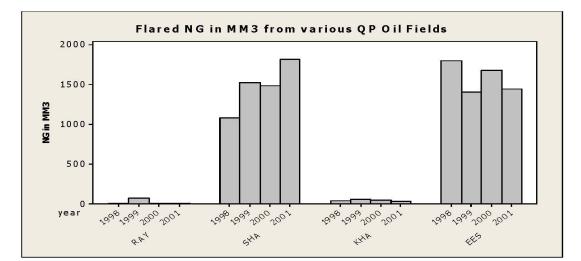
(Figure 3-11): Flared natural gas by Qatargas Plants during 1998-2002.



(Figure 3–12): Flared quantities of natural gas in million cubic meters [Mm<sup>3</sup>] from Rasgas.



Run charts figures 3-13 show flared quantities between 1998 – 2002 obtained from the individual sites, Qatargas, Rasgas, Al-Rayyan, Al-Khaleej, Eid El-Shargi and Al-Shaheen, respectively have been showing as new sources of gas flaring due to the new developments in the oil & gas industries While emissions from Al-Rayan and Khaleej seem rather low, Al-Shaheen and Eid El-Shargi are considerably higher.



(Figure 3–13): Flared quantities of natural gas in (Mm<sup>3</sup>) from Oil Fields.

The amount of gas flared is not, however, constant and to gain information on the types of variation experienced, the data in Table 3-2 [plotted in figures 3-14, 15 and 16] were obtained for the Al-Rayyan, Eid El-Shargi and Al-Shaheen Oil Fields. Much of the variation arises because of operational and the prevailing supply and demand conditions.

Table (3-7): Joint venture offshore operations of flared gas in (mm<sup>3</sup>).

Year / Mm <sup>3</sup>	Al-Rayyan	Eid El-Shargi	Al-Shaheen
1998	4.35	1798	1079
1999	69.7	1398	1522
2000	9.89	1671	1480
2001	10.62	1438	1809.4

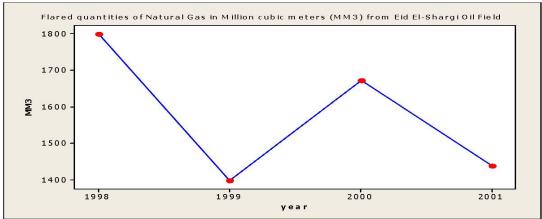


Figure (3-14): Flared natural gas from Eid El-Shargi Oil Field.

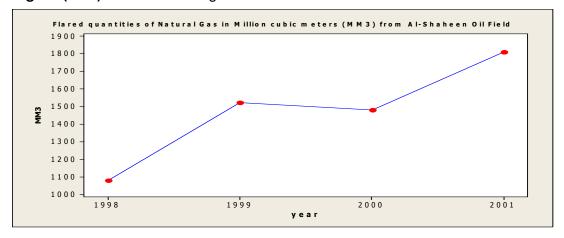
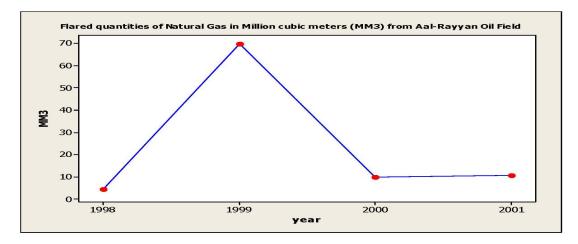


Figure (3-15): Flared natural gas from Al-Shaheen Oil Field.

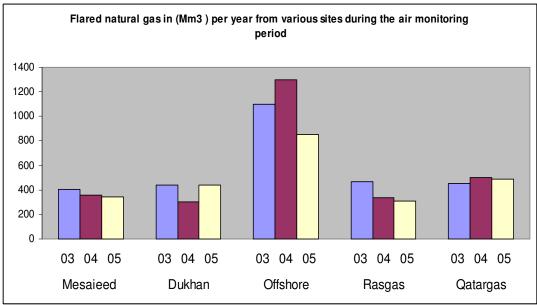


**Figure (3-16):** Flared natural gas in (Mm<sup>3</sup>) from Al-Rayyan Oil Field.

**Table (3-8):** Flared natural gas in million cubic meters (Mm<sup>3</sup>) per year from various sites during the air monitoring period.

Year / Mm <sup>3</sup>	Mesaieed	Dukhan	Offshore	Rasgas	Qatargas
2003	405	440	1100	470	450
2004	355	305	1300	334	502
2005	344	441	850	310	490

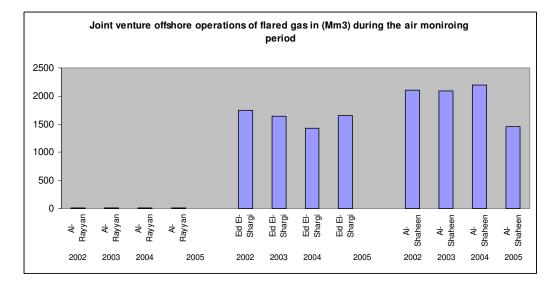
**Figure (3-17):** Flared natural gas in (Mm<sup>3</sup>) per year from various sites during the air monitoring period.



Year / Mm <sup>3</sup>	Al-Rayyan (02/03/04/05)	Eid El-Shargi (02/03/04/05)	Al-Shaheen (02/03/04/05)
2002	8.56	1750	2100
2003	7.7	1644	2086
2004	11.55	1432	2200
2005	12.6	1650	1450

**Table (3-9):** Joint venture offshore operations of flared gas in (Mm<sup>3</sup>) during the air moniroing period.

**Figure (3-18):** Joint venture offshore operations of flared gas in (million cubic meter) during the air monitoring period.



 $H_2$ S levels in the natural gas flared from the sites are in Table 3-5 [shown in figure 3-19]. Mesaieed and Offshore operations seem to register the highest. This is because offshore gas is normally sent to Mesaieed while the Dukhan, Rasgas and Qatgas sites have different gas composition with a much lower  $H_2$ S content.

Site	H <sub>2</sub> S (volume percent)
Mesaieed	2.39
Offshore	2.39
Dukhan	0.75
Rasgas	0.46
Qatargas	0.42

 Table (3-10): H<sub>2</sub>S levels in the natural gas flared from the sites

Figure (3-19): Volume %H<sub>2</sub>S in flared natural gas from various sources.

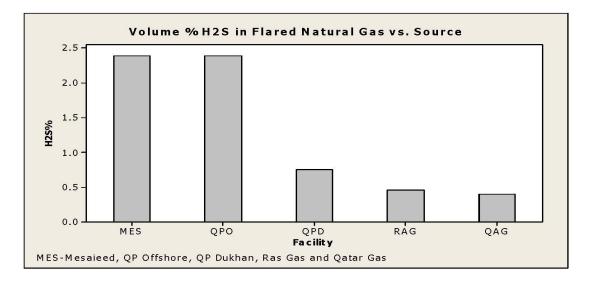


Figure 3-20 shows green house gas emissions (GHG) reported for the year 2001 for the two main LPG affiliate Operators in the country, Rasgas and Qatargas. Qatargas  $SO_2$  emissions are considerably less than that of Rasgas. This is attributed to the installation of a sulfur unit.

 Table (3-11): Fugitive emissions from Rasgas and Qatargas in 2001

Ton/yr.		CH <sub>4</sub>	N <sub>2</sub> O	NMHC	PM10	CO	NOx	SO <sub>2</sub>
Ras Gas	2200	2600	120	250	150	1300	6300	8000
Qatar Gas	2800	3000	150	200	180	1400	6800	0

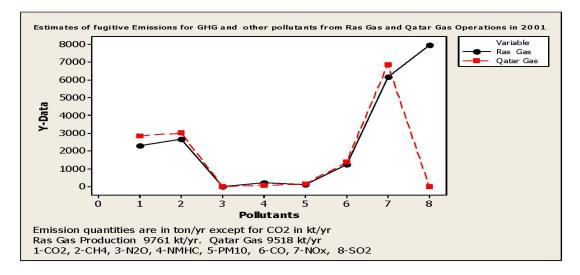


Figure (3-20): Fugitive emissions from Rasgas and Qatargas in 2001.

#### 3.4 Qatar Refinery Emissions

Because of the fact that emissions from refineries are of common concern, due to their variety and varying impact, and the fact that the refineries in Qatar were the first of the down stream industries of the oil industry in the country, this chapter the following section addresses the history of the refining operations and the corresponding associated emissions.

Refining operations in the State of Qatar dated back to the 1960 when the first 6800 barrels per day (BPD) crude refinery was commissioned. This was later upgraded to 12000 BPD. Four more refineries were added; crude, a fluidized catalytic conversion (FCC) unit, and a condensate and cap condensate refinery. Currently, the total capacity of the refining activities is 137000 barrels per day [84].

The data of Table 3-7 and the pie chart of figure 3-21 show the production in barrels in year 2000 and the percentage of each product. As gasoline, both RON 90 and RON 97 is nearly 30% of the total production.

Table (3-12): Output of refined products from Qatari refineries in the year 2000

Product	LPG	Gasoline 90R	Gasoline 97R	Jet A-1	LGO	Fuel Oil
Barrels/ yr	662,260	2,395,521	1,734,609	3,022,480	4,591,007	6,348,838

Figure (3 - 21): Output of refined products from refineries in the yr 2000.

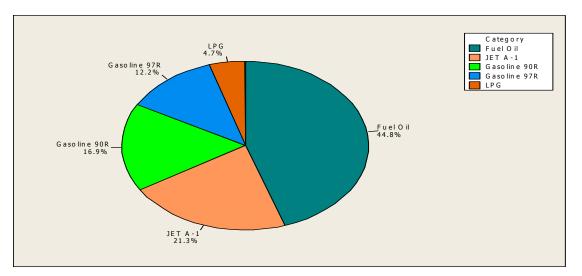
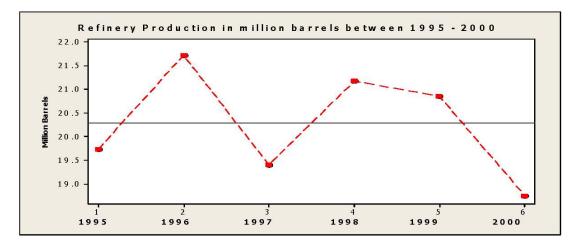
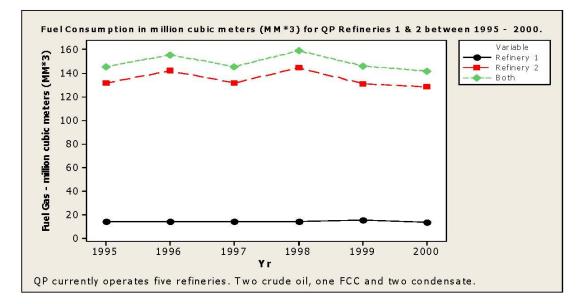


Figure (3-22): Run chart for refinery production in million barrels between 1995 and 2000.

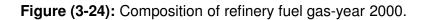


The higher consumption associated with refinery 2 has to do with the much larger production capacity of 50,000 BPD versus refinery 1 of 12000 BPD. The figures nevertheless seem to be steady over the years since neither complex had any major revamps during that period of time. The additions made recently to the refining operations included standalone condensate and cap condensate plants Figs (3-22&23).

**Figure (3-23):** Fuel consumption in million cubic meters (Mm<sup>3</sup>) for refineries 1&2 between 1995 and 2000.



The elemental composition of the refinery fuel gas is shown in Table 3-8 and figure 3-24. Hydrogen makes nearly 60% and Propane 20% with very little Nitrogen and virtually no  $CO_2$ . Fuel gas parameters including M.Wt, Density, Calorific value and  $H_2S$  are shown in Table3-8. From the operational point of view, the calorific value is the most indicative of the gas quality of course being the higher the better. Meanwhile, the hydrogen sulfide (H<sub>2</sub>S) is relatively low.



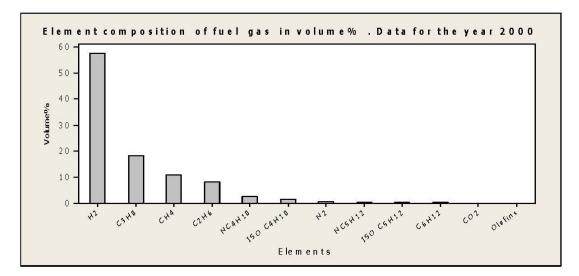


Table (3-13): Elemental composition of refinery fuel gas in the year 2000

Element	Volume %
Hydrogen	57.6
Propane	18.3
Methane	10.8
Ethane	8.1
Normal Butane	2.5
ISO Butane	1.4
Nitrogen	0.5
Normal Pentane	0.2
ISO Pentane	0.3
C <sub>6</sub> Hydrocarbons	0.2
Total Olefins	0.02

Parameter	1995	1996	1997	1998	1999	2000
Molecular Weight (kgm/mole)	16.06	16.06	16.06	15.62	16.17	16.39
Density (kg/m <sup>3</sup> )	0.72	0.72	0.72	0.69	0.71	0.73
Heating Value (kcal/m <sup>3</sup> )	9121	9121	9121	8947	9139	9272
H <sub>2</sub> S (ppm)	15	15	15	15	15	15

(Table 3-14): Refinery fuel gas parameters between 1995 - 2000

Table 3-9 represents parameters including molecular weight, density, heating and hydrogen sulfide content in refined fuel gas.

#### 3.5 Fugitive Emissions

This chapter also deals with fugitive emissions registered for Qatar Petroleum refineries and two of the affiliates RasGas and QatarGas.

If one wants to get a hand on all emissions, for whatever reason, one would definitely need to accommodate those fugitive emissions [uncontrolled emissions emanating from process equipment, i.e., valves, flanges, pumps, storage tanks].

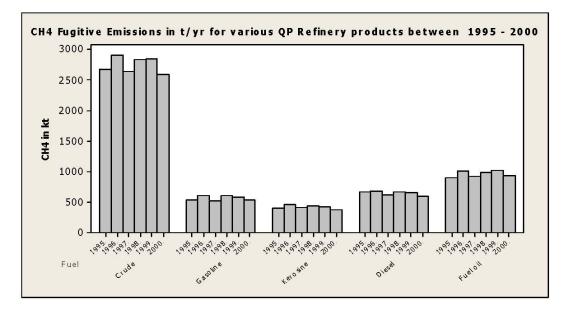
Data in Table 3-10 and in figure 3-25 shows quantities in thousand tons [kilo ton, kt] of  $CH_{A}$  emissions from various fuel types.

Crude oil has the highest emission inventory; most likely due to instability induced by the entrained light end / volatile hydrocarbons. During 1995 - 2000 for instance, nearly 3000 tons of  $CH_4$  were almost regularly emitted each year. The lowest emissions observed are from kerosene. The tank type, design and operational parameters do have an effect on the emissions.

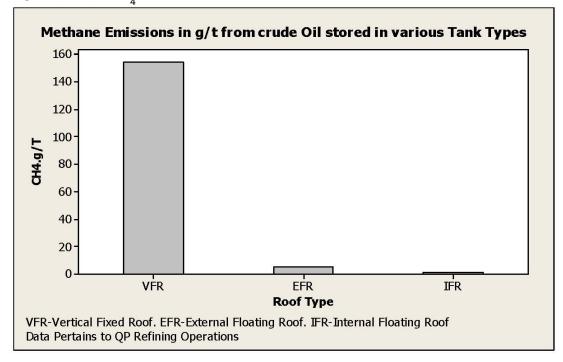
Fuel Type	1995	1996	1997	1998	1999	2000
Crude Oil	2672.9	2903.8	2639.1	2837.8	2849.8	2590.8
Gasoline	535	607.8	523.3	610.5	579.1	534.1
Kerosine	400.6	456.4	413.2	437.1	424.3	376.4
Diesel	672.6	684.4	622.1	668	662.1	600.1
Fuel Oil	898.3	1008.7	923	983.3	1016.3	940.6

Table (3-15): CH4 fugitive emissions in kt from various refinery fuel tanksduring 1995-2000

**Figure (3-25):**  $CH_4$  fugitive emissions for refined products between 1995 and 2000 grouped by fuel type.



The data in figure 3-26 compares  $CH_4$  emissions for various types of crude storage tanks [13].



**Figure (3-26):** CH<sub>4</sub> emissions from crude stored in various tanks.

Data on the emissions of green house gases from refinery are in Table 3-11 and in figure 3-27. The highest levels are those of non methyl hydrocarbon (NMH) followed by those of CO. The lowest of these emissions is for  $N_2O$ . CO<sub>2</sub> emissions are low and show little variation.

Emitted Gases included GHG (tones/year)	1995	1996	1997	1998	1999	2000
CO2	120.5	128.9	120.5	120.9	119.5	124.3
N <sub>2</sub> O	8.3	8.9	8.3	8.9	8.4	8.3
CH <sub>4</sub>	522	558.3	440.7	440.7	524.8	566.6
NMHC	1571.6	1680.8	1566	1661.6	1574.4	1551.3
SO2	3.5	3.7	3.5	3.6	3,5	3.5
NO <sub>x</sub>	316.6	338.5	316.5	339.5	318.2	313.6
CO	833	890.9	893	893.4	837.5	835.2

**Table (3-16):** Emissions in tones per year of emitted gases including GHG due to fuel combustion from refinery during 1995-2000.Quantities for  $CO_2$  in thousand tones (kt).

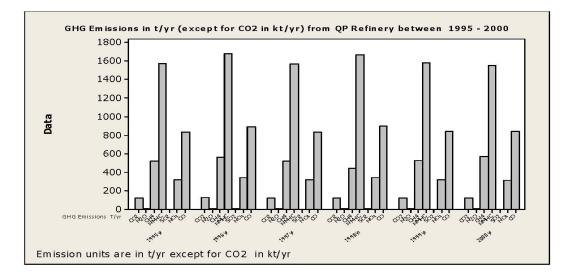


Figure (2-27): Greenhouse gas emissions (GHG) from refineries.

The importance of greenhouse gas emissions monitoring in the environment has been stressed in the Kyoto protocol. It has been recorded based on possible future demographic, economic, socio-political, technological, and behavioral changes. [85, 86]

IPCC have projected that the atmospheric concentration of carbon dioxide, for example, will increase from the current level of about 370 ppm to between 540 and 970 ppm by 2100.

The Earth's climate, without policies to combat climate change, would then warm an additional 1.4 to  $5.8^{\circ}$  C between 1990 and 2100. Environmental limitations, however, should neither hinder nor slow down the economic growth if there are factors of growth in the economy. In fact, it should promote development of new factors of growth. [87, 29]

The latter half of the last century witnessed increasing the share of new factors of growth- human capital, ideas, inventions and technological innovations, in economies of industrialized countries. Such new factors of growth do not essentially depend on the supply of natural resources and are not affected by environmental restrictions. [88, 89]

In the mid-1990s, Qatar witnessed the establishment of a progressive environmental legislation and a strong government agency in charge of environmental protection, the "Supreme Council for Protection of the Environment and Natural Resources, SCENR."

The formal establishment of this governmental body "The Supreme Council for the Environment and Natural Resources, SCENR", in July of the year 2000 has had, no doubt, a very positive impact on the overall environmental conditions, including atmospheric emissions, in the State of Qatar. While it would be somewhat difficult for me to assess the outcome of such positive impact, just by sitting in on the board of directors of the Supreme Council, I can confirm that it is very much there.

These improvements, however difficult to assess and came about through the enforcement of laws and bylaws on all industrial operators in the country whereby all operators may only obtain and / or renew their permit to operate after fulfilling the newly placed environmental laws and bylaws. [28, 90 & 91]

As per the environmental law number 30, for example, existing operations have been given a grace period of two years, starting from April 2005, to assess their emission sources; file validated quarterly reports and rectify non-complying process operations [2].

#### 3.6 Climate Change action plan in Qatar

State of Qatar ratified the Kyoto Protocol in 2004 although team of specialists in climate change negotiations has been participating since 1992.

I have personally been in the Qatar National Team on the climate negotiation since 1997. Furthermore, I represented the state of Qatar & the Asian region in the executive board bureau for two years (from 2002 - 2003) and lead the negotiations on behalf of the developing countries by chairing the group of 77 and China in 2004 [27, 92].

Currently I am Board member of the Adaptation Fund responsible for the management and the operational activities of the Fund. The Board develop the strategic priorities and the operational modalities for the Fund this include eligibilities, accessibilities and competency of the adaptation projects. The Adaptation Fund will receive 2% of the certified emission reductions Carbon credit CERs issued by the CDM Board as per the decision of the Conference of the parties to the Kyoto protocol. The Fund Board will monetize the CERs to fund essential projects in developing countries that are vulnerable to the adverse effects of climate change. [93]

I started establishing formal Designated National Authority (DNA) to create new emission reduction projects in the State of Qatar using Kyoto Protocol Clean Development Mechanism (CDM) [94] and successfully completed full registration of flared reduction of Al-Shaheen Project. This project in brief are associated with the development of the Al-Shaheen Oil Field Gas Recovery and Utilization. [95]

The project aims to recover Methane emitted as an associated gas mixture of various types (hydrocarbons and others) which also are been emitted as a result of this activity.

Year	Base	High case		
1998	0.76	0.76		
1999	0.88	0.88		
2000	0.92	0.92		
2001	1.22	1.22		
2002	1.26	1.30		
2003	1.87	2.13		
2004	1.54	1.53		
2005	1.32	1.46		
2006	1.07	1.67		
2007	0.90	1.87		
2008	0.82	1.85		
2009	0.75	1.78		
2010	0.62	1.75		
2011	0.44	1.60		
2012	0.39	1.40		
2013	0.32	1.20		
2014	0.26	0.99		
2015	0.22	0.86		
(Dec 2001 – Nov 2011)	10.62	16.85		

**Table (3-17)**: Projected GHG emissions as a result of flaring of associated gas in Al-Shaheen Field (Million tonnes  $-CO_2$ )

Utilizing Kyoto Protocol Mechanism CDM a methodology was developed for Al-Shaheen gas flare reduction; the most economically attractive options which are not prohibited under law. In the case of this project activity, was flaring and local consumption, which are both current practices. Therefore, this methodology is assumed that the recovered gases would have been flared in the absence of CDM project activities. In practice, flaring does not guarantee complete combustion. All methane recovered will be delivered to the power plant, which consumes both gas and diesel. It can be reasonably assumed that the gas delivered as a result of this project activity at least partly offset diesel consumption, which further contributes to GHG emission reduction.

The economic worth of associated gas is the main factor that influences an operator's decision to use or flare. In theory, if the benefits of using associated gas are higher than its costs, operators will refrain from flaring and venting. In practice, this is not always the case, as many developing countries focus on producing crude oil, and often consider finding ways to use associated gas a hindrance to crude oil production. [96, 97 & 98]

Furthermore, projects designed to use associated gas often are associated with marginal economics, as the production and optimization of widely varying qualities and quantities of associated gas from different oil fields is complex, time consuming and capital intensive. In many countries, gas development prospects have been hindered by the low valuation placed on natural gas compared with other energy sources, i.e. oil and coal.

This low valuation was initially reflected in very low natural gas prices either determined by the market or set by governments. In addition, energy sources have often been subsidized (mainly nuclear, hydropower, and coal, resulting in low prices for competing fuels), which has hindered the development of the upstream and downstream gas industry in many developing and industrial countries. Sour gas processing created additional problems linked to sulfur recovery, handling and storage in a very congested area.[99]. The commercial value from AI-Shaheen field comes mainly from the oil production associated gas is a by product of only marginal value.

The level of investment required is such that the project is not economically viable. It is not the best option for to make an additional 150 MMSCFD of gas available at Mesaieed.

Al-Shaheen gas flaring reduction was developed and successfully registered as CDM project recording the biggest oil and gas project in the energy sector worldwide which can create 2.5 million tones of certified CO<sub>2</sub> carbon credit which can generate a value 50 million dollars per year of CRs [100].

This project is really a success story for developing countries especially those who highly dependant on production and consumption of fossil fuels utilizing Kyoto Protocol Mechanism to combat climate change. Furthermore, it is also a starting point for the State of Qatar to eliminate major flaring sources such as Eid Al-Sharji, Mesaieed, Dukhan, Rasgas and Qatargas where their flaring represent almost 50% of Qatar CO<sub>2</sub> emission and the combined flaring reaching 500 mm ft<sup>3</sup>/day. [69, 101]

### 3.7 Carbon Capture and Storage CCS & Enhanced Oil Recovery EOR in Qatar

CCS has been identified as a promising technology which has the potential to reduce CO<sub>2</sub> emissions and at the same time permit the continued use of fossil fuels. CCS can achieve this by removing combustion related CO<sub>2</sub> from individual, large combustion sources (e.g. power stations) and transporting it to long term storage in geological formations, where it cannot contribute to global warming. [102, 103]

The use of  $CO_2$  for EOR in the right circumstances improves the financial case for  $CO_2$  capture and injection. This technology is already being developed and implemented in a range of projects, including for example the Weyburn project – which has investigated the potential of storing  $CO_2$  securely in geological formations during a commercial EOR operation at the Weyburn oilfield in Canada. [104]

Similarly in Qatar oilfields & gas fields have the potential to store CO<sub>2</sub> in underground geological formations. A pilot project was proposed jointly between Qatar petroleum & Qatar Foundation on research development.

The cost effectiveness of EOR depends strongly on the oil price. However, although this currently exceeds \$50 a barrel, over the last 20 years the average has been substantially lower, so market appraisals are based on a figure closer to \$25-\$35/barrel. At these prices, CCS by EOR will be about \$8-20/teCO<sub>2</sub> and so is an attractive option.

CCS will not happen without additional support. Government action is needed to establish market mechanisms for CO<sub>2</sub>, and to set up a sound regulatory framework. [105]

It is important to start the development of a country CO<sub>2</sub> Master plan, in order to reach an integrated understanding of the current and future CO<sub>2</sub> situation in Qatar, CO<sub>2</sub> network analysis (source, outlet, technology assessment & infrastructure / network scenarios) most be developed and the Potential for CO<sub>2</sub> reduction from existing assets by e.g. by efficiency improvements is essential. Assessment of the latest CO<sub>2</sub> technologies are added (e.g. cement industry as source or CO<sub>2</sub> mineralization as outlet) and their potential use for Qatar. This will include the latest R&D developments being undertaken in this area including GTL technology around the world. [106, 107& 108]

#### Chapter 4

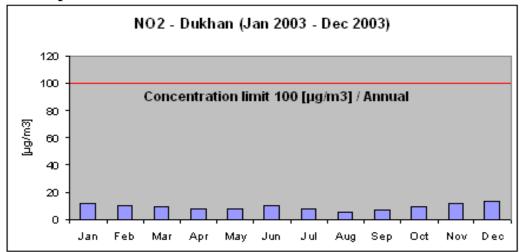
#### 4.1 Data from monitoring stations

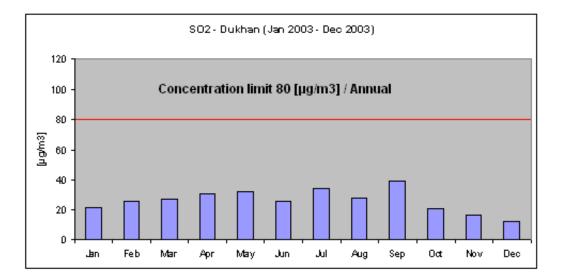
In this chapter, the residual levels of the more common air pollutants generated by such emissions, namely  $NO_2$ ,  $SO_2$ , CO,  $O_3$  and PM10, were recorded at several monitoring stations placed in three locations in the country; Mesaieed Industrial City (MIC) (South), Dukhan (East) and Halul Island, (North). These sites are characterized by major industrial activities.

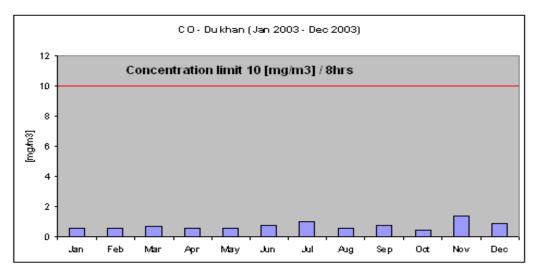
All three sites have varying industrial activities, with Mesaieed being the heaviest and most versatile of all. Halul Island would be the ideal place for monitoring intrinsic air quality parameters if there were no industrial activity on the island. Earlier however, for reliability considerations the data collected a year after, during 2003, 2004 and 2005 were analyzed at the time of composing this thesis in 2006. Each station monitors, on a continuous basis, the following parameters; NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, and O<sub>3</sub> besides wind speed, relative humidity and temperature. The results are electronically transmitted on to a PC where tabulation logs are produced. Data was extracted from these logs and analyzed in this work. The results are reported in this chapter.

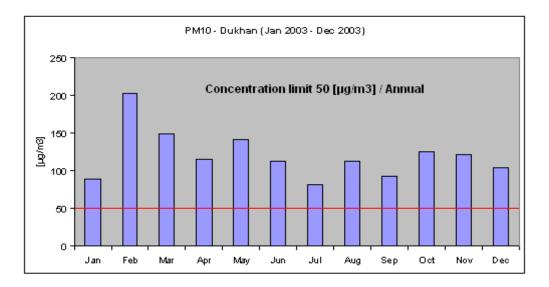
The following graphs (fig 4-1 to fig 4-3) represent the annual concentrations of  $NO_2$ ,  $SO_2$ , CO,  $O_3$ , PM10 and Wind Speed during 2003 in Dukhan, Halul and Mesaieed where the level of PM10 in Dukhan and Mesaieed exceeded the Qatar standard in 2003 but in Halul, it exceeds the standards in five months.

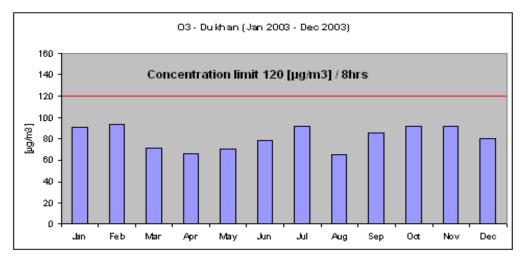
Fig (4-1): Dukhan Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2003

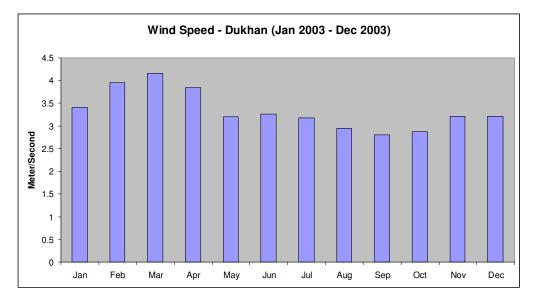




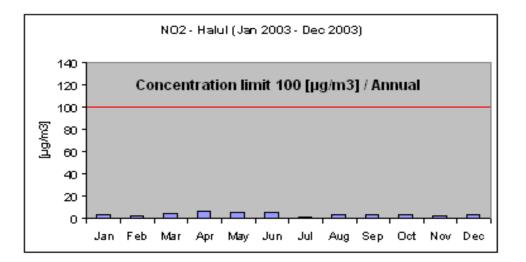


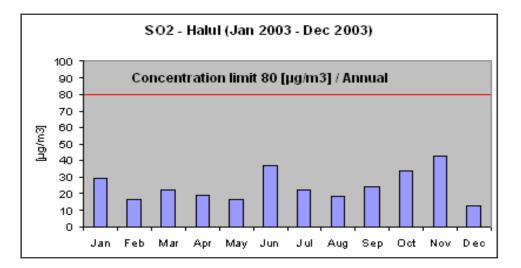


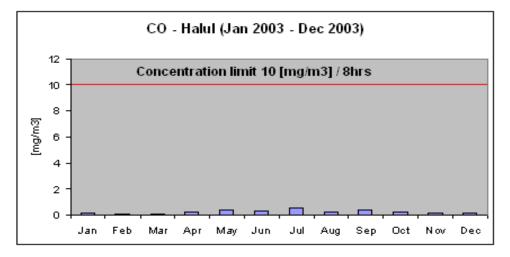


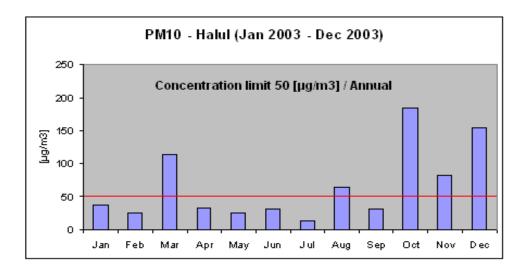


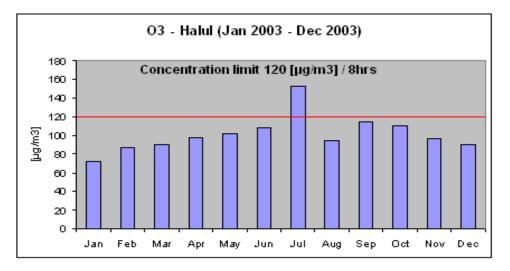
# Fig (4-2): Halul Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2003











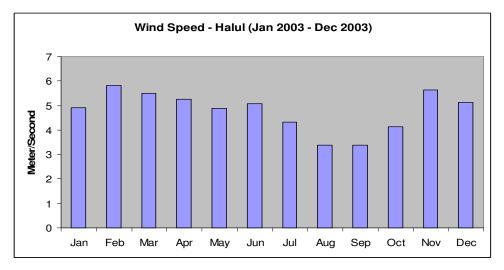
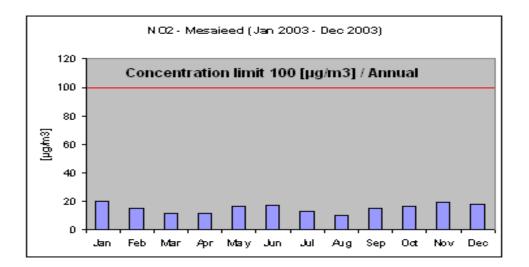
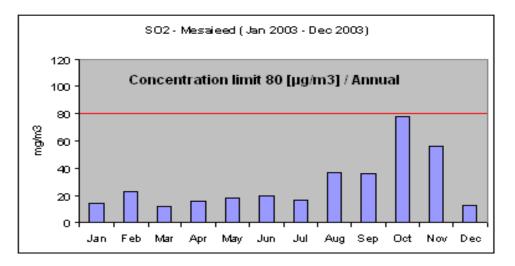
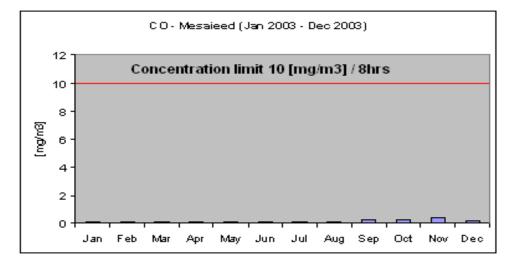
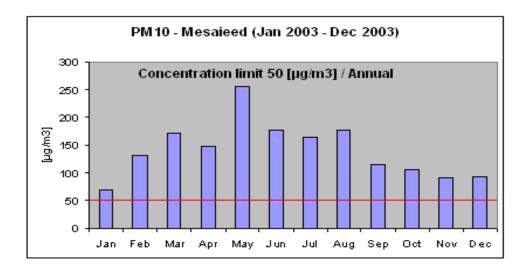


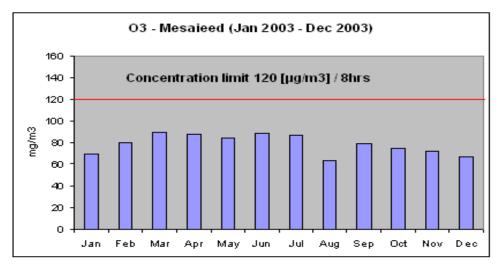
Fig (4-3): Mesaieed Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2003











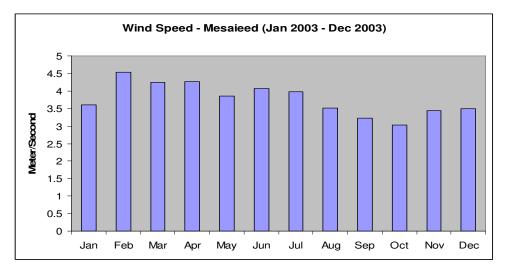
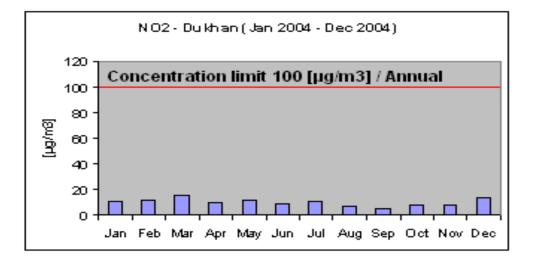
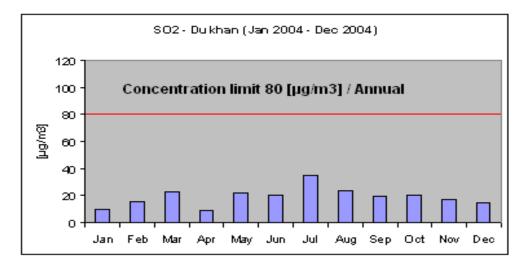
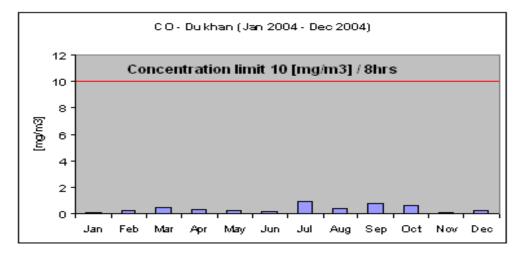
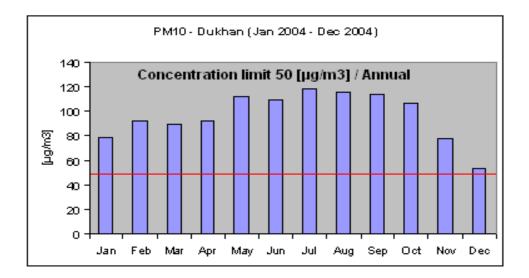


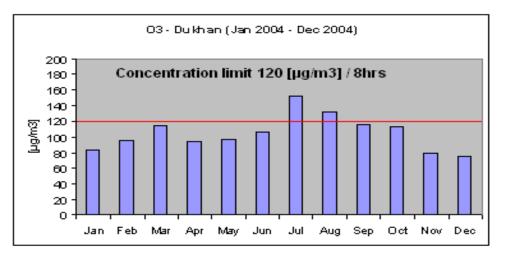
Fig (4-4): Dukhan Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2004

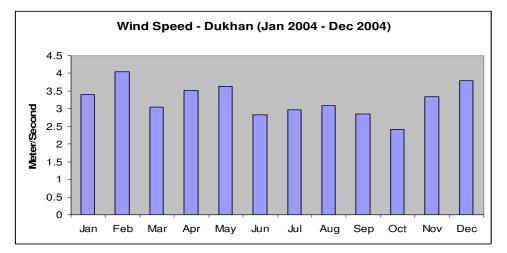




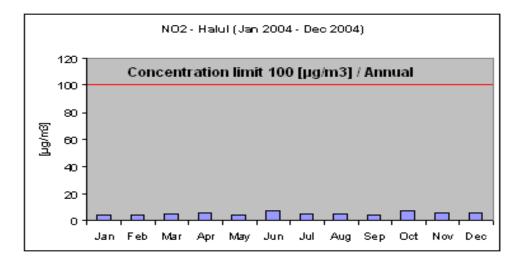


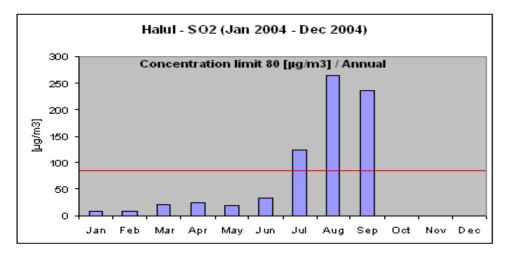


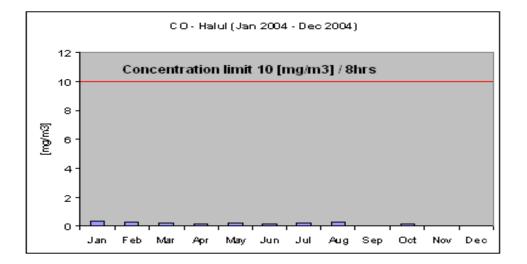


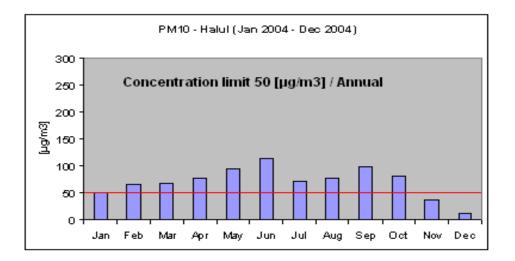


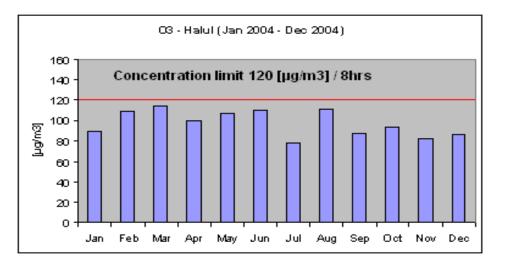
# Fig (4-5): Halul Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2004

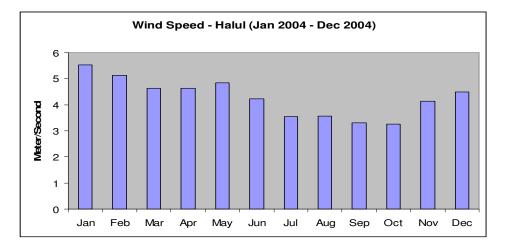




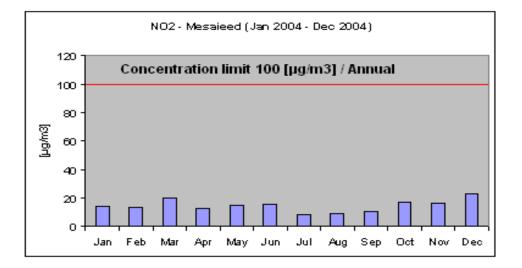


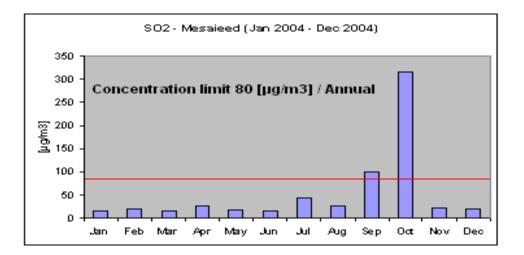


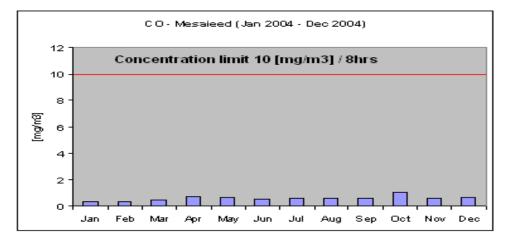


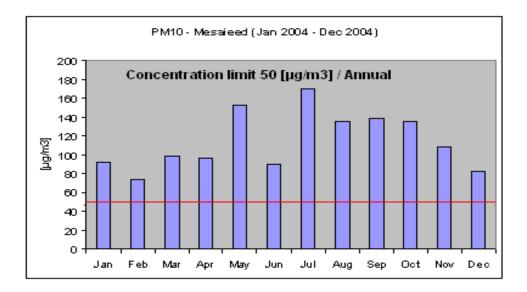


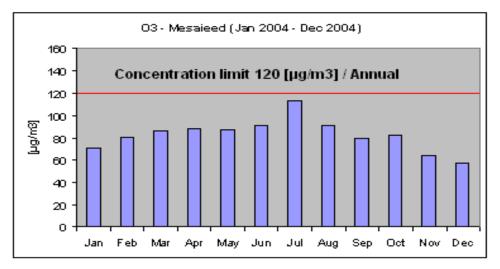
# Fig (4-6): Mesaieed Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10, O<sub>3</sub> and Wind Speed 2004











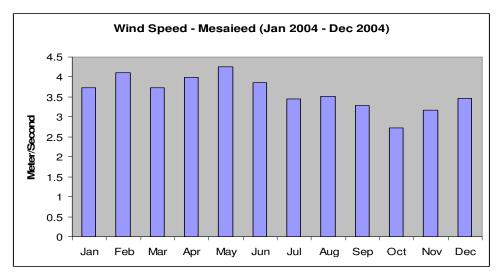
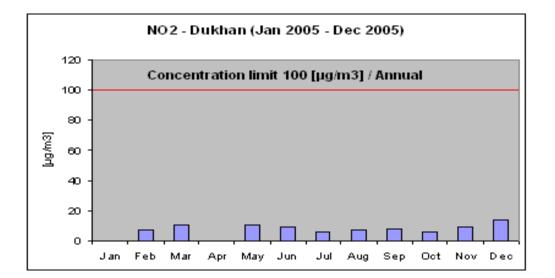
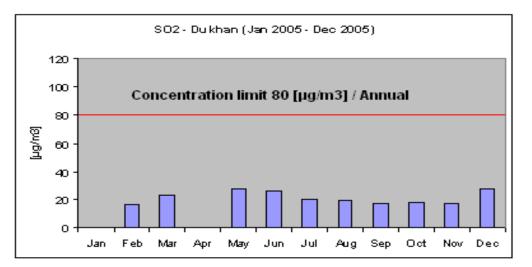
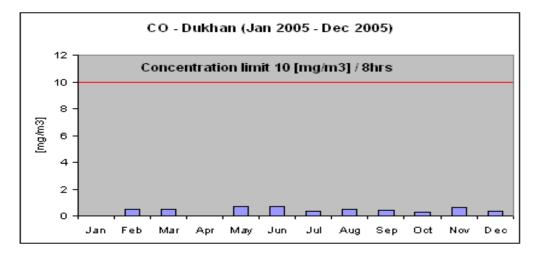
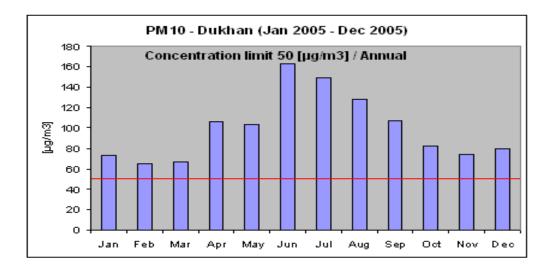


Fig (4-7): Dukhan Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10 and O<sub>3</sub> in 2005









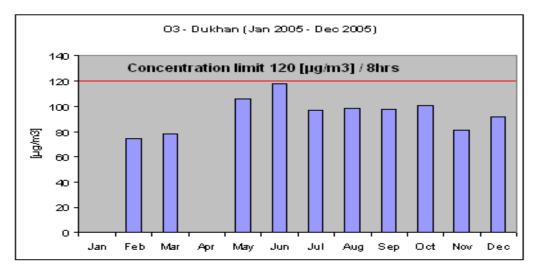
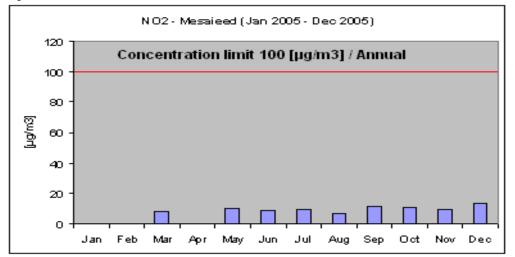
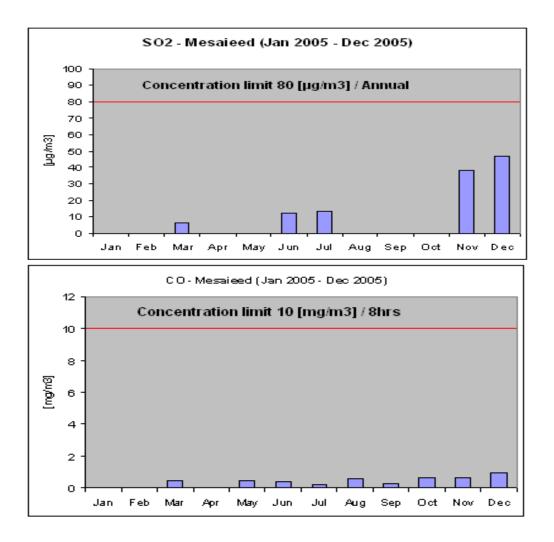
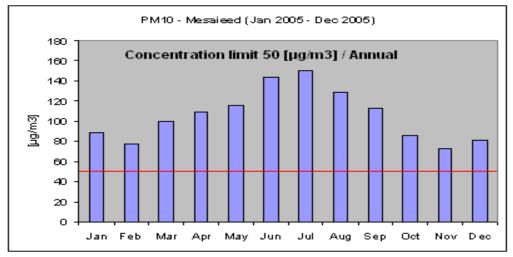
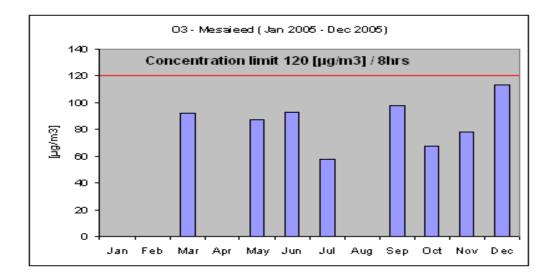


Fig (4-8): Mesaieed Monthly Average for NO<sub>2</sub>, SO<sub>2</sub>, CO, PM10 and O<sub>3</sub> in 2005









### Chapter 5

#### 5.1 Discussion

We should agree on the importance and the requirements of protecting the characteristic quality for the ambient air of the State of Qatar as the pollutants have harmful effects on the human general health as well as the ambient environment. However with the amount of industrial development in Qatar especially the Natural Gas Processing this may not lead to the environmental desirable goal.

With regard to the total volume of the emission as per the International Energy Agency IEA in 2004, it is estimated that Qatar emitted almost 100 thousand tonnes of NO<sub>2</sub> [109, 110], while the total emission released from natural gas operations in Ras Laffan in 2001 reached 26 thousand tonnes of NO<sub>2</sub> and 15 thousand tonnes of VOC as a result of the flaring emission and energy combustion from analysis of the industrial data.

Moreover, there is a real problem relating to the level of ozone gas concentration in the environment as shown by the industrial data gathered and several local reports by the state authorities i.e. ministry of health & the Environment authority which rise this concerns.

It should be agreed that the requirement of adapting comprehensive policies and strategies to control the emission in order to fulfill the state standards requires the use of better control techniques (type: BAT Best Available Technology) instead of (BATNEEC Best Available Technology Not Entailing Excessive Cost) which currently applied in Qatar industry, though it will be necessary to implement major upgrading to most of the existing industries in Qatar to fulfill these requirements. [16, 111]

The data gathered from the monitoring stations indicated low level of pollutants during the three-year survey, however there are some indications of several local violations of the level of Ozone and PM10 with some amounts of H<sub>2</sub>S emitted.

In fact the total emissions processed in Qatar industries are not matching the readings presented by the monitoring stations. So, it is important to go through the data and analyze separately each pollutant's readings.

First some explanations relating to specific pollutants during the years 2003, 2004 and 2005 in three sites; Dukhan, Halul and Mesaieed, as an interpretation for the monthly graphs in Chapter 4 is needed

In Fig 4-2 (Halul – 2003): The PM10 monthly graph shows an exceeding over the concentration limit  $50\mu g/m^3$  in five months where O<sub>3</sub> in July's reading has exceeded the concentration limit ( $120\mu g/m^3$ ) due to fluctuation in the daily readings across the month.

In Fig 4-3 (Mesaieed - 2003): The SO<sub>2</sub> reading during the first week of October, 2003 recorded high gradual increase of concentration limit. It could be due to flaring or operational activities. However, PM10 reading in May shows high level of concentration limit and exceeds the monthly limit by four times. This reading was impacted by six readings from days  $(16^{th} - 21^{st})$  May 2003 (Mesaieed) where readings recorded very high without apparent relation with other pollutants.

In Fig 4-4 (Dukhan - 2004): PM10 readings recorded high levels all over the year.

In Fig 4-5 (Halul - 2004): SO<sub>2</sub> 2004-monthly graph in Halul, the readings started from the months (Jul, Aug and Sep) registering sharply high records. These readings are unstable during some days of each of the above distinct months. These fluctuations have impacted the overall readings of the average concentration in these months. This happened with unapparent reason or relation with other pollutants. The last three months (Oct, Nov and Dec) were not plotted due to unrealistic recorded readings of concentration that probably illustrates an instrumental failure while gauging these concentrations. Alternatively, the readings of PM10 monthly graph in Halul 2004 are relatively

high compared with the high records noticed in PM10 readings in Dukhan and Mesaieed 2004. In these two sites, the readings have sharply exceeded the concentration limit.

In Fig 4-6 (Mesaieed - 2004): SO<sub>2</sub> 2004-monthly readings in Mesaieed shows a distinct high reading in October. The days of (7<sup>th</sup>, 8<sup>th</sup> and 9<sup>th</sup>) of Oct registered high levels that could take place due to operations' activities. The readings also recorded spiking level of NO<sub>2</sub> and O<sub>3</sub>.

In Fig 4-7 (Dukhan - 2005): PM10 12-month readings in Dukhan 2005 are noticed exceeding the average limit.

With regards to individual pollutant NO<sub>2</sub> is expected to be released mainly through vent stacks of process and power generation as well as transportation activities. The levels of NO<sub>x</sub> emitted from power plants vent stacks fall within the range of 50-1000 ppm [66]. Both NO and NO<sub>2</sub> production is favored kinetically and thermodynamically by high temperatures and excess oxygen concentrations and therefore these parameters must be considered for reducing NO<sub>x</sub> concentration.

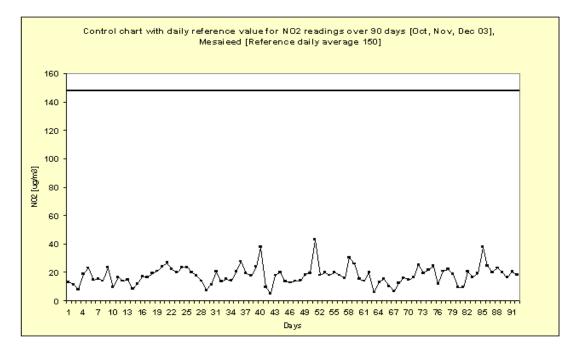
In reducing such emissions, the use of two-stage combustion, a high temperature with substoichiometric amount of air, which would limit NO formation, followed by a lower temperature with excess air thereby prevent its formation. As much as 90% reduction in NO emission has been achieved by the two-stage technology. [112, 113] Other technologies include catalytic decomposition, reduction and sorption of NO<sub>x</sub> by liquids or solids.

The NO<sub>2</sub> entering the atmosphere is converted into Nitric Acid and salt.

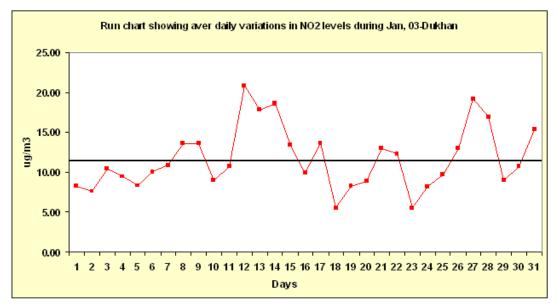
2NO2 +	$\frac{1}{2}O_2 +$	H₂O →	2HNO₃
HNO3 +	NH3	<b></b>	NH4NO3

This phenomenon is classified as "regional air pollution problem", since it can spread out several hundred miles. It is most direct impact in the case of the State of Qatar, in the absence of forestry and/or river waters. The State however is blessed with sea water (of high buffering capacity) surroundings, as well as soils of the calcareous type. It is important to see how steady the natural process of disseminating the NO<sub>2</sub> levels in the atmosphere, the data of fig 5-1 was used to produce control charts for the process. This is shown with the reference lines for the daily and yearly averages of 150 and 100 ppb, respectively. As is shown by the graph, although the process seems to be statically out of control, the readings are very well below the specification lines of 150 and 100 ppm.

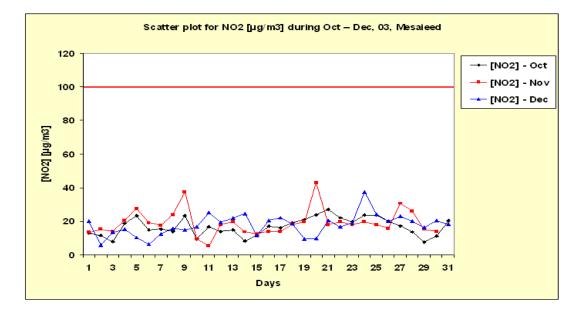
(Fig 5-1): Control chart with daily reference value for NO<sub>2</sub> readings over 90 days in Oct, Nov and Dec 03 in Mesaieed.



(Fig 5-2): Run chart showing aver daily variations in NO<sub>2</sub> levels during Jan, 03-Dukhan.



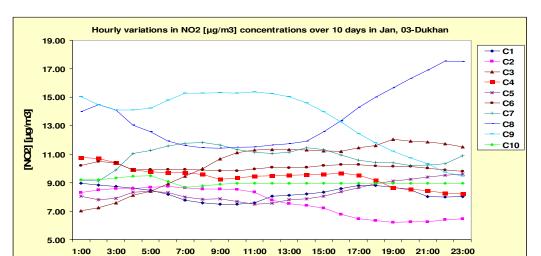
NO2 Data tabulated during January,03 was also analyzed in fig 5-2 for Dukhan station. Reading was stable throughout the month.



(Fig 5-3): Scatter plot for NO<sub>2</sub> during Oct – Dec, 03, Mesaieed

Fig 5-3 shows a scatter plot for NO<sub>2</sub> in microgram per cubic meter [ $\mu$ g/m<sup>3</sup>] over 30 day periods, Oct – Dec, 2003, recorded for MIC station.

The measurement is taken every hour around the clock, as is shown by the graph, readings throughout the month fall well below the reference (annual value) of 100  $\mu$  g/m<sup>3</sup> (ppb) set by the Supreme Council (Qatar Standard) and of course the standard daily average of 150 ppb.



(Fig 5–4): Hourly variations in NO<sub>2</sub> concentrations over 10 days in Jan, 03-Dukhan.

The variations in  $NO_2$  concentrations are shown in Fig 5-4 for several days over 24 hr periods.

Hours

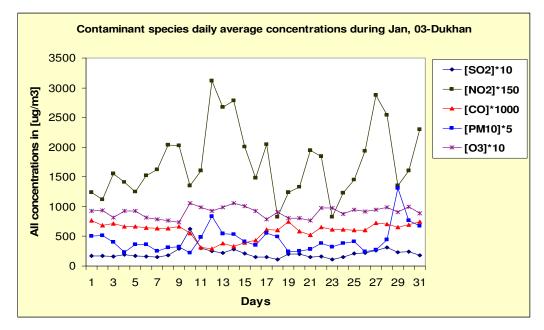
Many factors play parts in inducing this variation including the flaring activities, temperature, humidity, wind direction and speed. Generally speaking, NO<sub>2</sub> levels for Dukhan station seem considerably lower than that of MIC. This is very much expected since MIC houses a lot more industries / power plants as well as the largest ammonia / urea making fertilizer plants world wide.

Annual mean nitrogen dioxide concentrations, in urban areas throughout the world, are generally in the range 20 - 90 microgram per cubic meter (ug/m3) [66, 114 & 115]. Urban levels have been found to vary with time of day, season and meteorological factors. NO<sub>2</sub> concentrations are naturally affected by traffic peaks, i.e., rush hour emissions of Nitric Oxide (NO) which is oxidized in the atmosphere to Nitrogen Dioxide (NO<sub>2</sub>).

Ozone gas is deemed a secondary pollutant that is formulated in the spherical air atmosphere as a result of compounded photo-chemical reactions in the presence of nitrogen oxides and VOC's and with the providing of ultraviolet rays. These reactions are characterized by their chain reactions and leads to multiple free-radicals as well as they are reversible reactions. The reaction takes place in the atmosphere that leads to ozone formation and number of other oxidants in the areas that are along the wind direction of the emission sources of these pollutants (precursors) and also where they are loaded with prevailing winds towards these areas. Although the formation of ozone depends mostly upon the photo degradation for Nitrogen Dioxide and the ability of this reaction to make a reflection as a result of the accumulation of ozone due to the chemical equilibrium. [55, 116]

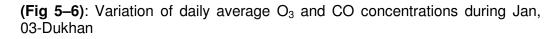
In presence of reactive hydrocarbons in the atmosphere, the chemical reaction takes place among the peroxylalkyl free radicals with nitrogen monoxide. Consequently, this process leads to producing and accumulating ozone in the air environment and also weakening the reversible reaction that could lead to its reduction. Concentration during the month of January 2003 in Dukhan is showed in fig 5-5 depicting all the pollutants with the representative values.

(Fig 5– 5): Contaminant species daily average concentrations during Jan, 03-Dukhan



Elevated concentrations of ozone have been measured in rural areas where local sources of ozone precursors are insignificant. Hourly concentrations exceeding 200  $\mu$  g/m<sup>3</sup> have been observed in rural areas of northern Europe and concentrations exceeding 300  $\mu$  g/m<sup>3</sup> have been observed in rural areas of the United States. [117, 118 & 119]

Generally ozone concentrations are lower in urban areas than in the suburbs, mainly as a result of the scavenging of ozone by nitric oxide originating from traffic. Ozone peaks typically occur in the afternoon. During the night, ozone is scavenged by nitric oxide. Seasonal variations in ozone concentrations occur and are mainly caused by changes in meteorological processes. Higher concentrations are generally observed in the spring and summer.



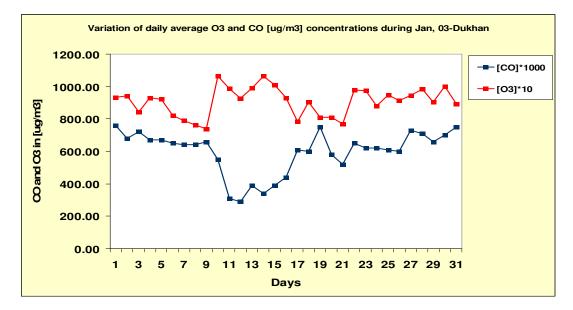
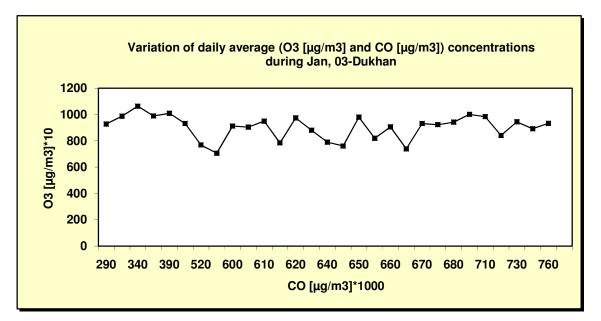
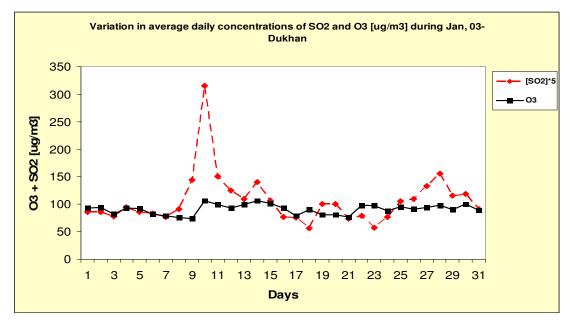


Fig 5-6 depicts the variation of concentrations between  $O_3$  (the squares) and CO (represented by the circles). Perhaps the most obvious relationship shows up between the days 10 and 20. The higher the  $O_3$  concentration is the lower the CO. Of course since the concentrations are rather low [ppb level], the rate is not going to be very high, especially that CO is involved, fig 5-7 shows the correlation between CO and  $O_3$ .

(Fig 5-7): A graph demonstrating the correlation of the two variables CO [ug/m3] with the O<sub>3</sub> [ug/m3] during Jan, 03 – Dukhan



(Fig 5–8): Variation in average daily concentrations of  $SO_2$  and  $O_3$  during Jan, 03-Dukhan



In comparison of the reading in the month of January 2003 in Dukhan for  $SO_2$  and  $O_3$  in figure 5-8, it shows an indication of relation specifically with the Day 10.

Ozone gas formed in Qatar environment attributed to heavy industries at Ras Laffan industrial city at the north and on the Westside from Dukhan operation and from the south at Mesaieed industrial city. Moreover, ozone could be formulated in the atmosphere and travel through long –range transboundary winds in the northern west where there are multiple regional sources and appropriate factors are available to formulate ozone gas. Since the age of these pollutants (residue time of  $O_3$ , NOx and VOC) in the atmosphere air may be several days they could be transported over large distances, maybe hundreds of miles.

The published result about the volume of air pollutant emission from the region; i.e. VOC from Iran are up to 1 million tones in 2003 and 600 thousand tones of NO<sub>2</sub>. Saudi Arabia also has produced more than one hundred thousands tones of VOC. [120, 121, 122 & 123]

SO<sub>2</sub> in Qatar, is primarily emitted from gas combustion, gas processing and to a much lesser extent, transportation fuels. SO<sub>2</sub> affects the Earth's radioactive budget through its photochemical transformation into sulfate aerosols that can either scatter solar radiation; affect cloud formation and impacts atmospheric chemical composition. Although it is considered to be short lived, it contributes to the formation of regional haze which can promote respiratory diseases. Exposure to the gas may increase the effort required to breathe and/or eventual death. In December 1952, approximately 4000 deaths took place in London because of excess levels of SO<sub>2</sub>. [66, 124 &125]

SO<sub>2</sub> can undergo several reactions in the atmosphere including photochemical and chemical types. It is worth noting that the atmosphere is a highly dynamic medium with great variations in temperature, composition, humidity and intensity of light that variably impacts the nature and extent of reaction processes. (Fig 5-9): Variation of SO<sub>2</sub> concentration average daily readings during Jan, 03-Dukhan

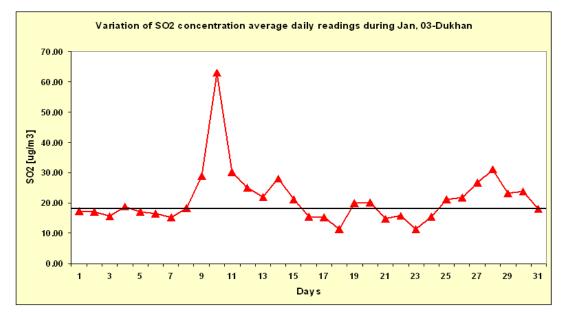
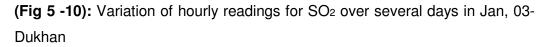
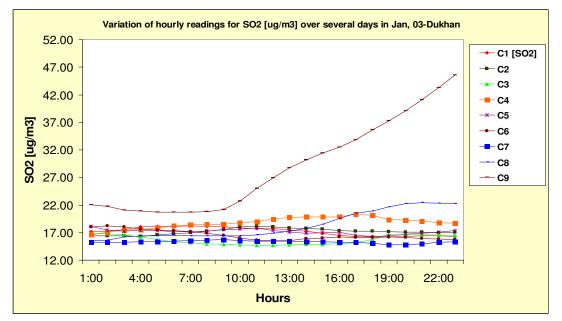


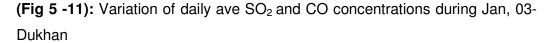
Figure 5 – 9 shows average daily readings, registered over 31 days, during January 2003 for Dukhan. Here again the data show a spike of 70 ppb for SO<sub>2</sub> concentration on day 10, still way below the daily Qatari standard for 365 ppb, that subsided back to average levels on the next day.

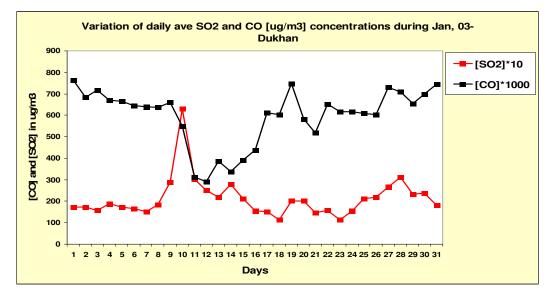


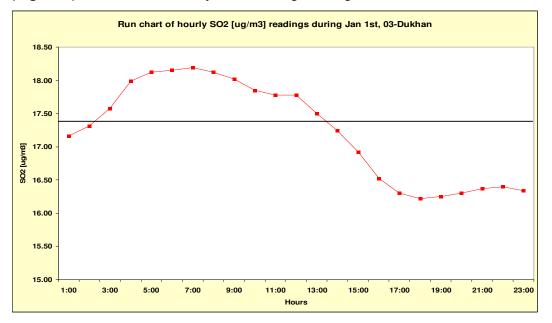


The Data of figure 5-10 shows variations of SO<sub>2</sub> concentrations in  $\mu g / m^3$  in the atmosphere during the day [over 24 hour period] on several days, C<sub>1</sub> – C<sub>10</sub>, in January 2003 registered at the Dukhan station. The data of Figure 62 show SO<sub>2</sub> level to start increasing, on day C<sub>10</sub>, at about 9 AM from nearly 20 ppb reaching 45 ppb at around 11 PM. This rise of course must have come from a flaring activity. It would be difficult to attribute this rise to a particular source / reason without consulting the records of several process plants spread over several process plants spread over several operational sites.

The daily basis concentration of  $SO_2$  and CO in January 2003 in fig 5-12 relatively shows a proportional relation between the both pollutants.



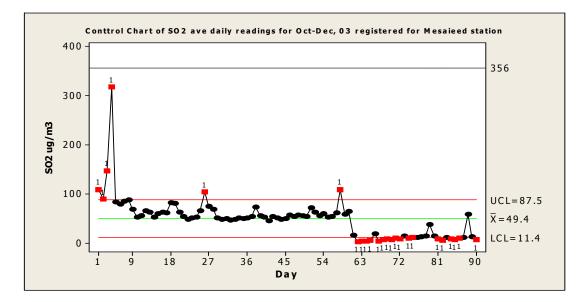




(Fig 5-12): Run chart of hourly SO<sub>2</sub> readings during Jan 1<sup>st</sup>, 03-Dukhan

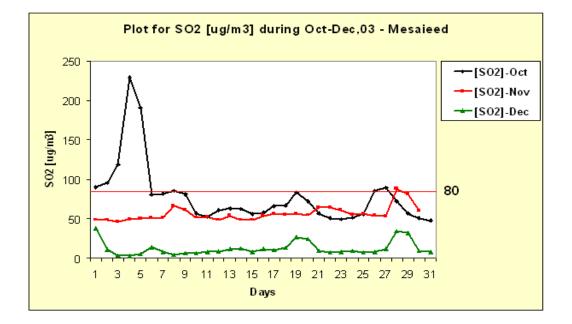
Fig 5-12 is hourly reading over 24hours period in January 2003 for  $SO_2$  was plotted reflecting correspondence to the area activities in Dukhan.

(Fig 5-13): A control chart for average daily SO<sub>2</sub> concentrations during Oct – Dec, 03 registered at Mesaieed station.



The philosophy behind constructing this chart 5-13 is to see how successful/steady the dissipation process in the atmosphere for SO<sub>2</sub>. The markings 1 indicate the points that are statistically out of control. The graph

also shows the upper and lower control limits as well as the average. As is seen in the graph, all the points are well below the average daily standard of 356 ppb.



(Fig 5-14): Plot for SO2 during Oct-Dec, 03-Mesaieed

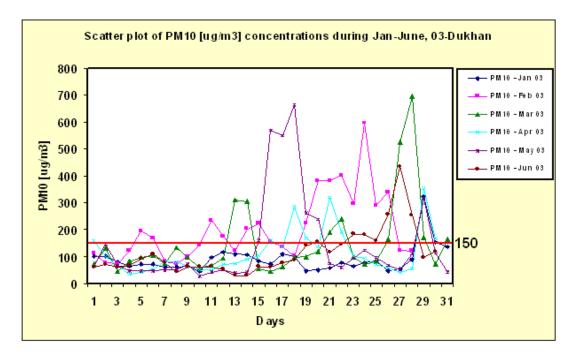
The plot of SO<sub>2</sub> concentrations over a 30 day period Fig 5-14 shows that all readings including the one on the 4th day of nearly 230, fall below the 24 hr (daily mean reference value) of 365 set by the Supreme Council (Qatari Standard). That higher than average reading registered in early October, must have been a result of a plant upset that necessitated flaring of a higher sulfur content gas.

Since SO<sub>2</sub> isn't very stable in the atmosphere, even under ambient conditions, due to many factors that can influence its stability including temperature, humidity, light intensity, atmospheric transport and particulate matter, that higher reading subsided back to average in November and continued to be that way in December too. The 80 is the reference annual value.

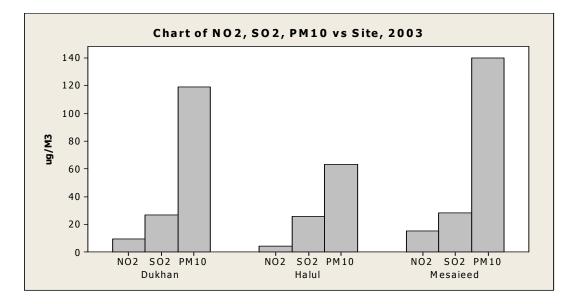
Particulate matter makes up the most visible and obvious form of air pollution. Pollutant particles in the 1 to 10 micron range are commonly suspended in the air near sources of pollution, i.e., highways, industrial and power plants, etc. Very small solid particles include carbon black, combustion nuclei, and sea salt nuclei. Larger particles include cement dust, wind blown soil dust, etc. Liquid particulate matter may be organic or inorganic; both types are atmospheric contaminants.

The effects of particulate matter may be detrimental to human health, damage materials, scatter light, reduce visibility, etc. [56]. Particulate emissions can be controlled using a variety of particle removal systems, (i.e., filtration, scrubbing, electrostatic, etc.) depending upon the nature of particles (size distribution), effectiveness, complexity and cost.

The data of fig 5-15 show recorded daily averages during the months Jan-June of 2003 at Dukhan station. Of interest is that considerably higher than the average daily reference value of 150 ppb was registered from January throughout April. Of more interest is that those higher levels subsided back to very low levels during the following months of May and June as is shown by the graph. In Europe, the annual average is between 20 and 98  $\mu$  g/m<sup>3</sup>



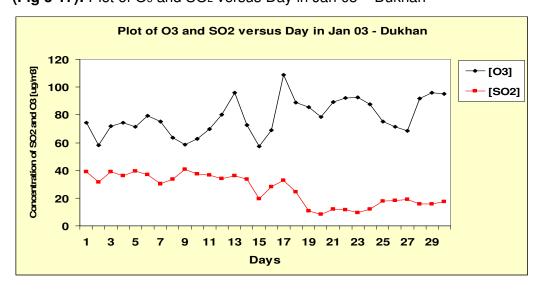
(Fig 5 -15): Scatter plot of PM10 concentrations during Jan-June, 03-Dukhan



(Fig 5 -16): Yearly concentrations of NO<sub>2</sub>, SO<sub>2</sub> and PM10 for 2003 vs. site

The data of fig 5-16 shows the average levels of daily measurements for NO<sub>2</sub>, SO<sub>2</sub> and PM10 through out 2003. As is shown by the graph, both NO<sub>2</sub> and SO<sub>2</sub> are very much below the reference yearly values of 100 and 80 ppb, respectively at all sites. As for PM10, MIC seems to be the highest reaching nearly 140 ppb. Both MIC and Dukhan are above the yearly reference value of 100.

Concentration of SO<sub>2</sub> and O<sub>3</sub> was plotted in fig 5-17 for January 2003. The interaction between the both pollutants is not significant. (Fig 5-17): Plot of O<sub>3</sub> and SO<sub>2</sub> versus Day in Jan 03 – Dukhan



## 5.2 Evaluation of Ambient Air Quality

## 5.2.1 Comparison with State of Qatar Environmental Protection Standards

A direct comparison with air quality standards provides an assessment of what is acceptable and can provide a bench mark to determine if air quality is improving or deteriorating. An analysis was undertaken of the monitoring data from each station against the Qatar national standards.

The data from each station for sulfur dioxide, nitrogen dioxide, carbon monoxide, PM10 and ozone was statistically sampled and compared with the Qatar Environmental Protection Standards (EPS) on the basis of percentile quoted in the standard. The data is summarized in Table 5.1. It's apparent that the ozone and PM10 levels exceeded the Qatar standards for all three stations.

In the case of the PM10 particulate data, it is difficult to separate the industrial from the anthropogenic sources on the basis of the data collected. The Qatar standard stipulates that the particulate matter should not be of natural origin. Previous experience in Qatar demonstrates that high PM10 values can be obtained during sand storms and periods of high wind speed. Exceedance of the PM10 standard is therefore not definitive.

Parameter	Averaging Time	Percentile	Di	ukhan	ŀ	lalul		MIC	Qatar	Units
	(1)		Value	Flag	Value	Flag	Value	Flag	Standard	
SO <sub>2</sub>	24 hr	99.7	34.3		42.5		109.7		365	μg/m <sup>3</sup>
	Annual (1)	Mean of hourly	14.2		6.94		12.4		80	µg/m³
	Overall			MEETS		MEETS		MEETS		
	1 hr	99.98	79.2		36.8		97.1		400	μg/m <sup>3</sup>
NO2	24 hr	99.7	24.3		13.8		41.9		150	µg/m <sup>3</sup>
	Annual (1)	Mean of hourly	11.9		2.8		12.4		100	µg/m³
	Overall			MEETS		MEETS		MEETS		
	1 hr	99.98	1.2		0.7		2		40	mg/m <sup>3</sup>
СО	8 hr	99.8	0.7		0.6		1.1		10	mg/m <sup>3</sup>
	Overall			MEETS		MEETS		MEETS		
	24 hr	99.7	858.5		310.2		524		150	μg/m <sup>3</sup>
PM10	Annual (1)	Mean of hourly	125.1		40.8		70.4		50	µg/m³
	Overall			EXCEEDS		EXCEEDS		EXCEEDS		
	1 hr	99.7	168.2		153.8		142.7		235	μg/m <sup>3</sup>
O3	8 hr	98	129.7		144.7		136.1		120	μg/m <sup>3</sup>
	Overall			EXCEEDS		EXCEEDS		EXCEEDS		

 Table 5-1: Comparison of Monitoring Data with Qatar EPS

## 5.3 Air Quality Banding Assessment

The banding of air quality data allows more meaningful information to be provided to the general public and those exposed to the air quality in question. The United Kingdom uses a banding system based on ambient concentrations of ozone, nitrogen dioxide, carbon monoxide and PM10 particles. The UK system is designed to inform and protect the general population. Most of the monitoring stations are located in urban environments where traffic makes a considerable contribution to local air quality. Since the three stations are in fact on site of each of the industrial locations. it's likely that the concentrations recorded would be conservative in comparison with measurements made in nearby population centers, unless the stations are located upwind of point sources or are sited in close proximity of point sources of emissions at some height above the monitoring height, in which case plume effects may be observed. The banding system can be combined with health advice to the population affected by periods of poor air quality.

The bandings included in Table 5-2 are therefore proposed based on the UK system.

Pollutant Banding Concentrations					
BAND	Ozone	Nitrogen Dioxide	Sulfur Dioxide	Carbon Monoxide	PM10 Particles
	Hourly mean [µg/m <sup>3</sup> ]	Hourly mean [µg/m <sup>3</sup> ]	15 minute mean [μg/m <sup>3</sup> ]	8 hour mean [μg/m³]	24 hour mean [μg/m <sup>3</sup> ]
GOOD	0 - 99	0 - 286	0 – 265	0 – 11.5	0 - 49
ACCEPTABLE	100 – 179	287 - 572	266 – 531	11.6 – 17.3	50 – 74
POOR	180 – 359	573 – 763	532 – 1063	17.4 – 23.1	75 – 99
BAD	360 or	764 or	1064 or	23.2 or	100 or
	more	more	more	more	more

 Table 5-2: Boundaries between Banding System for Each Pollutant

On the basis of the above banding for each pollutant, the rolling average values were determined for each station to correspond with the observation period stated. The upper end of each band was then inserted as a limit in the statistical analysis package to determine the number of observations which

exceeded each the band limit. This data was then summarized in Tables 5-3, 5-4 and 5-5 as the percentage of time, over the 3-month monitoring period from 1<sup>st</sup> December 2003 until 29<sup>th</sup> February 2004, when the air quality was within that band for each parameter for Dukhan, Halul and MIC respectively.

BAND	Ozone	Nitrogen Dioxide	Sulfur Dioxide	Carbon Monoxide	PM10 Particles
GOOD	67.58	100	100	100	14.29
ACCEPTABLE	32.28	0	0	0	24.17
POOR	0.14	0	0	0	17.58
BAD	0	0	0	0	43.96

Table 5-3: Percentage of Monitoring Period within Each Band for Dukhan

#### Table 5-4: Percentage of Monitoring Period within Each Band for Halul

BAND	Ozone	Nitrogen Dioxide	Sulfur Dioxide	Carbon Monoxide	PM10 Particles
GOOD	51.89	100	99.87	100	51.65
ACCEPTABLE	48.31	0	0.13	0	21.98
POOR	0	0	0	0	8.79
BAD	0	0	0	0	17.58

Table 5-5: Percentage of Monitoring Period within Each Band for MIC

BAND	Ozone	Nitrogen Dioxide	Sulfur Dioxide	Carbon Monoxide	PM10 Particles
GOOD	51.69	100	99.50	100	30.77
ACCEPTABLE	48.31	0	0.39	0	21.98
POOR	0	0	0.06	0	15.38
BAD	0	0	0.05	0	31.87

High levels of any of these pollutants can affect the elderly, sufferers from heart or lung diseases including asthmatics and the very young. Air pollution can result in short term effects on such sensitive individuals. Health advice associated with air quality in each band, based on UK guidance, is provided in Table 5-6.

Table 5-6: Health Advice	Associated with Each Band
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BAND	Health Advice
GOOD	Effects are unlikely to be noticed even by those sensitive to air pollutants.
ACCEPTABLE	Sensitive people may notice mild effects but these are unlikely to need action.
POOR	Sensitive people may notice significant effects and may need to take action to avoid or reduce these effects (e.g. reducing exposure by spending less time in polluted areas outdoors). Asthmatics will find that their 'reliever' inhaler is likely to reserve the effects on the lung.
BAD	Effects on sensitive people described under the POOR band may worsen.

Effects on sensitive people can be reduced by spending less time outdoors. "Reliever" inhalers should lessen effects on asthma sufferers. During periods of high particulate concentrations, such as sand storms, breathing protection such as month filters may be required.

## 5.4 Overview on international standard limit exceedance of pollutants:

## 5.4.1 Ozone

Elevated concentrations of ozone have been measured in rural areas where local sources of ozone precursors are insignificant. Long-range transport of ozone and/or its precursors from upwind sources or tropospheric infolds has been cited as being responsible. Maximum hourly ozone concentrations exceeding 200µg/m<sup>3</sup> have been observed in rural areas in northern Europe and concentrations exceeding 300µg/m<sup>3</sup> in rural areas of the United States. High episodes exceeding 500µg/m<sup>3</sup> as an hourly average have been also recorded around the Mediterranean. Maximum hourly ozone values of 430µg/m<sup>3</sup> and 520µg/m<sup>3</sup> have been also measured in the Netherlands and the United Kingdom respectively [51]. The maximum hourly concentration of ozone recorded at Ras Hayyan, a remote location at the east coast of Bahrain in August 1987 was 128µg/m<sup>3</sup> [52].

In some areas of Europe, urban 1-hour average ozone concentrations exceed  $350\mu g/m^3$ , while in the United States, urban 1-hour mean

concentrations often exceeds  $400\mu$ g/m<sup>3</sup>. Generally ozone concentrations are lower in urban centers than in the suburbs, mainly as a result of the scavenging of ozone by nitric oxide originating from traffic.

Diurnal variations in ozone vary according to the location and the balance of the various ozone formation, transport and decomposition mechanisms. In the early morning, some time is required for the development of photochemical reactions. Ozone peaks typically occur in the afternoon. During the night ozone is scavenged by nitric oxide.

Seasonable variations in ozone concentrations occur and are mainly caused by changes in meteorological processes. Higher quarterly mean ozone concentrations are generally observed in the spring and summer.

The monitoring data from all three stations indicates ozone concentrations to be within the observed range for European population centers. The occasional high levels of ozone observed at MIC and Halul, are typical.

## 5.4.2 Nitrogen Dioxide

Maximum 30 minute or 1-hour average and maximum 24-hour concentrations of nitrogen dioxide have been reported elsewhere at concentrations of up to 940µg/m<sup>3</sup> and 400µg/m<sup>3</sup> respectively. Annual mean nitrogen dioxide concentrations in urban areas throughout the world are generally in the range 20 to 90µg/m<sup>3</sup>. Urban levels have found to vary with time of day, season and meteorological factors. Typically urban data is affected by traffic related peaks with correspond to the rush-hour emissions of nitric oxides which are oxidized in the atmosphere to nitrogen dioxide.

The monitoring data from all three stations indicates nitrogen dioxide concentrations to be within the observed range for European population centers.

## 5.4.3 Sulfur Dioxide

Data on concentrations of sulfur dioxide are based either on national monitoring networks, which tend to be concentrated in urban areas, or on cooperative programs for the study of long-range transport of pollutants. As a result of the reduction of fuel sulfur content in Europe, annual mean levels of sulfur dioxide in major European cities are now largely below  $100\mu g/m^3$ . Similarly there has been a decline in maximum daily mean values which are now generally below  $500\mu g/m^3$ . Peaks over shorter averaging periods in Europe, such as 1-hour, can extend to  $1000 - 2000\mu g/m^3$  and in certain situations higher transient peaks may occur. Natural concentrations of sulfur dioxide are normally below  $5\mu g/m^3$ , although annual mean concentrations may exceed  $25\mu g/m^3$ , in rural areas as a result of using high stacks for dispersion of major combustion sources such as power plants.

The monitoring data from all three stations indicates sulfur dioxide concentrations to be within the observed range for European population centers. However,

## 5.4.4 Carbon Monoxide

Natural background levels of carbon monoxide range between 0.06 and 0.14 mg/m<sup>3</sup>. Concentrations in urban areas typically depend on weather and traffic density. They also vary greatly over time and with distance from source. The 8-hour mean concentrations are generally less than 10 mg/m<sup>3</sup>. However, maximum 8-hour mean values of up to 60 mg/m<sup>3</sup> have been occasionally observed.

The monitoring data from all three stations indicates carbon monoxide concentrations to be within the observed range for European population centers.

#### 5.4.5 PM10 Particles

Airborne particulate matter is a complex mixture of organic and inorganic constituents. The smaller particles represent the greatest risk since they are able to enter the lower respiratory tract. PM10 (Particulate matter in which

50% of particles are less than  $10\mu$ m in size) is regarded by the US EPA as an indicator of health related particles. Data on PM10 for dry arid climates is difficult to obtain as most monitoring sites are not in the public domain.

Occurrence in air as an annual average, in Europe is generally between 20 and  $98\mu g/m^3$  (measured gravimetrically). High 24-hour PM10 values have been recorded at the three stations. the annual average values are exceeding the observed range for European population centers.

## 5.5 Wind and Pollution Roses

Breuer plots were prepared of 95 Percentile values of each pollutant for each station to determine the direction of sources. Plots were also made using 95 Percentile wind speed values (effectively a wind rose) for comparison. The plots are included in Appendix-2 [ Fig 2-1 to Fig 2-6 ]. It is useful to know the locations for nearby sources to the stations as this would aid interpretation of the observed data.[126&127]

## 5.6 Halul Breuer Plots

The wind rose for Halul in Appendix-2 does not show a distinct pattern although it does show higher frequency of winds from the northwest and south-southeast. Marked differences are apparent between pollutants. Nitrogen dioxide shows sources from a southwesterly and to a lesser extent south easterly direction.

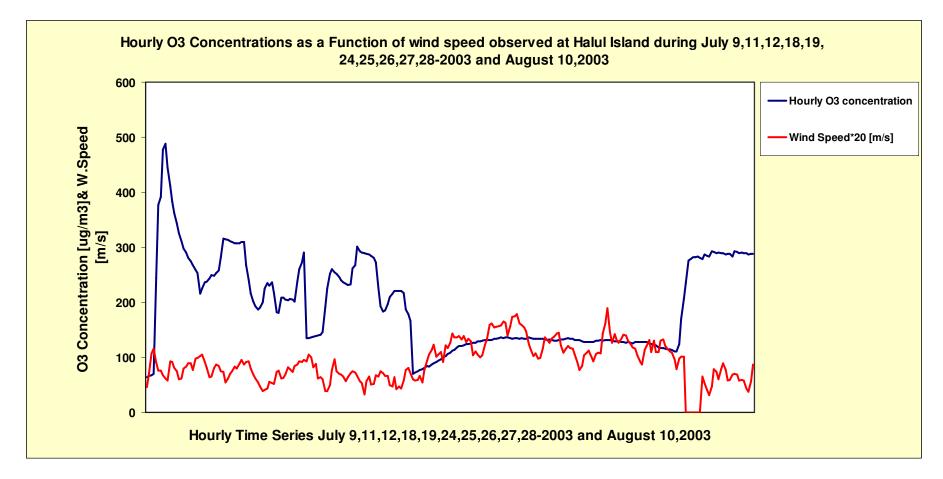
Carbon monoxide and ozone do not show a distinctive source. Sulfur dioxide shows a definitive source from a southeasterly direction, whilst PM10 shows sources from several directions, with a notable peak to the north and south.

For comparison reasons, selected days during July 2003 and Aug 10, 2003 were plotted to develop a possible relation between the wind speed and the concentration of ozone. In table 5-7, we see the 24 hour readings for these days and a wind rose was plotted to show the prevailing wind direction and figure 5-18 shows an important relation that when the wind speed reduces, ozone concentrations increase and when the wind speed increases, ozone concentration reduces. This can be considered a serious observation for this phenomena where local harmful ozone can be created and can impact the health and safety of the public.

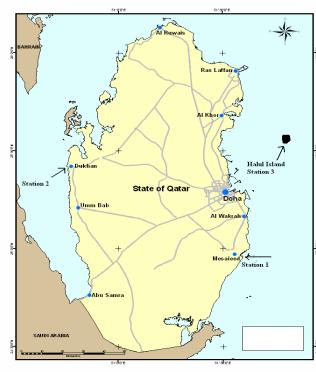
	9 <sup>th</sup> Jul	y, 2003	11 <sup>th</sup> July	/, <b>200</b> 3	12 <sup>th</sup> Ju	ly, 2003	18 <sup>th</sup> Jul	y, 2003	19 <sup>th</sup> Ju	ly, 2003	24 <sup>th</sup> Ju	ly, 2003	25 <sup>th</sup> Jul	y, 2003	26 <sup>th</sup> Ju	ly, 2003	27 <sup>th</sup> Ju	ly, 2003	28 <sup>th</sup> Jul	y, 2003	10 <sup>th</sup> Au	g, 2003
	<b>O</b> <sub>3</sub>	W.Spd	O <sub>3</sub>	W.Spd	O <sub>3</sub>	W.Spd	O <sub>3</sub>	W.Spd	O₃	W.Spd	O₃	W.Spd	<b>O</b> <sub>3</sub>	W.Spd	O <sub>3</sub>	W.Spd	O <sub>3</sub>	W.Spd	<b>O</b> <sub>3</sub>	W.Spd	<b>O</b> <sub>3</sub>	W.Spd
00:00	С	2.31	С	5.22	С	2.72	С	4.07	С	3.24	С	3.84	С	5.03	С	5.38	С	5.08	С	6.01	С	3.25
01:00	64	3.55	215.16	4.59	201.4	2.36	134.7	4.39	293	2.52	69.53	4.71	124.28	5.21	133.5	4.87	133.6	4.62	126.91	6.58	123.88	2.65
02:00	66.72	5.34	225.84	4.05	192.3	1.91	135.3	3.06	290.3	2.58	72.31	5.32	123.85	6.15	134.8	4.93	131.8	5.3	127.58	5.5	170.45	1.96
03:00	68.06	5.79	236.65	3.18	187	2.04	136.3	3.21	289	3.38	74.52	5.65	125.63	6.65	133.4	5.8	131.5	5.4	126.8	6.51	206.3	1.58
04:00	70.23	4.53	236.99	3.27	189.9	2.17	137.2	3.01	288.4	3.25	76.52	6.12	126.46	7.98	134.1	6.83	131.4	5.38	125.31	5.48	235.39	2.36
05:00	244.28	3.79	243.87	4.06	200.3	2.75	138.4	1.95	286.2	3.71	78.91	5.08	126.94	8.04	135.7	6.54	128.8	7.19	127.16	5.46	276.17	3.99
06:00	377.63	3.82	249.13	4.34	225.8	2.63	139.5	1.92	283.9	3.56	80.59	5.24	129.42	7.47	134.7	6.33	127.9	8.06	127.46	6.51	278.21	3.67
07:00	391.22	3.39	247.82	4.24	235.3	2.61	140.5	2.5	280.7	3.31	84.02	5.46	128.92	7.75	134.2	6.76	128	9.44	127.6	6.61	281.87	3.04
08:00	476.59	3.07	253.03	3.73	230	3.7	146.2	3.48	272.8	3.29	83.71	4.55	129.87	7.85	133.7	6.89	128.3	7.27	128.14	6	282.41	4.36
09:00	488.31	2.9	258.36	3.65	236.7	3.8	191.2	4.82	225.2	2.44	86.16	6.11	131.37	7.9	133.7	7.17	127.1	6.3	127.21	5.73	282.78	4.44
10:00	445.05	4.61	281.43	2.73	217	3.09	225.1	3.73	192.3	2.33	89.12	5.83	131.13	8.27	133.7	7.25	127.3	7.1	127.3	5.57	280.45	3.84
11:00	411.05	4.58	315.65	3.06	182.2	3.13	252	3.49	182.6	3.19	91.22	6.31	131.61	8.14	133.2	6.15	129.7	6.59	125.29	5.41	278.23	2.88
12:00	383.56	4.03	314.96	3.48	181	3.44	259.7	3.46	186.1	2.08	94.09	7.14	131.31	6.96	132.9	5.44	130.1	6.35	124.27	4.8	287.31	2.93
13:00	361.88	3.75	312.75	3.73	209	4.11	254.7	3.23	196.9	2.37	96.03	6.79	133.79	7.84	130.8	5.74	131	6.77	122.94	3.9	284.58	3.46
14:00	342.99	3.02	310.57	4.17	207.9	3.89	251.3	2.83	209.8	2.17	100.1	6.79	133.39	8.66	131.9	6.03	129.7	7.03	121.19	4.88	282.57	3.51
15:00	325.06	3.08	309.27	3.95	204.9	3.7	245.8	3.22	215.7	2.9	102	6.91	134.61	8.76	131.8	5.87	130.8	7.01	118.43	5.07	292.33	3.45
16:00	310.53	3.96	307.07	4.4	204.1	4.22	240.2	3.56	220.3	3.84	106.1	6.6	135.7	8.91	129.8	5.88	131.2	6.5	116.82	5.09	291.12	2.9
17:00	298.18	4.16	307.17	4.73	205.7	4.33	236.5	3.71	220.4	4.03	108.5	6.99	135.42	8.1	130.2	5.23	131.1	6.2	116.34		289.25	2.97
18:00	289.98	4.46	307.74	4.31	204.7	4.64	233.9	3.6	220.2	3.53	111.6	6.41	136.02	7.93	131.4	4.54	130.3	5.92	115.13		289.95	2.92
19:00	280.98	4.43	309.22	4.59	201.3	4.59	231.8	3.31	220.7	3.04	113.8	6.66	136.15	7.71	132.4	3.84	128.8	5.78	115.06		289.18	2.17
20:00	274.28	3.84	310.15	4.61	237.6	4.75	232.9	2.86	217.4	2.89	118	6.46	134.52	7.33	132.8	4.2	128.7	5.16	114.23		288.79	1.87
21:00	267.42	4.9	267.03	3.97	260.2	4.62	261.2	2.68	186.9	2.93	120.5	5.21	133.94	6.18	133.4	5.17	128.5	4.63	113.16		286.75	2.81
22:00	259.47	4.95	240.83	3.46	272	5.42	267	1.65	178.6	3.33	120.7	5.57	134.8	5.67	135	5.4	127.6	4.34	111.43		288.49	4.33
23:00	252.72	5.12	216.12	3.09	291	4.98	301.4	2.85	166.4	2.74	122.2	5.24	134.65	5.11	133.6	5.59	127.5	5.56	110.65		288.28	4.05
Ave	293.49	4.058	272.9	3.942	216.4	3.567	208.4	3.191	231.5	3.027	95.66	5.875	131.47	7.317	133.1	5.743	129.6	6.208	121.58	5.595	267.6	3.141

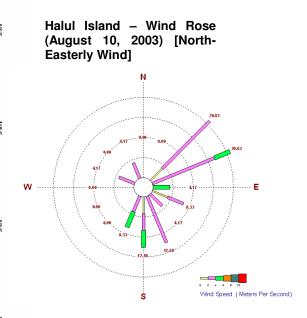
(Table 5-7): Datasheet of hourly O<sub>3</sub> concentrations & wind speed during 9,11,12,18,19,24,25,26,27 and 28 July, 2003 and 10<sup>th</sup> Aug, 2003

(Fig 5-18): Hourly  $O_3$  Concentrations as a Function of wind speed observed at Halul Island during July 9,11,12,18,19,24,25,26,27,28-2003 and August 10,2003

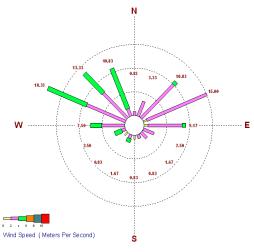


(Fig 5–19): A wind rose showing the elevation of Levels of  $O_3$  concentrations during July 03 at Halul islands in a relation with wind speed and wind direction.

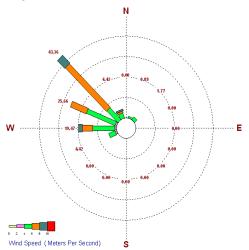




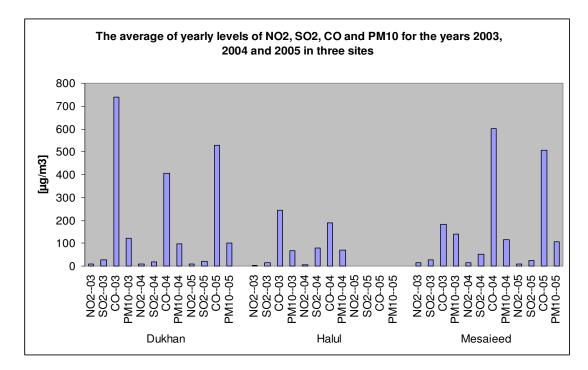
Halul Island – Wind Rose (July 9, 11, 12, 18-19) / 2003 [Low Wind Speed]



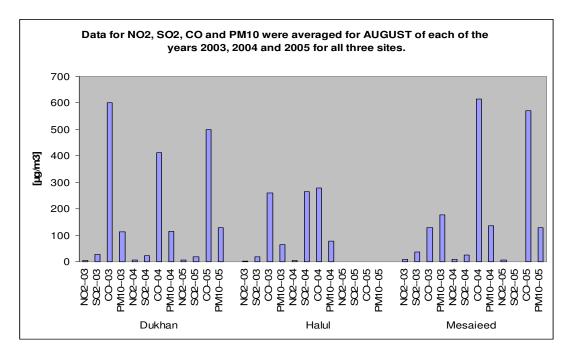
Halul Island – Wind Rose (July 24, 25, 26, 27-28) / 2003 [High Wind Speed]



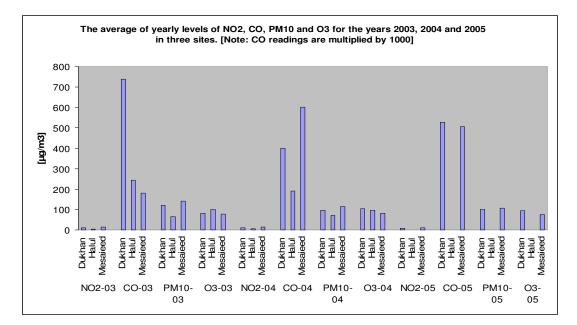
(Fig 5-20): The average of yearly levels of NO2, SO2, CO and PM10 for the years 2003, 2004 and 2005 in three sites [Note: CO readings are multiplied by 1000].



(Fig 5–21): Data for NO<sub>2</sub>, SO<sub>2</sub>, CO and PM10 were averaged for AUGUST of each of the years 2003, 2004 and 2005 for all three sites [Note: CO readings are multiplied by 1000].



(Fig 5–22): The average of yearly levels of NO2, CO, PM10 and O3 for the years 2003, 2004 and 2005 in three sites [Note: CO readings are multiplied by 1000].



It is firmly believed in challenging the status quo where this is warranted, to me accepting something simply because its there or been that way is threats to our progress & developments. Most of my work during the past ten years has been aimed at presenting new ideas and solutions to existing or unearthed problems. Therefore the need for a clear and close overview of the work outcomes are critical for the under standing of the comparison between both results.

The finding from the monitoring stations do not reflect the expected severe air pollution coming from our industries as per the real data collected from the reporting process due to not establishing a comprehensive air pollution network in Qatar.

Therefore the reading collected varies with wind direction and the mode of operation in the different industrial areas. The amount of expected emissions from Qatar industry was reported publicly by the IEA or UNEP on there reports on 1995 & 2005.

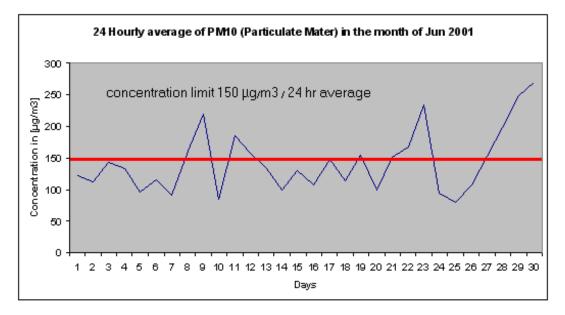
Several complaints from the resident of Halul Island, Messaied as will as Alkhor City on an H<sub>2</sub>S incident were reported. Reports on the phenomena of the excessive concentration of harmful and strong hydrocarbon gases in the atmospheric air were the topic of many local news papers this include medical repots on Asthma.

This led the ministry of health in the Qatar to ask the World Health Organization (WHO) to provide an expert to report on these concerns and the consequences which resulted from the emission of Nitrogen Oxides and Volatile Organic Compounds from the plants. An action plan on the risk of Ozone gas formation on Doha and Al-Khor was developed. The main outcome of the WHO expert report is as follow:

- The primary man-made sources of air pollution in the Ras Laffan industrial area, in northern Qatar, are mainly from Liquefied National Gas industries and the shipment of exported gas at Ras Laffan Port.
- The air pollutants emitted from stacks, flares, and fugitive emissions include sulfur oxides (SO<sub>x</sub>), hydrogen sulfide, nitrogen oxides (NO<sub>x</sub>), hydrocarbons (methane and nonmethane), toluene, benzene, xylene, mercaptans and particulates, mainly in the form of black smoke from flares.
- Major air pollutants to be considered in any air quality management programs from the Ras Laffan area.
- Atmospheric photochemical reactions involving hydrocarbons and nitrogen oxides have led to the local formation of ozone sometimes reaching levels higher than WHO guideline values level and Qatar air quality standards.

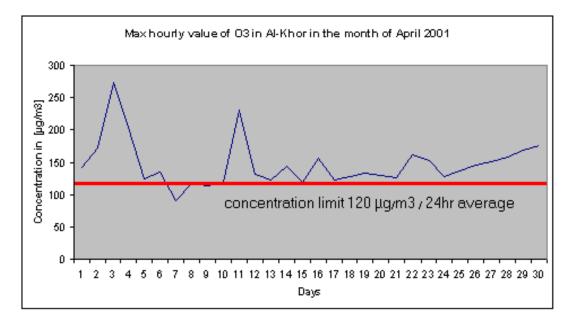
The report also indicated that during April 2001, Al-Khor residents complained about the strong smell of mercaptans. According to the Ras Laffan report to the Supreme Council for the Environment, a breakdown

occurred in an LNG sulfur recovery unit during April and May 2001, possibly leading to excessive emissions of pollutants. Examinations of air quality data monitored at RLC during April and May 2001 indicated that air pollutants such as sulfur dioxide and ozone sometimes reached concentrations higher than WHO guideline values. Three graphs (fig 5-23, 24, 25) from WHO expert report are below & the copy of the front page are in (Appendix 1.12).

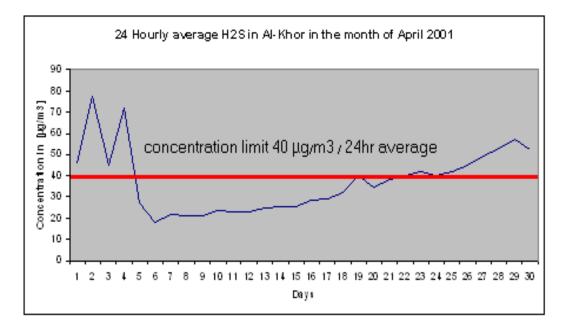


(Fig 5-23): 24 hourly averages concentration of PM10 in Al-Khor June, 2001

(Fig 5-24): Daily highest hourly concentration for O3 in Al-Khor April, 2001

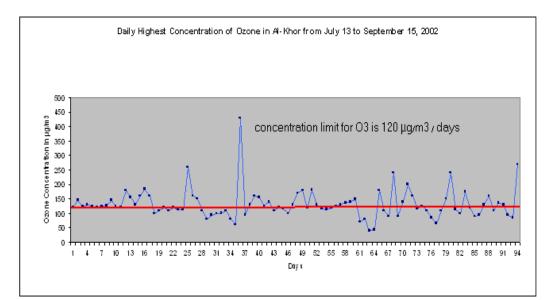


(Fig 5-25): Hourly average H<sub>2</sub>S (mercaptans) in Al-Khor area April, 2001

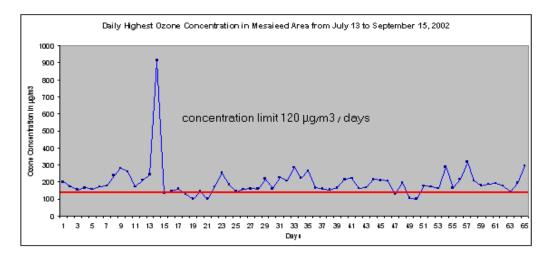


Furthermore, the Supreme Council of Environment in 2002 indicated severe increase in ozone gas level in Al-Khor (Fig 5-24) where the standards level of ozone was violated several times. Moveable air quality stations were mobilized to maintain air quality control. Two graphs from SCENR report are below.

**(Fig 5-26):** Daily Highest Concentration for O<sub>3</sub> in Al-Khor area from the period July 13 to September 15, 2002 .The Standard of the Council in hourly basis



(Fig 5-27): Daily Highest Ozone Concentration in Mesaieed Area from July 13 to September 15, 2002. The Standard of the Council in hourly basis



This comprehensive discussion of the data and calculated statistics in relation to the known issues over air-quality monitoring in Qatar in comparison to actual data collected from the industries and so many reports from authority, it is necessary that a national plan for controlling of air pollution is very much needed and the impact of the transboundery pollutants regulated through regional agreements and protocols. This needs to be developed to sustain the industrial prosperity, utilize the new technology and protect the people of Qatar from these development threats. It is also rewarding to see some of my new ideas in print, achieving the goal to serve the society and the global environment.

#### Chapter 6

#### 6.1 Conclusions

This thesis has analyzed the air quality in the State of Qatar using two independent data sets. The differences between these data sets have led to a major program of monitoring since the completion of data collection for this thesis. The major outcomes from this study of air quality in Qatar are given here.

- A questionnaire-based survey of Qatar industries early in this research, from 2000-2002, revealed a significant atmospheric pollution problem, with high levels of all pollutants in emissions from industry. Much of this pollution due to flaring.
- Subsequently, monitoring stations of air pollutants, stationed in various parts of the country, indicate that registered levels during 2003, 2004, 2005 for CO, NO<sub>2</sub> and SO<sub>2</sub> contaminants are within Qatari and European Standards. PM10 however was higher than standard in all three stations and measured daily O<sub>3</sub> levels were sometimes higher than reference. This requires further investigation.
- 3. Data show that the two most contributing factors to the warm temperature in summer time in Qatar, especially at night, are perceived to be the high levels of water vapor (relative humidity) and low winds speeds.

The results & reports show that air monitoring in Qatar requires development into a comprehensive network and better regulation of the industry. Reports should be made available for the concerned including the public throughout the country. For example, flaring and fugitive emissions can be brought under control however through smart planning and successful revamping of projects.

#### 6.2 Recommendations

- While the pace with which the gas production and processing has been developing is no doubt very fast this has impacted our environment. More time should be taken and better planning implemented in future developments projects.
- Air monitoring in Qatar requires development into a comprehensive network and better regulation of the industry.
- The state of Qatar needs to capitalize more on the international mechanisms (i.e., Kyoto protocol) the acquisition of contemporary technology for attaining cleaner processing operations, namely under the clean development mechanism (CDM) and Technology Transfer (TT).
- It is important to start the development of a country CO<sub>2</sub> Master plan, in order to reach an integrated understanding of the current and future CO<sub>2</sub> situation in Qatar, CO<sub>2</sub> network analysis (source, outlet, technology assessment & infrastructure / network scenarios) must be developed and the potential for CO<sub>2</sub> reduction from existing assets by e.g. by efficiency improvements is essential. Assessment of the latest CO<sub>2</sub> technologies are added (e.g. cement industry as source or CO<sub>2</sub> mineralization as outlet) and their potential use for Qatar.
- The use of electricity and water in the State should be better regulated.
- Flare mitigation projects should be looked into and encouraged for all public and private industries in the State.
- Waste gas scrubbers need to be installed for all public and private industries in the State.
- Monitoring stations for seawater temperature, level, salinity, etc., need to be installed.
- Forestry should be encouraged.
- Better lines of communications among the concerned parties, i.e., ministry of Health, Industry, the Supreme Council, etc., on emissions monitoring and control need to be installed.

- Regulatory functions on controlling all emissions from operating industries in the country need to be activated.
- Make sure that all incoming industries are of the emission free type technologies.
- Public transportation / car pooling should be encouraged.
- Gas phase kinetics research need to be conducted on these emissions to determine their ultimate impact on radioactive forcing and consequently climate change issues.
- The higher levels of CO, H<sub>2</sub>S & NO<sub>2</sub> at all industrial areas including Halul, Ras Lafan, MIC and Dukhan need to be investigated.
- The higher than reference levels of PM10 & Ozone in all stations need to be monitored and investigated immediately. Control measures to be installed in order to protect the cities of Al-Khor and the capital Doha.
- Major air pollutants shall be considered in any air quality management programs for the Ras Laffan area.

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#### **APPENDIX-1**

#### 1.1 Questionnaire for Industries & Plants

Emissions of Criteria Pollutants Due to Fuel Combustion (Data required for 1998, 1999, 2000, 2001 and 2002)

2) 3)	Facility Name Address Contact Person Address, Telephone etc
5)	Total Electric Power Generation CapMW
6)	Number of Units and capacities
7)	Number of Gas Fired Turbines, Generators, Gas Fired boilers and their heat input capacities (MW)
8)	Number of Stacks, Description, height (m), diameter (m) exit temperature (°C) and exit velocity. (m/s)
9)	Type of emergency liquid fuel used (Crude, diesel, fuel oil etc.)
10	)Total amount of gas fuel usedm <sup>3</sup> /yr.
11	)Total amount of liquid fuel usedm <sup>3</sup> /yr.
12	) Chemical Characteristics of natural gas used (%CH <sub>4</sub> , %C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> , C <sub>4</sub> , etc. N <sub>2</sub> S, CO <sub>2</sub> etc.)
13	Average molecular weight of natural gas, %C content, density and net heating value
14	Chemical composition of liquid fuel used. (%C content, S, N, density, Net heat value)
15	Air Pollution Control technology used and efficiency
16	Boilers Firing Angles (Vertical, Tangential etc.)

17) Available source emission estimates for  $CO_2$ ,  $CH_4$ ,  $N_2O$ ,  $NO_x$ , CO, NMHC.....

Parameter	Unit	Averaging period	Concentration Limit	Criteria					
	un (m. <sup>3</sup>	24 hr	365	A					
Sulfur Dioxide	$\mu g / m^3$	Annual	80	В					
Suspended Particulate Inhalable	$\mu g / m^3$	24 hr	150	А					
particles < 10 microns)	μg / m	Annual	50	В					
Nitrogen		1 hr	400	D					
Oxides, as	$\mu g / m^{3}$	24 hr	150	A					
NO <sub>2</sub>		Annual	100	В					
Photochemical	$\mu g / m^{3}$	1hr	235	С					
Oxidants, as $O_3$	μg i m	8 hr	120	G					
Carbon	$\mu g/m^3$	1 hr	40	D					
Monoxide	$\mu g / m$	8 hr	10	E					
B. Arithmetic me calendar year.	laily meas ean of all o	Key urements taken durir daily measurements asurements taken du	taken during the p	period of one					
D. 99.7% of al	I days co	ontaining 1 hour me	easurements at o						
standard during the period of one calendar year.E. 99.98% of all hourly measurements taken during the period of one year.F. 99.8 % of all 8 hour measurements taken during the period of one calendar year.G. 98% of all daily maximum 8 hour averages during one year.									

#### 1.2 Qatar Air Quality Emission Standard

## 1.3 Statistics of Natural Gas Flaring Disaggregated by Oil & Gas field and Operating Venture in Qatar (1998 - 2002)

FACILITY	Year	Flare (10 <sup>6</sup> m <sup>3</sup> ) NORTH FI LEAN GAS		Flare (10 <sup>6</sup> m <sup>3</sup> ) OFFSHOR STRIPPED	Yearly Total 10 <sup>6</sup> m <sup>3</sup>	
				GAS	1	
	1998	558.6	0.4	2.6	2.39	561.2
MES	1999	691.9	0.4	76.3	2.39	768.2
IVIL S	2000	453	0.4	150.2	2.39	603.2
	2001	174.9	0.4	10.2	2.39	185.1
	2002					384.4

		DU-GEN	ERAL	ARAB-D		
	1998	330.5	0.77	368.7	0.75	669.2
QPD	1999	469.3	0.77	195.2	0.75	664.5
	2000	535.3	0.77	168.6	0.75	643.9
	2001	265.5	0.77	34.6	0.75	300.1
	2002					261.3

		PS-2, 3		PS-4			
	1998	2164.5	2.39	103.8	0.4	2268.3	
QPO	1999	1013.5	2.39	195.8	0.4	1209.2	
	2000	946.5	2.39	99	0.4	1045.5	
	2001	1034.4	2.39	60.8	0.4	1095.2	
	2002					704.8	

	1998	ONSHO	RE	OFFSHOR	OFFSHORE			
RAG	1998	0	0	0	0	0		
hAG	1999	1167	0.45	4.4	3.8	1171.4		
	2000	343	2	5.8	0.48	348.8		
	2001	220.6	0 (SW)	8.5	0.46	243.8		
		14.7	11.4 (SO)					
	2002							

		ONSHORE		OFFSHORE		
	1998	0	0	0	0	0
QPO	1999	93.5	0.16	41.2	0.4	134.7
	2000	419.5	0.16	19.7	0.4	439.2
	2001	435.3	0.25	7.5	0.42	442.8
	2002					469.7

Table () Cont'd

FACILITY OIL FIELD	Year	Flare (10 <sup>6</sup> m <sup>3</sup> )	H₂S (%Vol)	Yearly Total 10 <sup>6</sup> m <sup>3</sup>
	1998	4.35	4.5	4.35
RAY	1999	69.7	3.4	69.7
<b>NAT</b>	2000	9.89	3.4	9.9
	2001	10.62	3.5	10.62
	1			
	1998	1079	0.8	1079
SHA	1999	1522	0.18	1522
ЭПА	2000	1480	0.18	1480
	2001	1809.4	0.3	1808.4
[				
	1998	38.3	N/A	38.3
КНА	1999	53.0	1.6	53.0
	2000	48.0	0	48.0
	2001	31.0	0	31.0
	2002	47.0	0	47.0
	1998	1798	1.0	1798
EES	1999	1398	1.0	1398
	2000	1671	1.77	1671
	2001	1438	1.35	1438

SW: Sweet Gas; SO: Sour Gas; N/A: Not Available

	MESAIEE	D FLARING	ì	OXY FLA	RING		MAERSK	FLARING		TOTALFI	NAELF	
Paramete r	Specific EF Estimate s (tonnes)	Default Estimate s (tonnes)	Uncertaint y (%)									
CO <sub>2</sub>	0.337 (×10 <sup>6</sup> )	0.488 (×10 <sup>6</sup> )	+ 54 %	3.335 (×10 <sup>6</sup> )	3.755 (×10 <sup>6</sup> )	+13 %	5.794 (×10 <sup>6</sup> )	4.722 (×10 <sup>6</sup> )	- 19%	91.110	68,955	- 25%
CH4	6.090	6484	+6%	48,554	50,364	+4%	64580	63,328	+2%	847	925	9%
NMHC	266	2,779	+945%	12,948	21,585	+67%	24,420	27,140	+11%	804	396	+53%
N2O	11.0	15.0	+36%	109	117	+7%	150	147	+2%	2.74	2.0	+28%
SO <sub>2</sub>	1.285	2,395	+86%	19,422	50,348	+160%	9,950	15,065	+50%	4.0	0.0	σσ
H <sub>2</sub> S	36	NA		543	NA		278	NA		0.10	NA	
NOx	205	278	+36%	2.020	2,158	+7%	2,781	2,714	-2%	51.9	40	-23%
со	1187	1,612	+36%	11,718	12,519	+7%	16,101	15,741	-2%	300	230	-24%
Density (kg/m <sup>3</sup> )	0.728	1.0	+37%	0.938	1.0	+7%	1.024	1.0	-2%	1.31	1.0	-24%
Volume Mm <sup>3</sup>	185.1	185.1		1,438	1,438		1,809	1,809		** 26.4	26.4	

1.4 Estimates of Greenhouse Gas and Criteria Pollutant Emissions due to Operational Flaring from Mesaieed, Oxy, MAERSK AND TOTALFINAELF using Country Specific Emission Factors and Default Coefficients (2001)<sup>\*</sup>

(Default Factors (t/t): CO<sub>2</sub> =2.61; CO =0.0087; NOx=0.0015; N<sub>2</sub>O=0.000081; CH<sub>4</sub> =0.0035; VOC = 0.015; USEPA, Oil Industry E&P Forum);

• \*\* weighted energy content = 1711.24 TJ

	1995	1996	1997	1998	1999	2000
Hydrogen	59.21	59.21	59.21	61.34	58.72	57.58
Nitrogen	0.53	0.53	0.53	0.38	0.72	0.5
Carbon dioxide	0.08	0.08	0.08	0.06	0.09	0.1
Methane	9.86	9.86	9.86	8.29	10.48	10.48
Ethane	7.82	7.82	7.82	7.61	7.75	8.11
Propane	17.55	17.55	17.55	17.63	16.74	18.27
Iso-Butane	1.57	1.57	1.57	1.46	1.46	1.41
Normal-Butane	2.56	2.56	2.56	2.39	2.81	2.48
Iso-Pentane	0.32	0.32	0.32	0.35	0.3	0.31
Normal-Pentane	0.25	0.25	0.25	0.21	0.32	0.22
C6 Hydrocarbons	0.23	0.23	0.23	0.25	0.23	0.2
Total Olefins	0.03	0.03	0.03	0.02	0.05	0.02
Molecular Weight	16.06	16.06	16.06	15.62	16.17	16.39
Density (km/nm <sup>3</sup> )	0.7165	0.7165	0.7165	0.6969	0.7114	0.7312
Net Heating Value	9121	9121	9121	8947	9139	9272
(k cal/nm <sup>3</sup> )						

#### 1.5 Refinery Gas Composition (Volume %)

#### 1.6 Industrial Output of Refined Products in BBLS

Year / Product	1995	1996	1997	1998	1999	2000	
LPG	866,015	971,596	753,169	851,015	716,170	662,260`	
90R	2,960,392	3,445,968	2,757,190	2,991,640	2,936,136	2,395,521	
97R	1,480,364	1,598,701	1,586,374	2,075,423	1,870,304	1,734,609	
JET A-1	3,216,888	3,664,512	3,317,665	3,510,069	3,406,884	3,022,480	
LGO	5,145,691	5,235,447	4,759,027	5,110,187	5,065,139	4,591,007	
FUEL OIL	6,063,836	6,808,583	6,232,387	6,637,265	6,860,330	6,348,838	

## 1.7 Country Specific CO<sub>2</sub>, CH<sub>4</sub>, NMVOC, SO<sub>2</sub> and H<sub>2</sub>S Emissions Factors from Combustion of Stripped Associated Natural Gas (G-1) Cement Manufacture Industry

		Sweet				
Parameter	Mole %	MW		C %		Mole Fraction
$\begin{array}{c} CH_4\\ C_2H_6\\ C_3H_8\\ C_4H_{10} \end{array}$	75.33 12.44 2.81 0.39	16 30 44 58		56.0 10.0 2.30 0.32		12.05 3.73 1.23 0.23
H <sub>2</sub> S CO <sub>2</sub> N <sub>2</sub> Total	1.25 7.3 0.44 100	34 44 28 		 2.0  70		0.43 3.21 0.12 
NHV (MJ/m <sup>3</sup> )		I	36.17			
Computed Av. MW			21.0			
Computed Density (Kg/ m <sup>3</sup> ) (20°C, IP)	0.874					
Specific Combustion	Emission Factors *		Country Specif	ic Emi	ssion Fa	ctors
EFCO <sub>2</sub> (Kg CO <sub>2</sub> / m <sup>3</sup> )	2.23		Lost Klin Dust Factor (CF)			1.05
EFCO <sub>2</sub> (tC/TJ)	16.8		%CaO in Clinko	ər	0.635	
EFSO <sub>2</sub> (g/ m <sup>3</sup> ) EFSO <sub>2</sub> (t/TJ)	20.5 0.57		EF Process (tC t Clinker)	:O <sub>2</sub> /	0.524	.#
Specific Combustion	Emission Factors **		IPCC Combustion Emission Factors <sup>@</sup>			
EF CH <sub>4</sub> (g/ m <sup>3</sup> ) EF CH <sub>4</sub> (t/TJ) EF NMHC (g/ m <sup>3</sup> )	3.3 0.09 0.68		EF CH4 (t/TJ) EF NOx (t/TJ)		0.0011 1.11	
EF NMHC (t/TJ) EF $H_2S$ (g/ m <sup>3</sup> ) EF $H_2S$ (Kg/TJ)	0.019 0.055 1.5		EFCO (t/TJ)		0.083	

\* Assuming Combustion Efficiency = 0.995

$$= \frac{CO_2}{CaO} \times CaO \times CF$$
$$= \frac{44}{56} \times 0.635 \times 1.05 = 0.524$$

- \*\* Total CH<sub>4</sub>, NMHC ratios = 0.75, 0.156
  - @ IPPC (1966)

#

		Activity										
	Cement		Klin Fuel Consumption		Electricity C	Consumption	Electricity	Klin Combustion				
	(Tonne)		N.G. (Mm <sup>3</sup> )	Energy** Eq (TJ)	KWh $\times$ 10 <sup>6</sup>	Energy Eq. (TJ) <sup>*</sup>	Energy (%)	(%)				
1997	513481	320053	136.3	4930	64.19	231.0	4.5	95.5				
1998	857105	841195	142.6	5158	103.89	374.0	6.7	93.3				
1999	958539	838877	158.5	5733	115.49	415.8	6.7	93.3				
2000	1029187	905443	163.2	5903	123.03	442.9	7.0	93				
2001	1209403	952248	163.21	5903	134.92	485.7	7.6	92.4				

1.8 Statistics on Energy Consumption and Clinker and Cement production in Qatar During (1998 – 2001)

\* 11kWh = 3600 KJ

\*\* NHV for natural gas = 36.17 MJ/m  $^3$ 

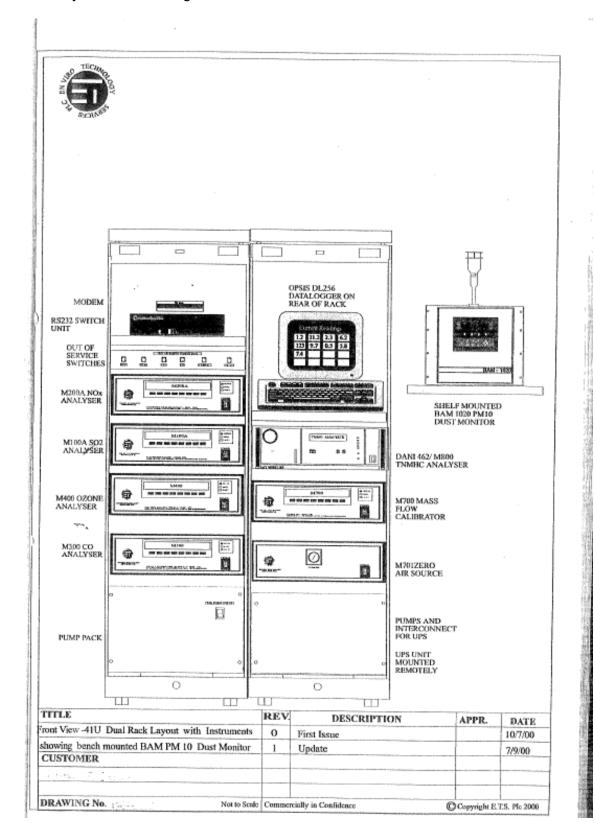
# 1.9 Country Specific CO<sub>2</sub>, CH<sub>4</sub>, NMVOC, SO<sub>2</sub> and H<sub>2</sub>S Emissions Factors from Combustion of NF Sweet and Sour Natural Gas by Power and Water Desalination Plants.

Deverseter		Sweet		Sour			
Parameter	Mole % C % Mole Fraction		Mole %	C %	Mole Fraction		
$\begin{array}{c} CH_4 \\ C_2H_6 \\ C_3H_8 \\ C_4H_{10} \end{array}$	91 3.2 0.83 	68.3 2.56 0.68 	14.56 0.96 0.38 	77.2 12.01 2.6 0.4	57.9 9.61 2.13 0.33	12.4 3.60 1.14 0.23	
$\begin{array}{l} H_2S\\ CO_2\\ N_2\\ Total \end{array}$	4 ppm 1.45 4.2 100	 0.40  71.94	 0.64 1.18 	1.0 6.5 0.25 100	0.94 (S) 1.77  71.74	0.34 2.86 0.07 	
NHV (MJ/m <sup>3</sup> )	33.2	I	I	36.4			
Computed Av. MW	17.7			20.64			
Computed Density (Kg/ m <sup>3</sup> ) (20°C, IP)	0.74			0.859			
Combustion Emission	ns						
EFCO <sub>2</sub> (Kg CO <sub>2</sub> / m <sup>3</sup> )	1.94			2.25			
EFCO <sub>2</sub> (tC/TJ)	15.95			16.85			
$EFSO_2 (g/m^3)$	0.0059			16.0			
EFSO <sub>2</sub> (t/TJ)	0.00018			0.44			
Incomplete Combustion Emissions							
$\begin{array}{l} EF\;CH_4\;(g/\;m^{\;3})\\ EF\;CH_4\;(t/TJ)\\ EF\;NMHC\;(g/\;m^{\;3}) \end{array}$	3.4 0.10 0.15			3.32 0.092 0.645			
EF NMHC (t/TJ) EF H <sub>2</sub> S (g/ m <sup><math>3</math></sup> ) EF H <sub>2</sub> S (Kg/TJ)	0.0045 15 × 10 <sup>-6</sup> 0.45 × 10 <sup>-3</sup>			0.018 0.0431 1.2			

Year	Private Passenger Cars	Private Trucks	Public Transport Vehicles	Taxis	Heavy Duty Mobile Equip.	Motor Bikes	90R Gasoline (Mm <sup>3</sup> )	97R Gasoline (Mm <sup>3</sup> )
1991	8260	6389	3	10	119	77		
1992	10835	4581	1	2	234	19		
1993	9781	4239	164	11	401	73		
1994	7227	3996	299	113	368	42		
1995	8557	3766	166	70	360	93	266.6	238.5
1996	10454	4026	120		422	36	257.8	256.0
1997	14606	4900	214	6	656	166	266.3	279.4
1998	14962	5541	94		632	152	270.8	298.3
1999	12996	3961			337	174	292.8	291.3
2000	14772	3991	1	15	388	156	311.4	300.6
2001	17917	5048	5	28	633	101		
TOTAL	130,367	50,438	1,067	255	4,550	1,089		
Fuel	Gasoline	Gasoline/ Diesel	Gasoline/ Diesel	Gasoline	Diesel	Gasoline		

1.10 Statistics of Road Transport Vehicles [Registration] and Gasoline Sales in the State of Qatar (1991 - 2001).

\* Sulfur content of 90R and 97R Gasoline are respectively 300 and 100 ppm (w/w)



1.11 Layout of monitoring instruments with dual rack

1.12 WHO Expert Report on Air pollution in Ras Laffan City, Qatar.

VINIO JEALTH MICANZATION Regional Utilics for the Eastern Meditorraness DREAMSATION MUMBALE BELA SANTE Derean righted do la Miditorranée originale

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EM/PEH/547/E/R/02.02/21 Distribution: Restricted

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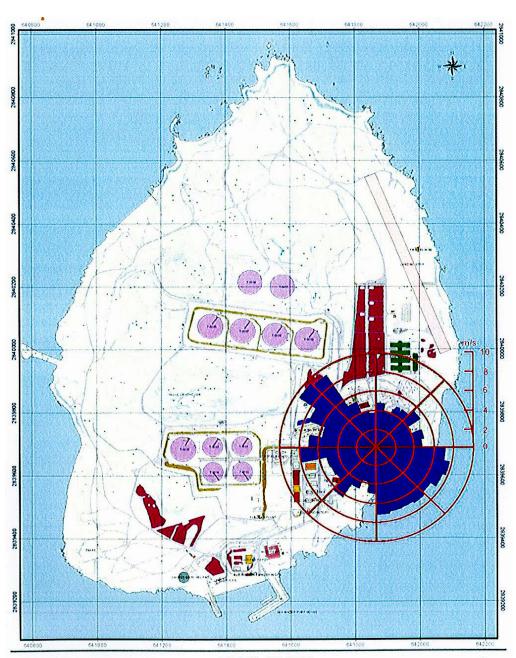
Assignment report on

# AIR POLLUTION IN RAS LAFAN CITY, QATAR

28 December 2001--7 January 2002

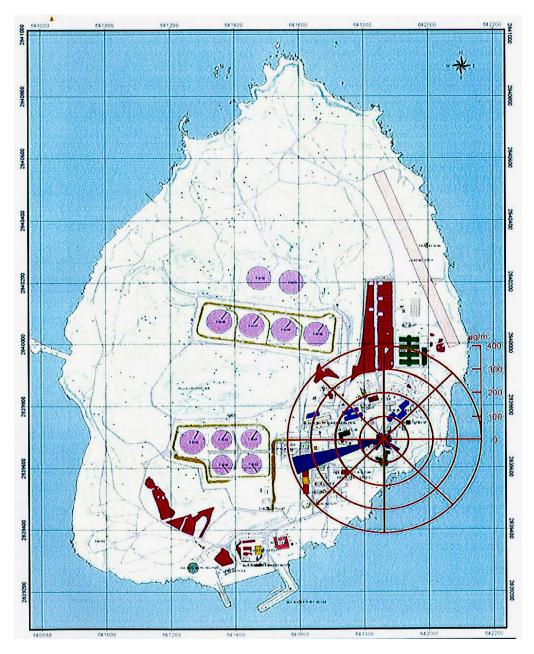
Dr Mahmoud M. Nasralia WHO Consultant

# <u>Appendix – 2</u>



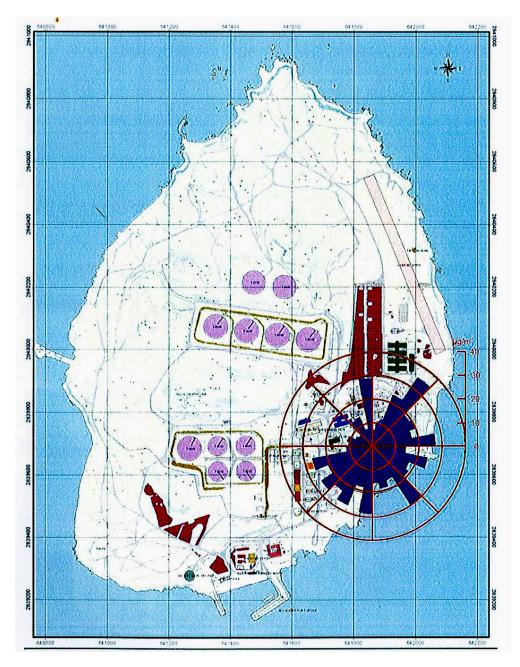
(Fig 2-1): Wind Rose graph for wind speed in Halul  $-1^{st}$  March to  $31^{st}$  May 2004

Halul Island



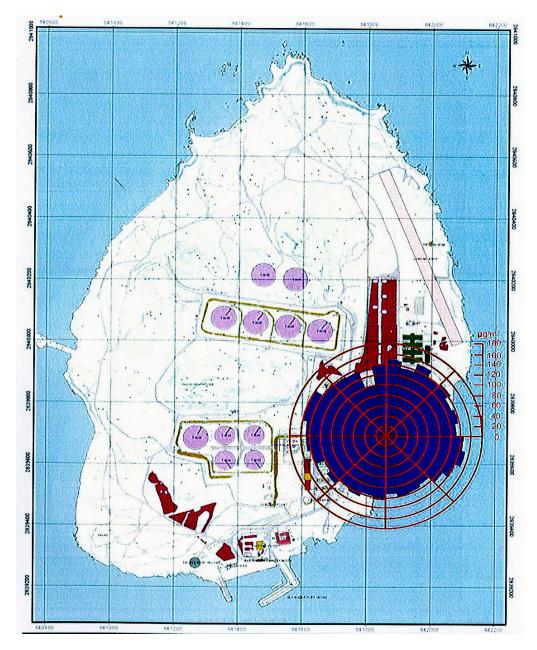
(Fig 2-2): Wind Rose graph for  $SO_2$  in Halul – 1<sup>st</sup> March to 31<sup>st</sup> May 2004

Halul Island



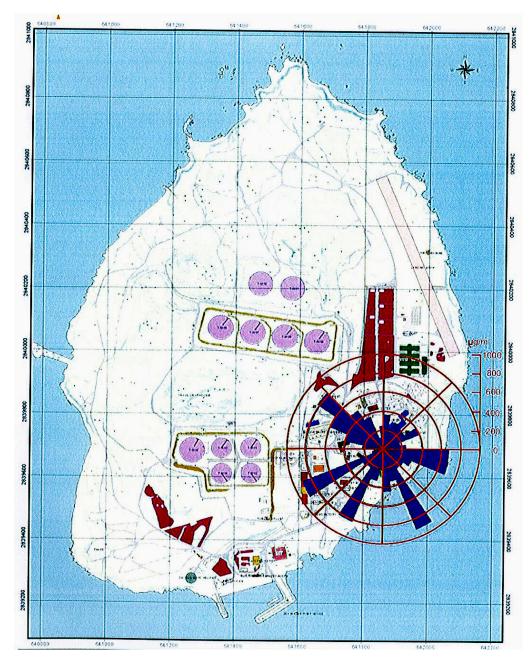
(Fig 2-3): Wind Rose graph for  $NO_2$  in Halul – 1<sup>st</sup> March to 31<sup>st</sup> May 2004

Halul Island



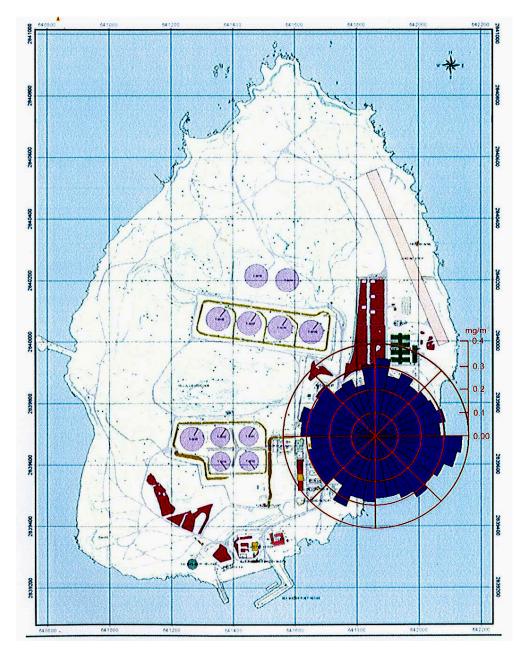
(Fig 2-4): Wind Rose graph for  $O_3$  in Halul – 1<sup>st</sup> March to 31<sup>st</sup> May 2004

Halul Island



(Fig 2-5): Wind Rose graph for PM10 in Halul –  $1^{st}$  March to  $31^{st}$  May 2004

Halul Island



(Fig 2-6): Wind Rose graph for CO in Halul –  $1^{st}$  March to  $31^{st}$  May 2004

Halul Island

**Table 2.1** Datasheet for the whole 2003 months in three sites; Dukhan, Halul and Mesaieed. All concentrations are measured in  $[\mu g/m^3]$  except CO in  $[mg/m^3]$ 

	2005													
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave/Yr
	Dukhan	11.6	10.29	9.11	8.22	7.91	10.31	7.87	5.11	7.36	9.33	11.87	13.89	9.40583333
NO2	Halul	3.64	2.78	4.58	6.56	5.51	5.53	2.28	3.32	3.02	3.69	2.71	3.37	3.91583333
	Mesaieed	20.11	15.06	11.95	11.64	16.9	17.05	12.6	10.05	15.65	16.71	18.97	17.7	15.3658333
	Dukhan	21.28	25.29	27.1	30.2	32.2	26	33.9	27.92	39	20.28	16.9	12.18	26.0208333
SO2	Halul	28.95	16.81	21.93	18.8	16.2	36.59	22.6	18.31	23.9	33.6	42.4	12.7	15.8215
	Mesaieed	14.64	23.1	12	15.4	17.8	19.5	16.2	36.61	36.4	78	56.4	12.5	28.2125
	Dukhan	0.596	0.569	0.67	0.546	0.58	0.76	0.98	0.6	0.78	0.48	1.38	0.927	0.739
CO	Halul	0.146	0.06	0.08	0.24	0.41	0.32	0.515	0.26	0.4	0.202	0.13	0.17	0.24441667
	Mesaieed	0.131	0.13	0.1	0.12	0.15	0.12	0.13	0.128	0.3	0.3	0.39	0.19	0.18241667
	Dukhan	89.57	202	149	115	142	113	81.8	112.5	92.6	125	122	103.6	120.6725
PM10	Halul	37.54	24.6	113.5	32.3	24.7	31.67	13.81	64.5	31.32	185	81.3	155	66.27
	Mesaieed	68.9	131	172	148	257	177	164	177.3	115	106	91.3	92.5	141.666667
	Dukhan	90.75	93.75	70.9	65.9	70.5	78.5	91.1	64.47	85.3	92.16	91.6	79.86	81.2325
O3	Halul	71.84	87.2	89.93	97.2	102	107.9	152.9	94.6	114	111	96.4	89.4	101.1975
R	Mesaieed	69.72	79.6	89	87.4	84.1	88.6	87.2	63.74	79.3	74.9	72.1	67.1	78.5633333
	Dukhan	3.41	3.96	4.16	3.85	3.2	3.26	3.18	2.95	2.8	2.87	3.22	3.22	3.34
Win/Spd	Halul	4.91	5.82	5.5	5.25	4.87	5.07	4.33	3.38	3.39	4.13	5.64	5.12	4.78416667
	Mesaieed	3.6	4.54	4.25	4.27	3.85	4.07	3.98	3.52	3.22	3.02	3.44	3.49	3.77083333

# <mark>2003</mark>

**Table 2.2** Datasheet for the whole 2004 months in three sites; Dukhan, Halul and Mesaieed. All concentrations are measured in  $[\mu g/m^3]$  except CO in  $[mg/m^3]$ 

	<mark></mark>													
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave/Yr
	Dukhan	10.54	11.23	15.30	9.74	11.83	8.49	10.49	7.41	5.45	7.73	7.90	13.16	9.94
NO2	Halul	4.08	4.07	4.80	5.84	4.56	6.79	5.04	4.85	3.97	7.50	5.62	5.38	5.12
	Mesaieed	14.59	13.51	20.05	12.88	15.16	15.45	8.37	9.04	10.77	16.65	16.61	22.89	14.66
	Dukhan	9.89	15.27	23.12	8.89	21.62	20.68	35.06	23.99	19.46	20.03	17.16	14.56	19.15
SO2	Halul	8.98	9.21	20.56	24.24	18.98	32.55	123.6	264.7	236.1	-	-	-	82.11
	Mesaieed	15.80	19.76	14.49	28	17.71	16.42	42.99	25.85	99.71	313.5	21.51	19.52	52.94
	Dukhan	0.12	0.25	0.46	0.34	0.28	0.20	0.98	0.41	0.81	0.65	0.08	0.22	0.40
CO	Halul	0.32	0.28	0.22	0.15	0.20	0.17	0.23	0.27	-	0.16	0.0095	0.037	0.19
	Mesaieed	0.34	0.35	0.43	0.74	0.67	0.54	0.57	0.61	0.61	1.08	0.57	0.66	0.60
	Dukhan	78.97	92.15	89.48	92.01	112.3	109.5	118.2	115.7	113.5	106.6	77.5	53.6	96.6
PM10	Halul	51.72	66.11	67.41	76.77	95.62	114.3	72.5	78.4	98.7	81.8	38.05	12.82	71.21
	Mesaieed	91.83	73.89	98.52	96.25	152.63	89.83	169.58	134.9	139.3	135.7	108.98	82.6	114.5
	Dukhan	83.2	95.2	114	94	96.7	105.5	152.3	132.4	115.6	112.8	79.4	75.13	104.7
O3	Halul	88.67	109.6	113.9	100.3	106.8	110	77.7	110.6	87.8	93.6	82.4	86.1	97.33
<b>-</b>	Mesaieed	70.98	80.60	86.16	88.59	86.91	90.57	113.4	91.63	79.85	82.39	64.15	56.60	82.65
	Dukhan	3.3	4.04	3.05	3.51	3.63	2.83	2.96	3.08	2.84	2.42	3.34	3.79	3.24
Win/Spd	Halul	5.5	5.1	4.6	4.6	4.8	4.2	3.5	3.5	3.3	3.2	4.1	4.4	4.27
	Mesaieed	3.73	4.10	3.72	3.99	4.24	3.86	3.44	3.50	3.29	2.72	3.16	3.47	3.60

# <mark>2004</mark>

**Table 2.3** Datasheet for the whole 2005 months in three sites; Dukhan, Mesaieed. All concentrations are measured in  $[\mu g/m^3]$  except CO in  $[mg/m^3]$ . Readings at Halul station are not available in the table.

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave/Yr
	Dukhan	-	7.26	10.67	-	10.66	9.3	6.13	7.34	8	5.59	9.25	13.57	8.777
NO2	Halul	-	-	-	-	-	-	-	-	-	-	-	- 1	-
	Mesaieed	-	-	8.03		10.46	8.97	9.65	7.01	11.38	10.66	9.93	13.35	9.937778
	Dukhan	-	16.15	23.3		27.36	25.98	20.26	19.33	17.12	17.99	17.45	28.12	21.306
SO2	Halul	-	-	-	-	-	-	-	-	-		-	-	-
	Mesaieed	-	-	6.21	-	-	12.56	13.09	-	-	-	38.43	47.14	23.486
_	Dukhan	-	0.46	0.5	-	0.67	0.73	0.37	0.5	0.39	0.27	0.65	0.73	0.527
CO	Halul	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mesaieed	-	-	0.44	-	0.42	0.41	0.25	0.57	0.29	0.61	0.64	0.94	0.507778
	Dukhan	72.97	65.26	66.76	106.3	103.4	163.2	149.2	128.6	106.5	81.81	73.74	78.88	99.71833
PM10	Halul		-	-			-			_			-	-
	Mesaieed	89.23	77.79	99.7	109.3	116	143.3	150.5	129.1	122.88	85.9	72.3	81.48	106.4567
	Dukhan	-	73.83	78.2	-	105.8	117.75	96.44	98.15	97.36	100.22	81.44	91.5	94.069
O3	Halul	-	-	-	-	-	-	-	-	-	-	-	-	-
<u> </u>	Mesaieed	-	-	92.38	-	87.17	92.86	57.45	-	97.59	67.55	78.51	113.5	85.87

# <mark>2005</mark>

Fig (2-7): Yearly average of NO<sub>2</sub> registered during the years 2003, 2004 and 2005 for various sites.

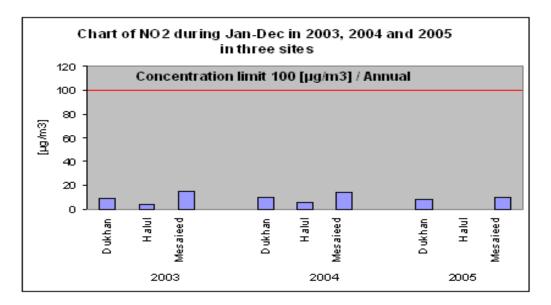
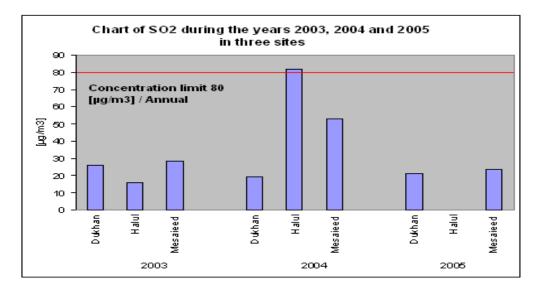


Fig (2-8): Yearly average of  $SO_2$  registered during the years 2003, 2004 and 2005 for various sites.



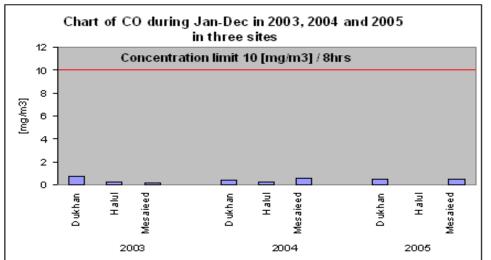


Fig (2-9): Yearly average of CO registered during the years 2003, 2004 and 2005 for various sites.

Fig (2-10): Yearly average of PM10 registered during the years 2003, 2004 and 2005 for various sites.

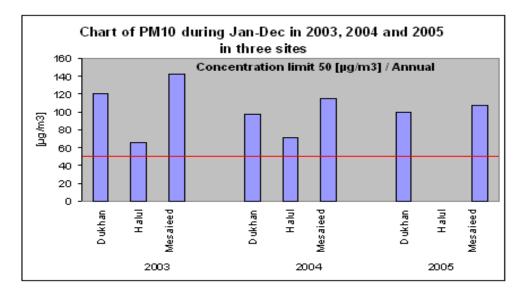
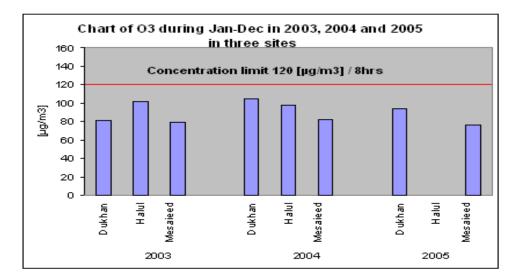
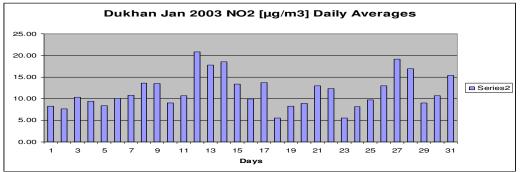


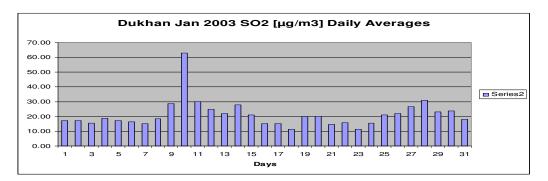
Fig (2-11): Yearly average of  $O_3$  registered during the years 2003, 2004 and 2005 for various sites.

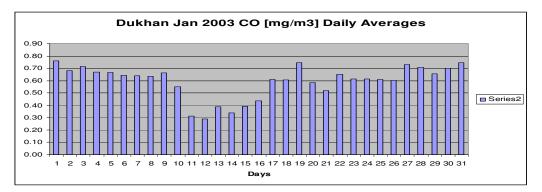


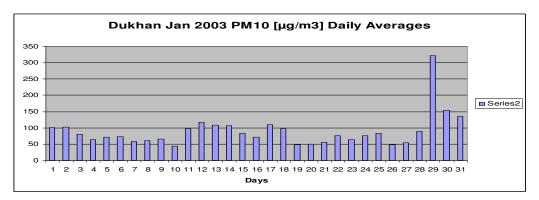
# 2.12 DUKHAN GRAPHS (24-Hour Averages of Data) / 2003

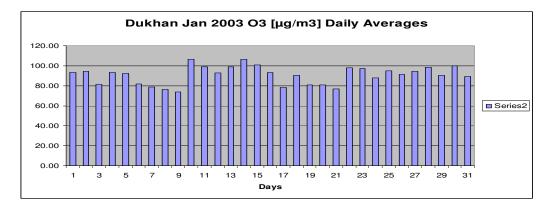
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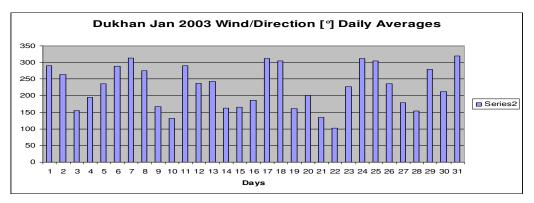


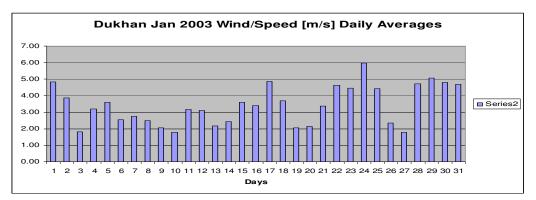




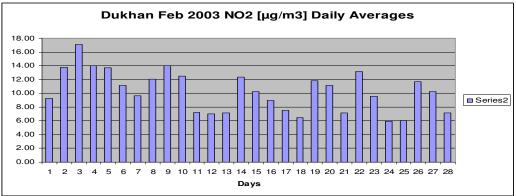


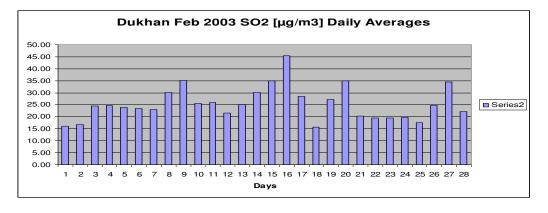


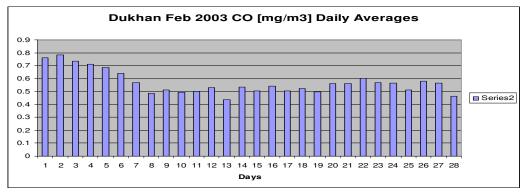


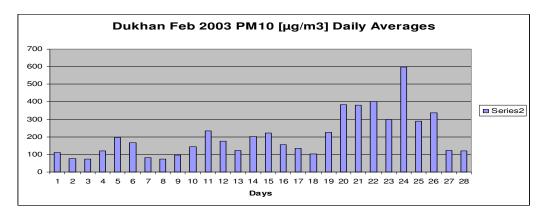


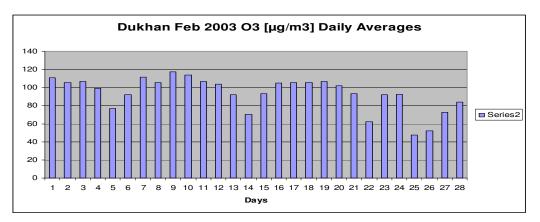
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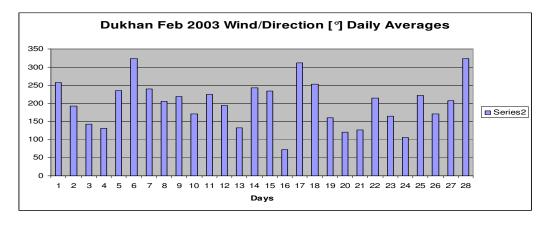


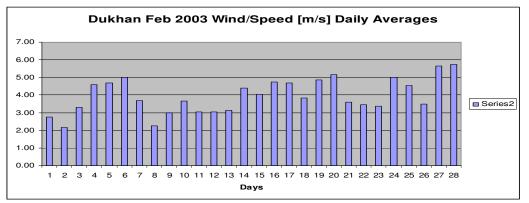




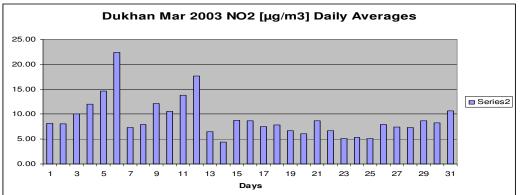


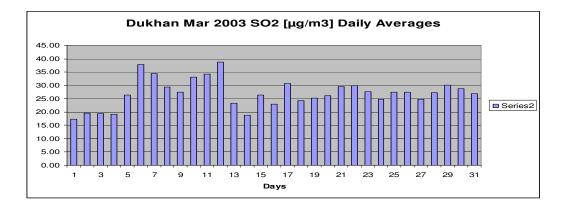


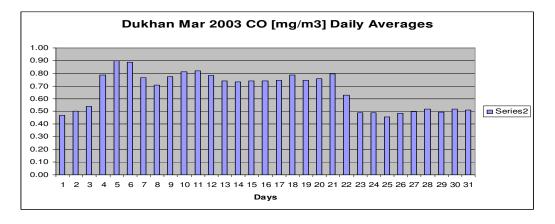


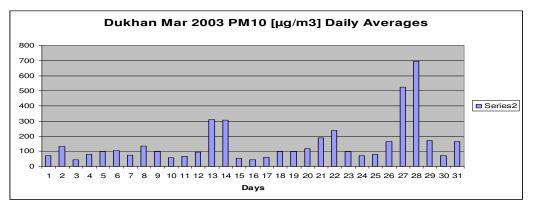


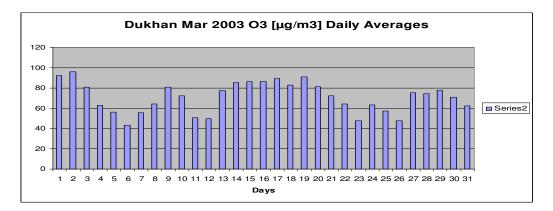
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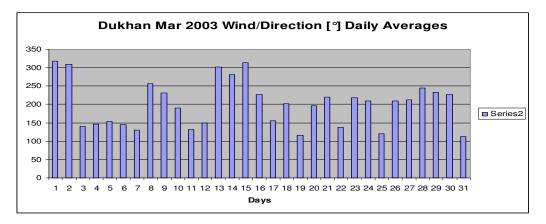


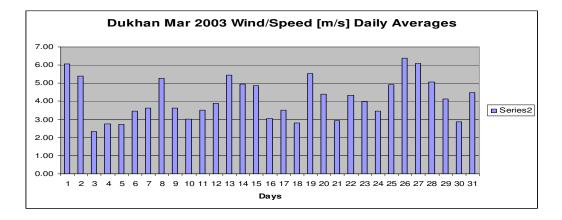




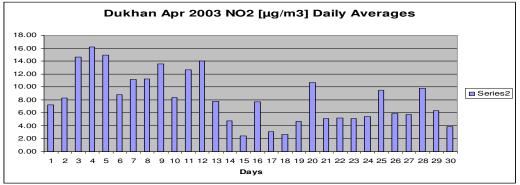


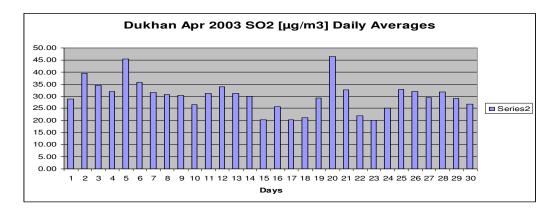


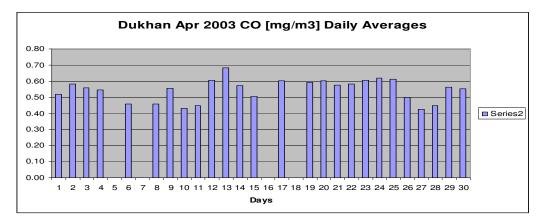


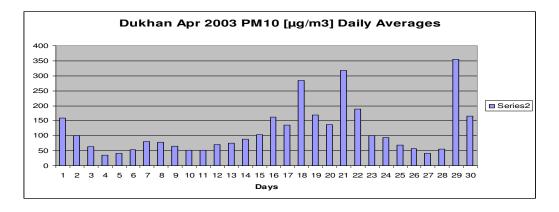


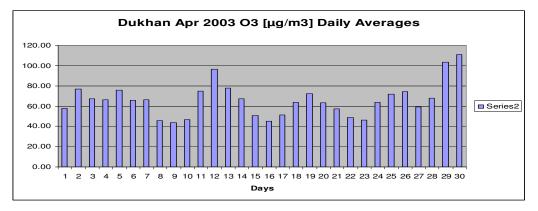
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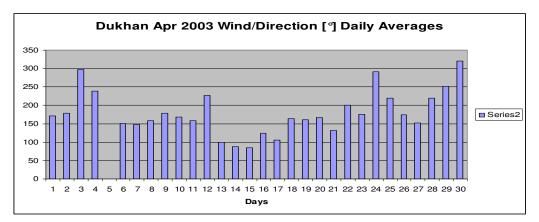


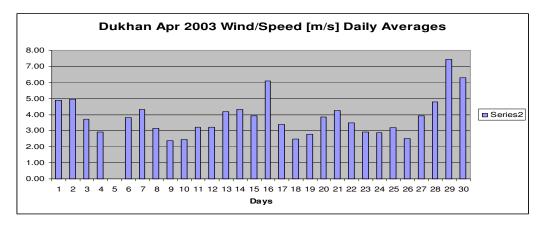




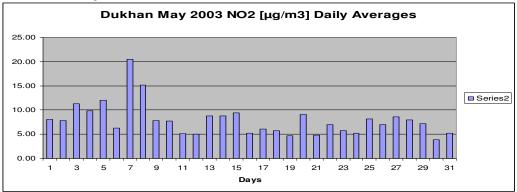


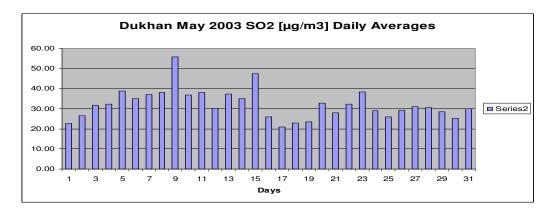


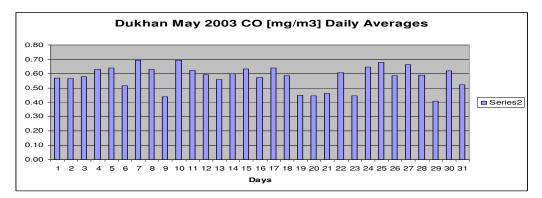


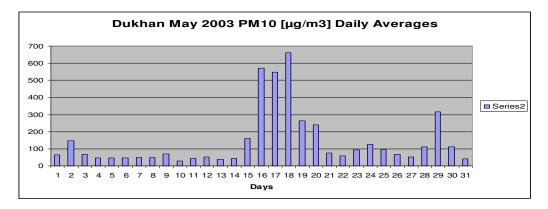


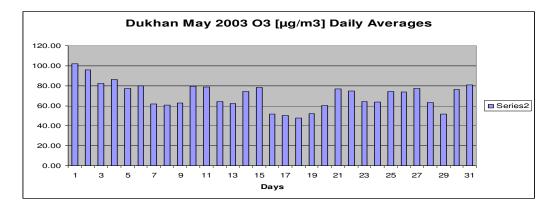
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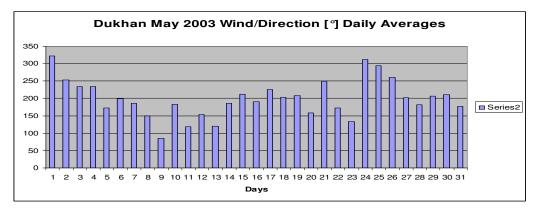


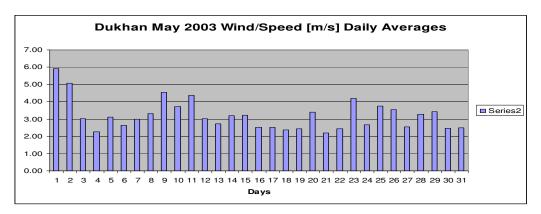




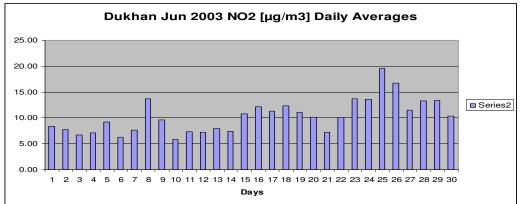


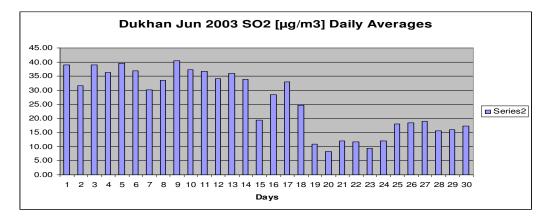


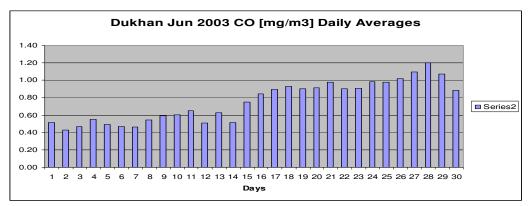


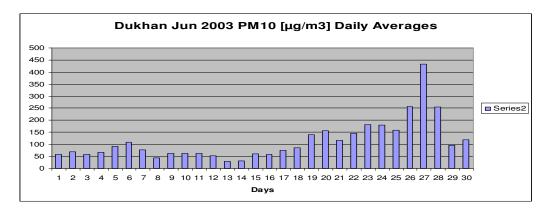


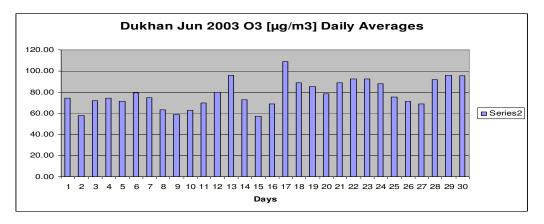
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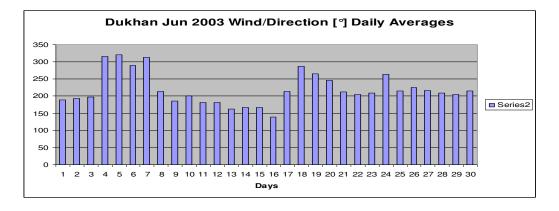


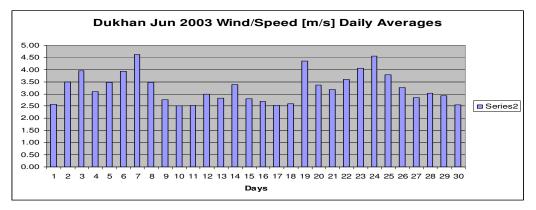




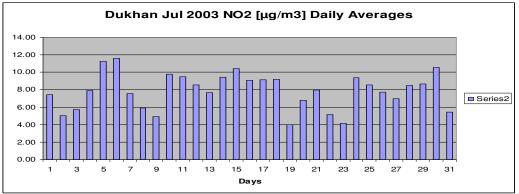


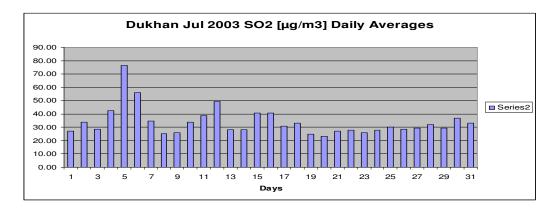


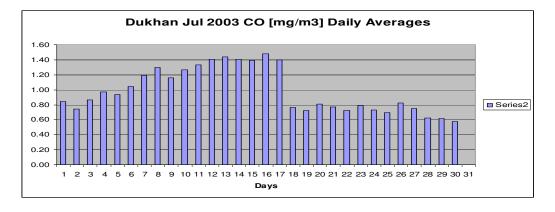


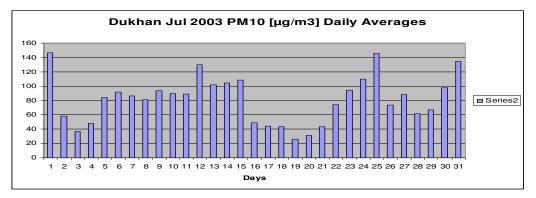


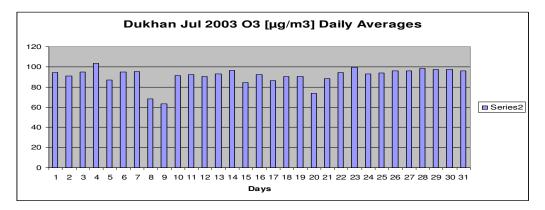
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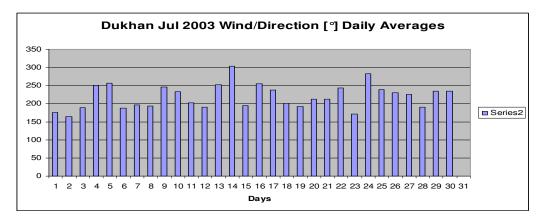


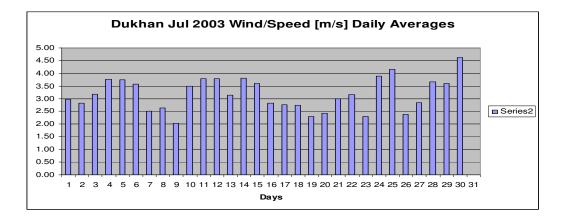




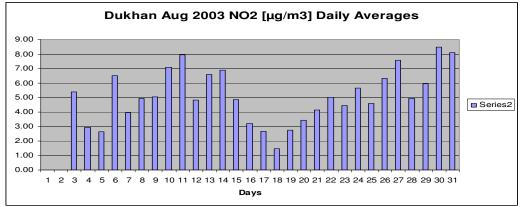


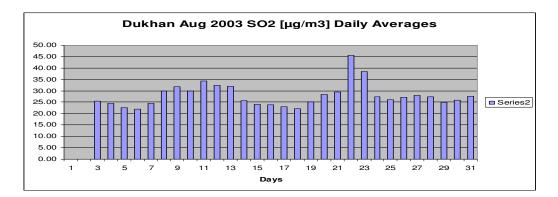


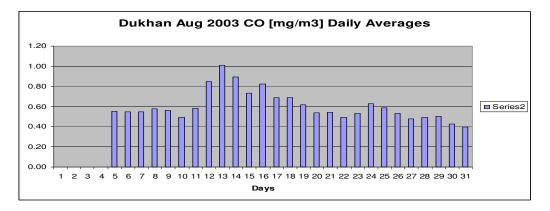


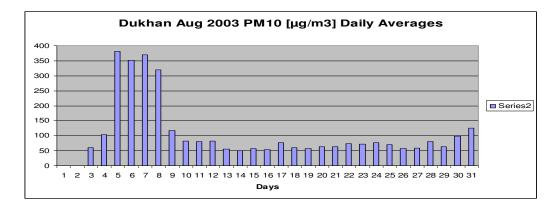


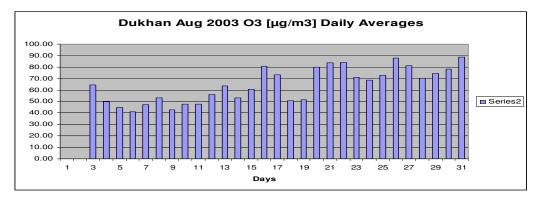
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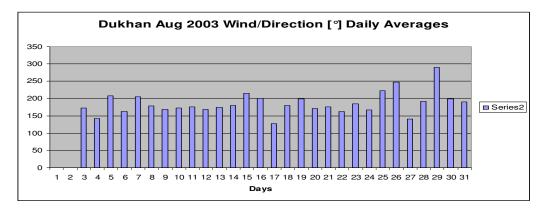


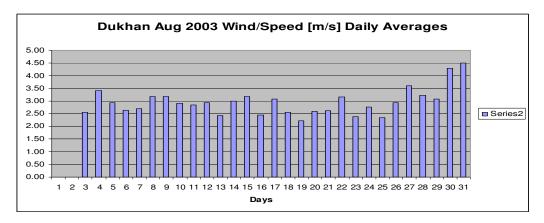




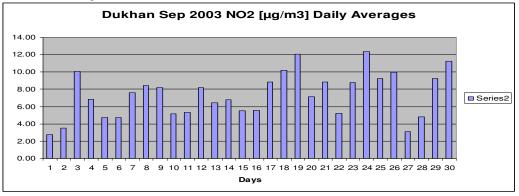


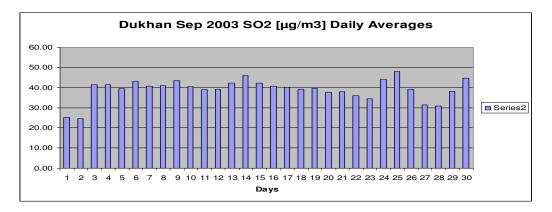


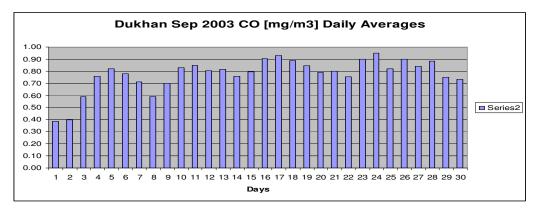


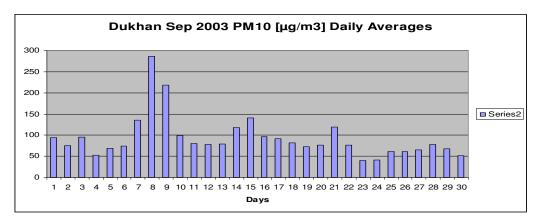


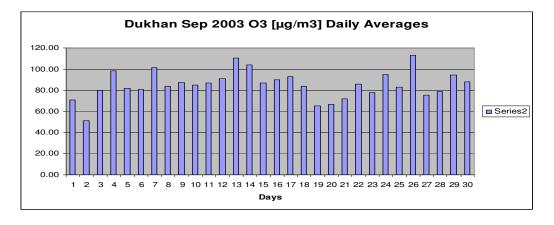
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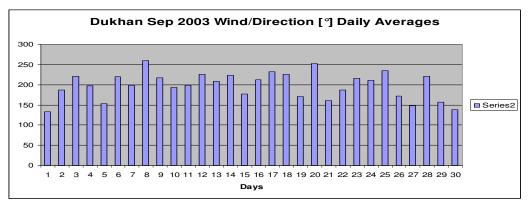


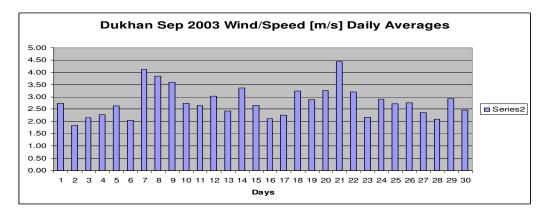




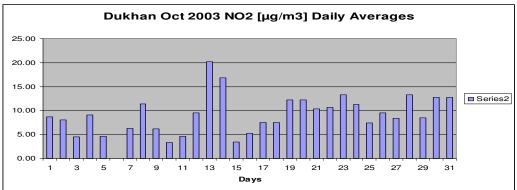


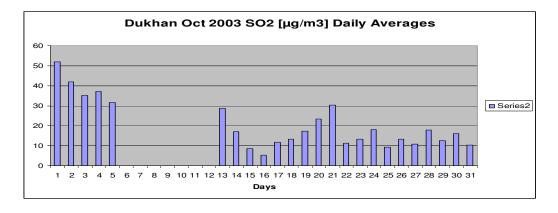


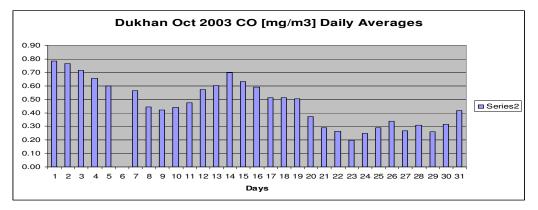


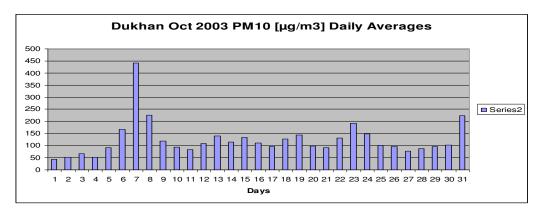


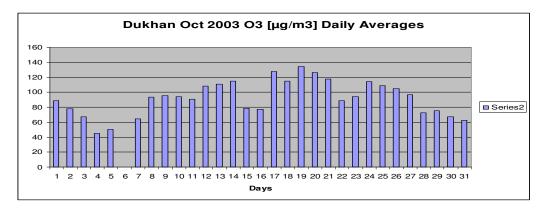
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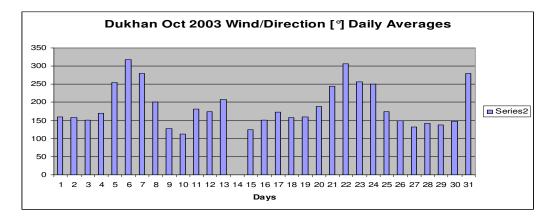


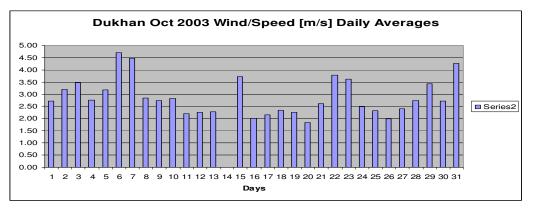




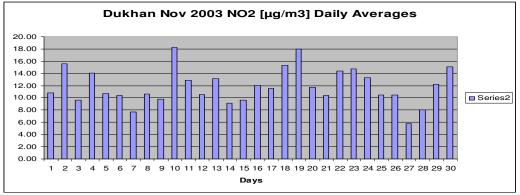


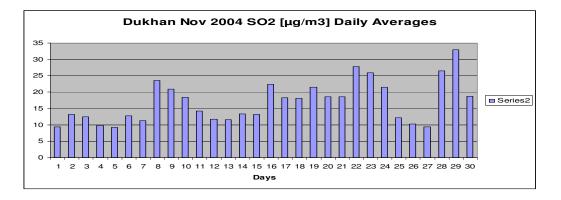


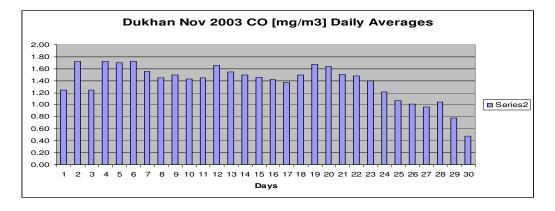


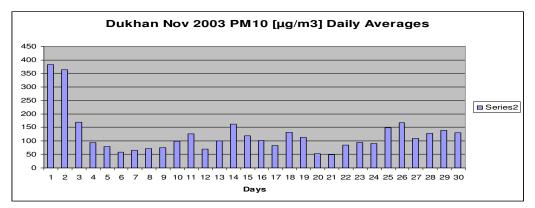


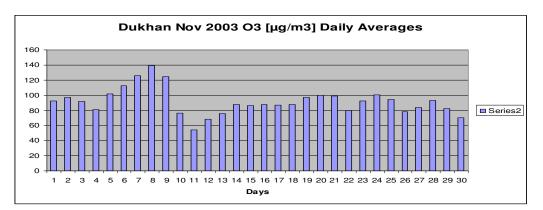
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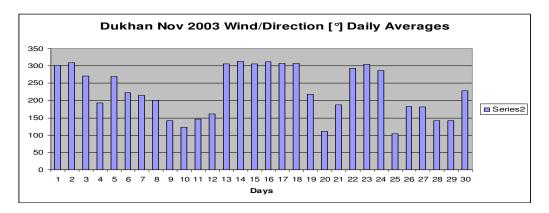


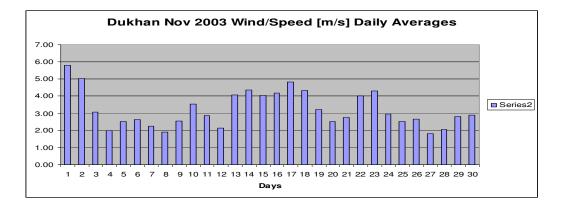




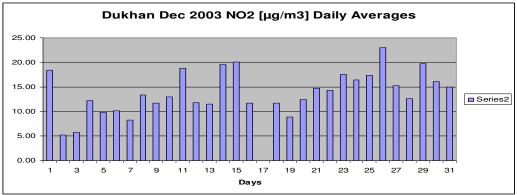


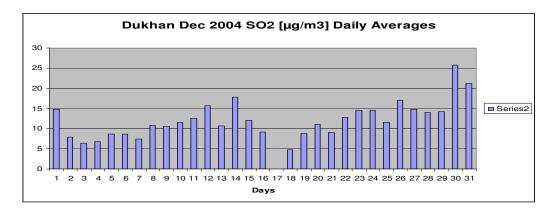


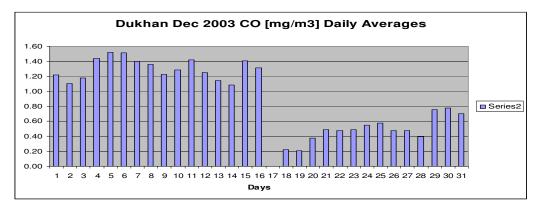


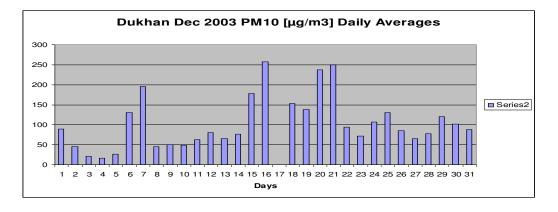


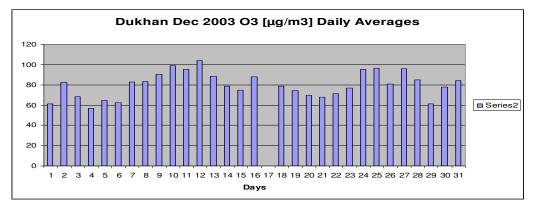
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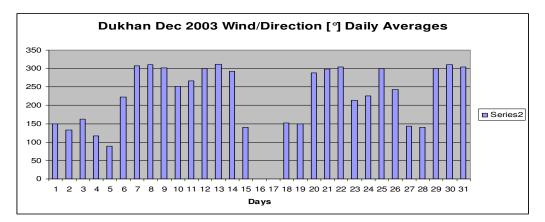


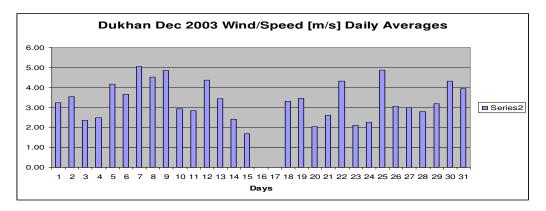






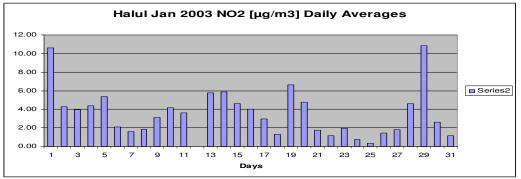


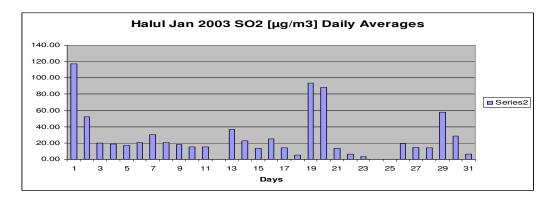


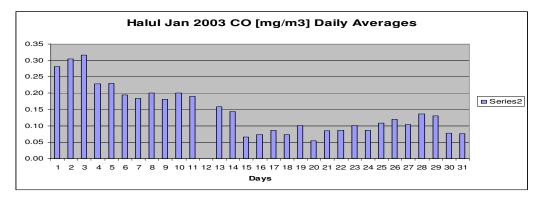


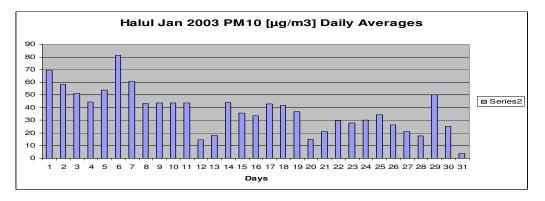
# 2.13 HALUL GRAPHS (24-Hour Averages of Data) / 2003

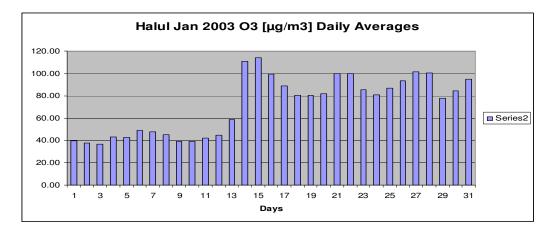
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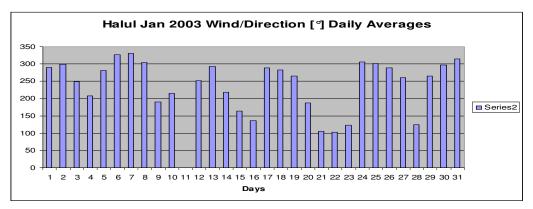


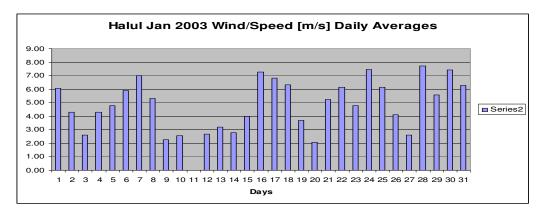




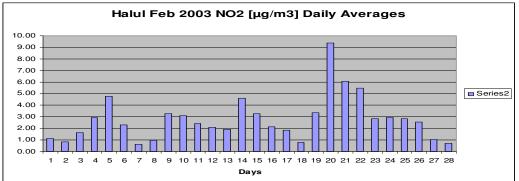


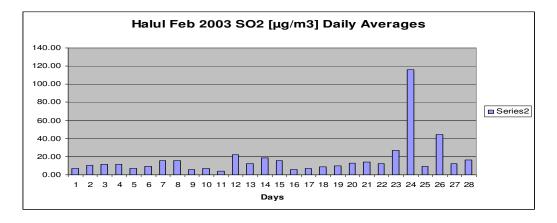


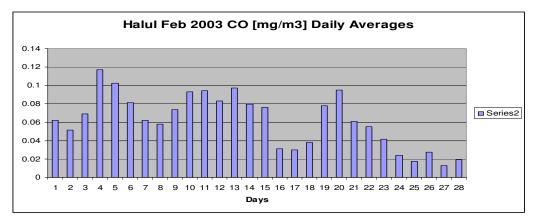


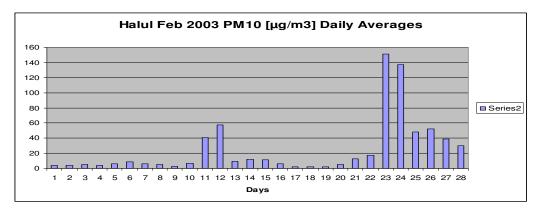


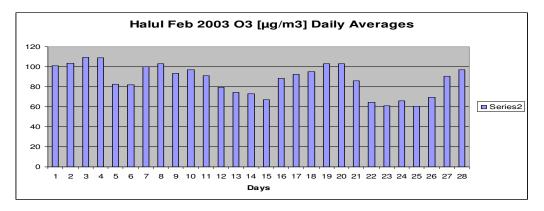
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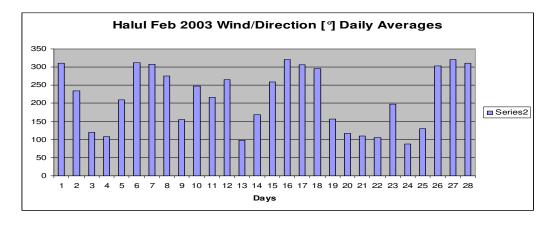


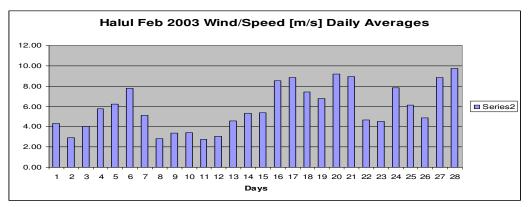




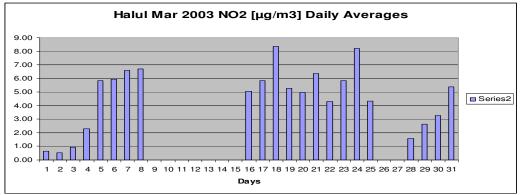


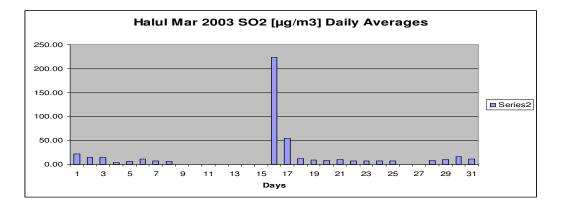


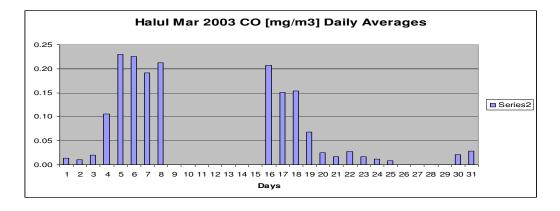


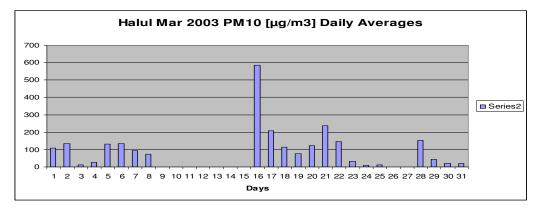


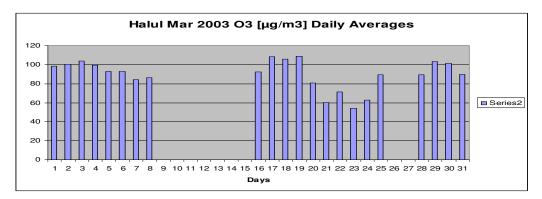
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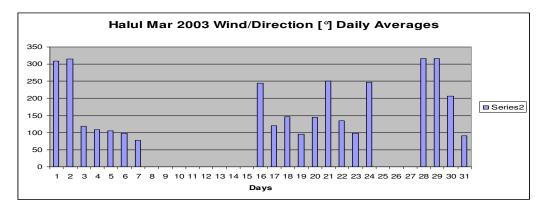


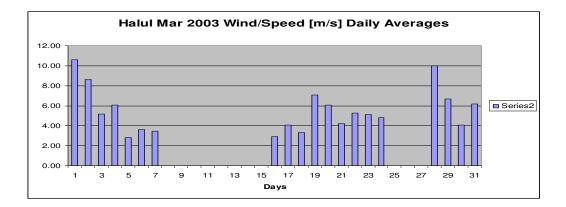




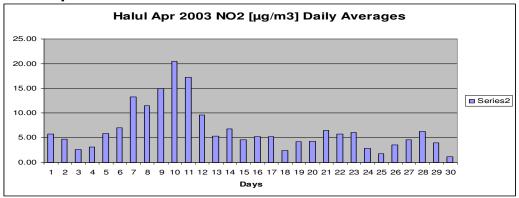


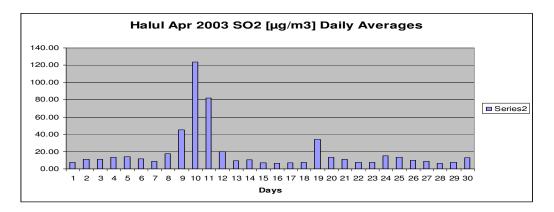


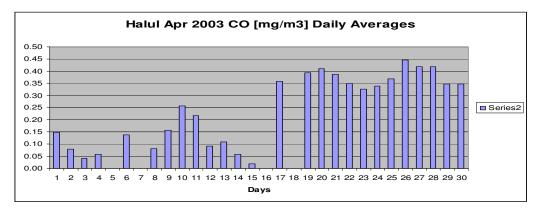


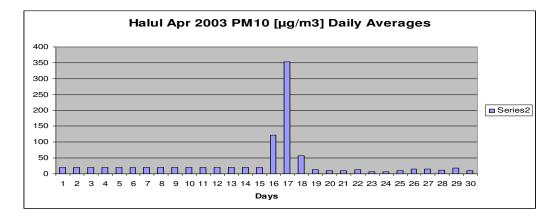


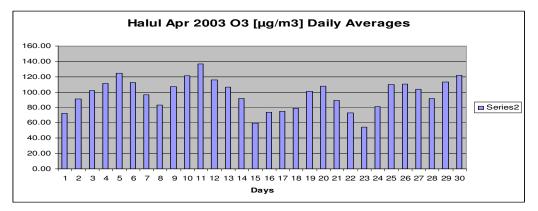
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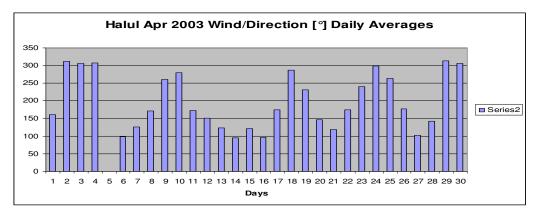


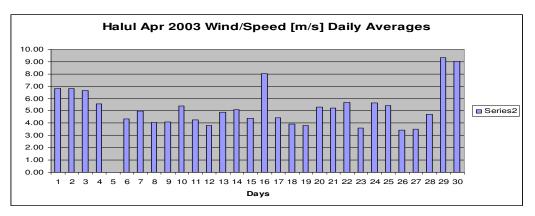




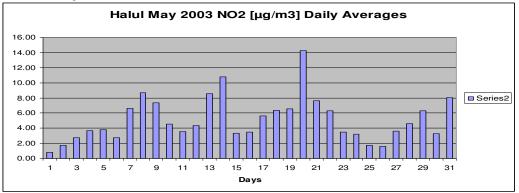


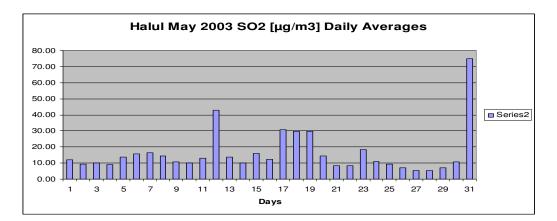


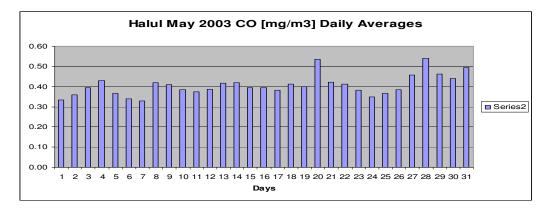


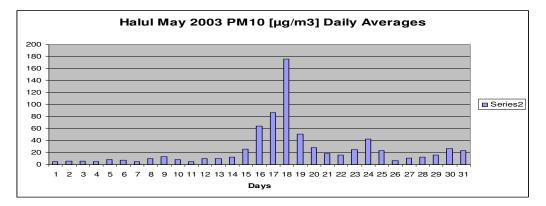


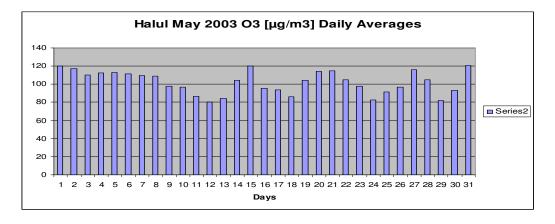
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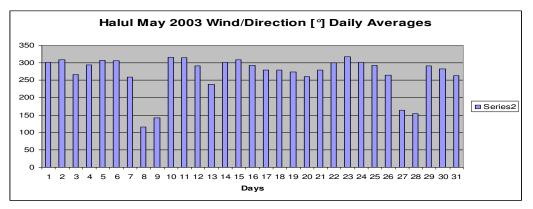


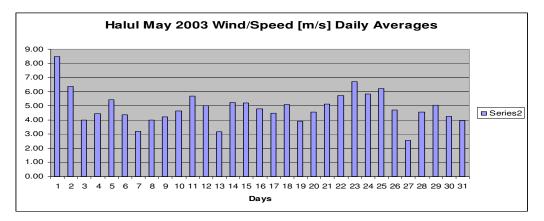




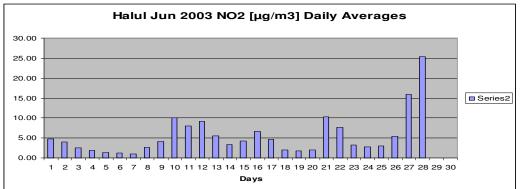


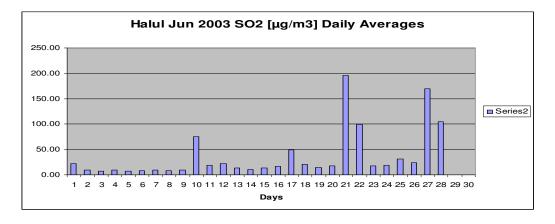


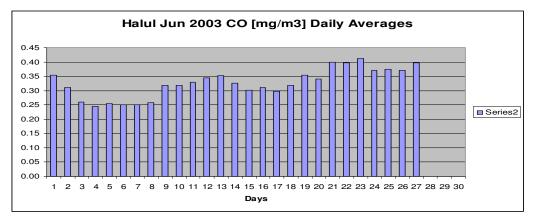


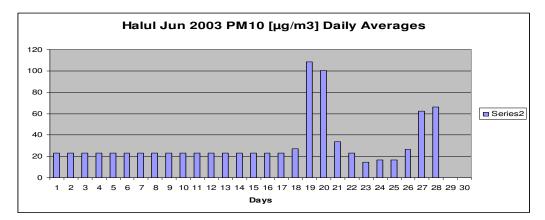


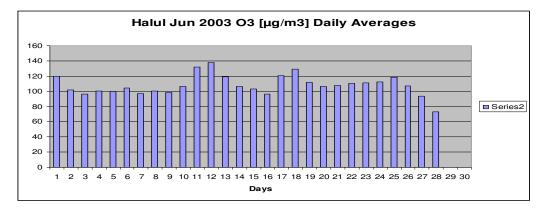
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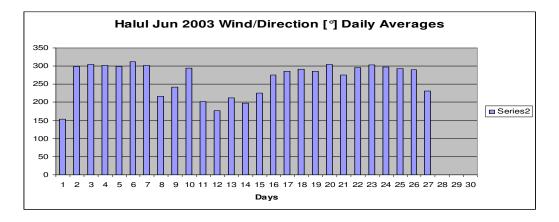


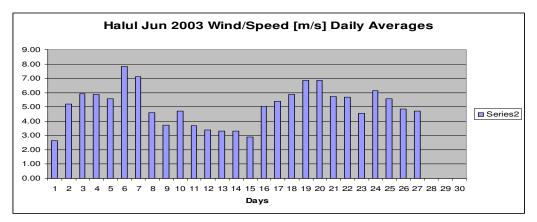




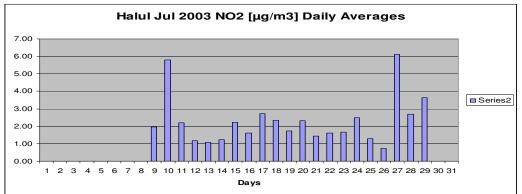


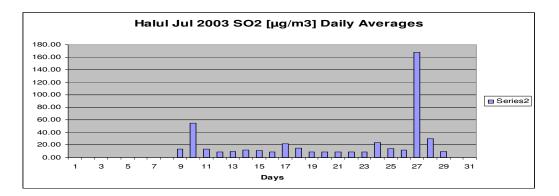


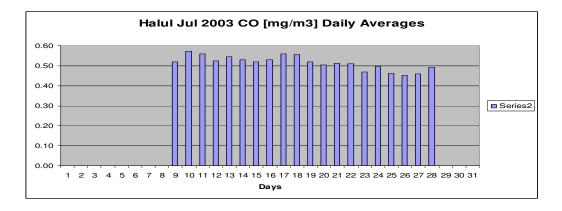


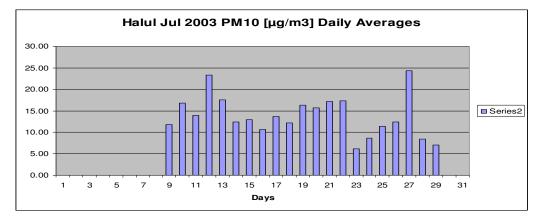


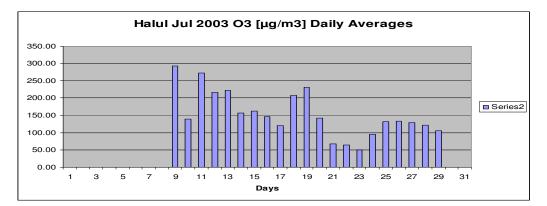
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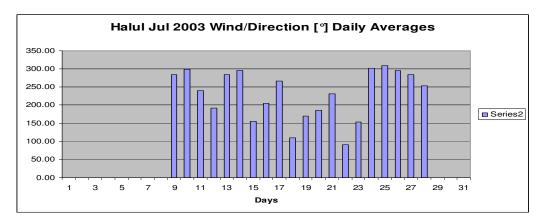


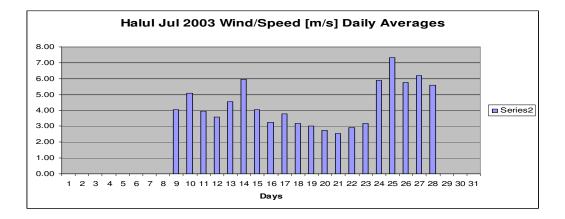




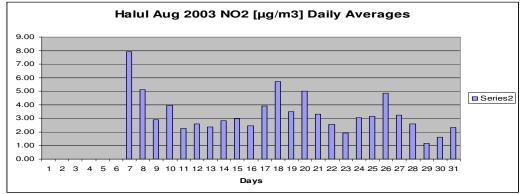


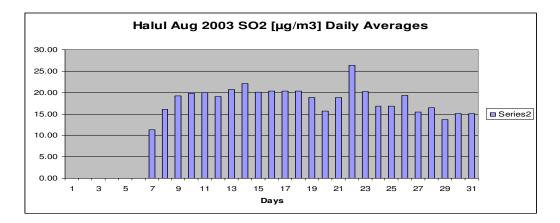


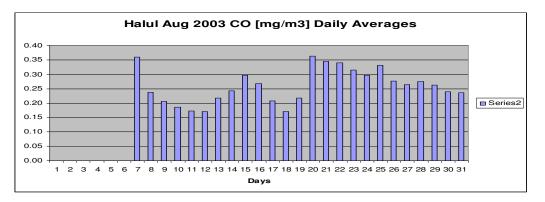


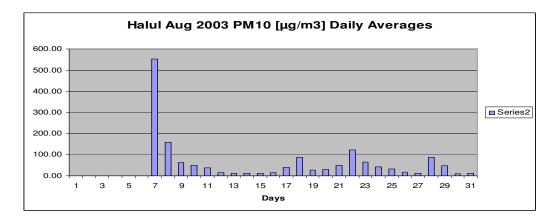


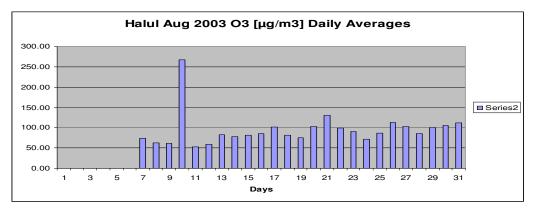
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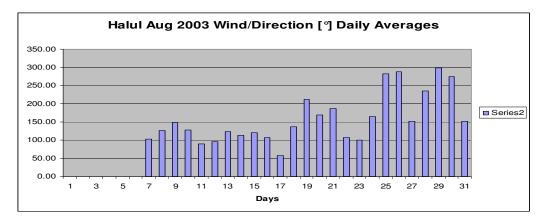


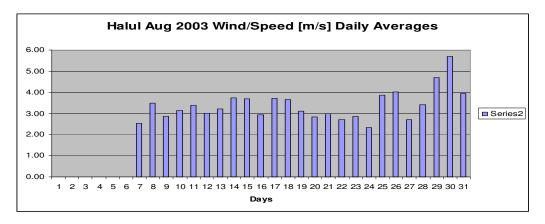




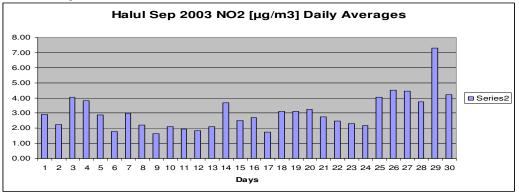


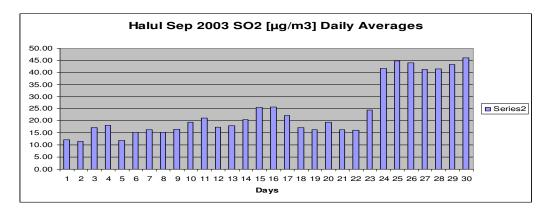


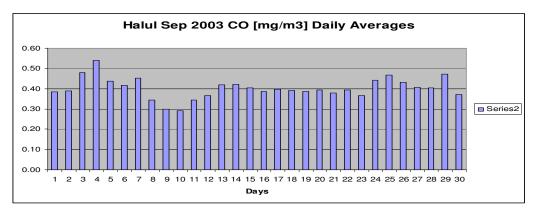


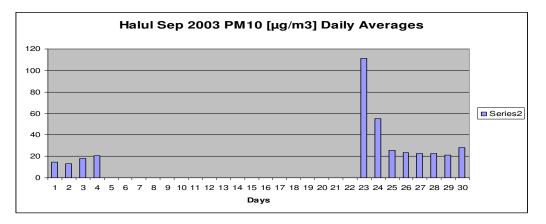


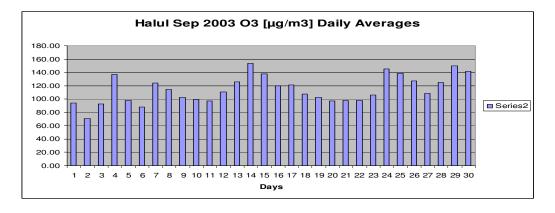
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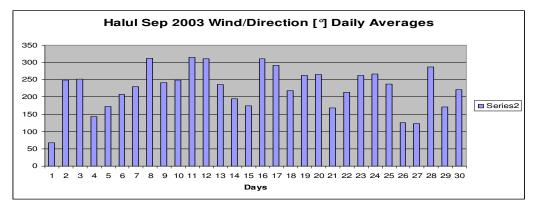


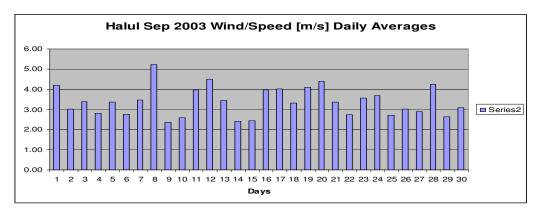




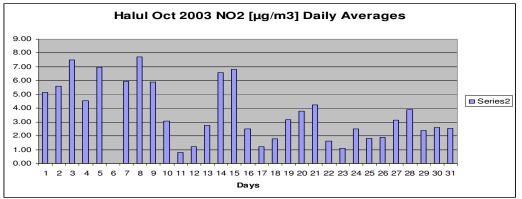


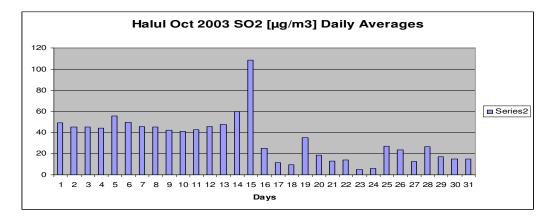


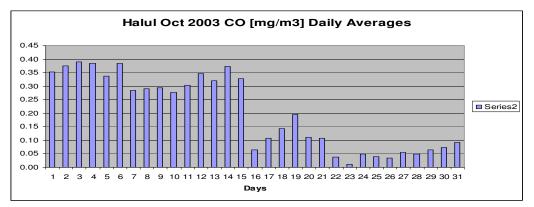


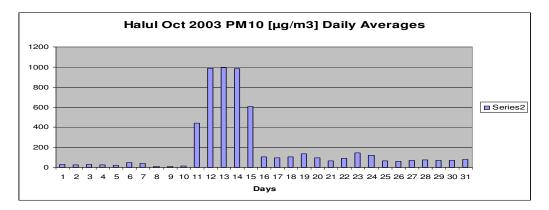


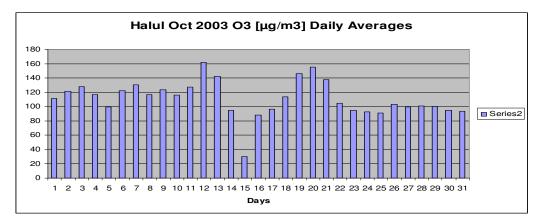
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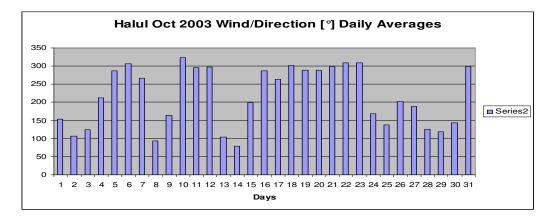


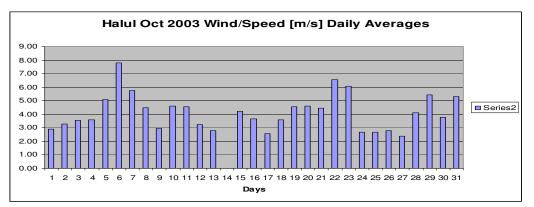




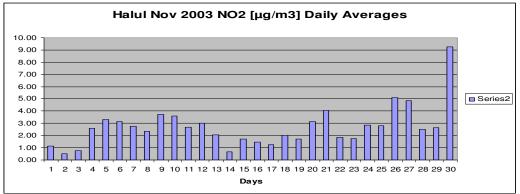


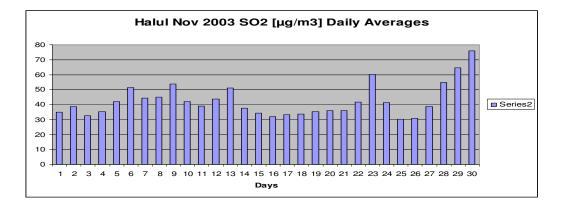


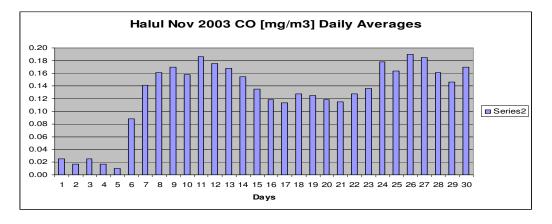


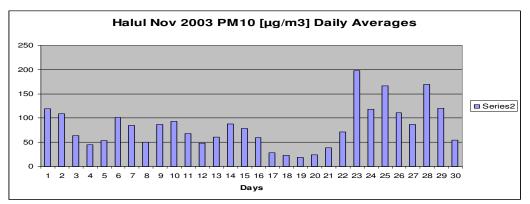


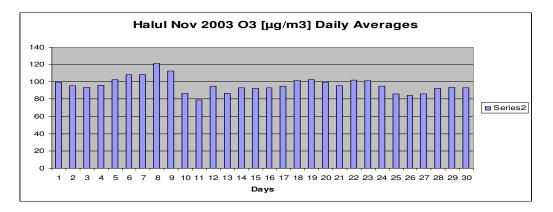
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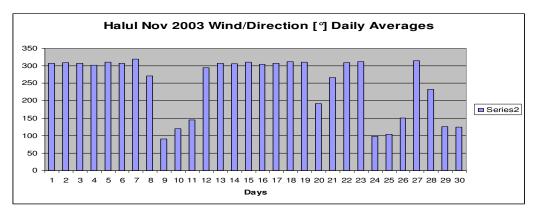


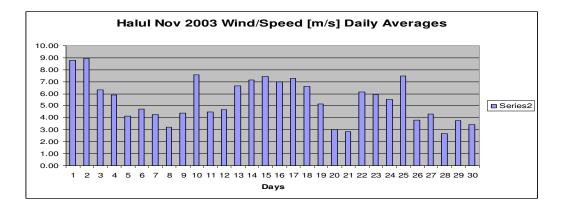




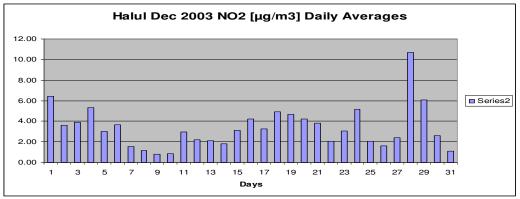


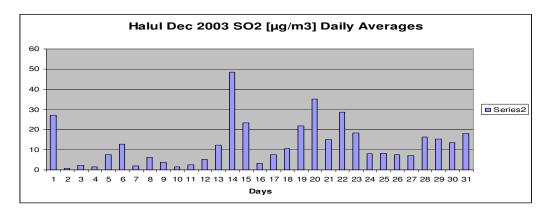


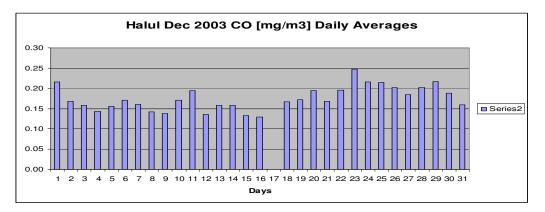


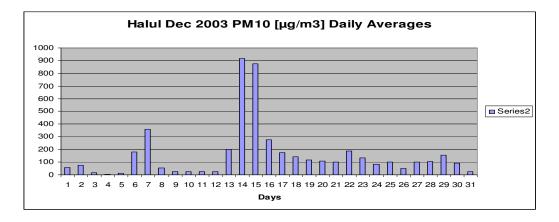


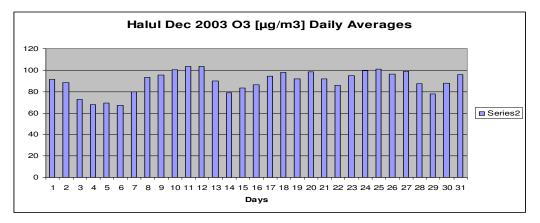
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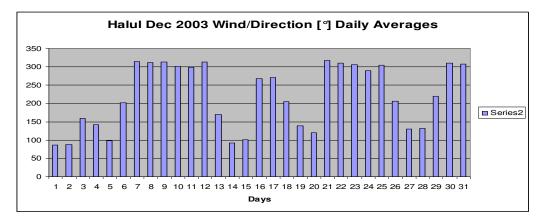


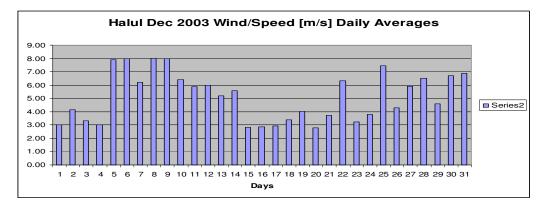




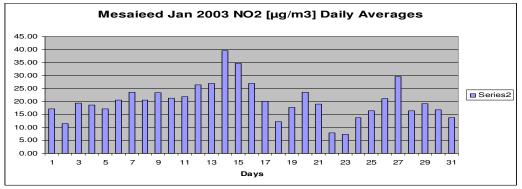


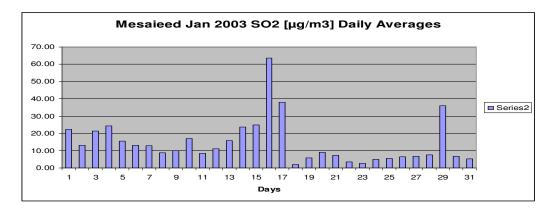


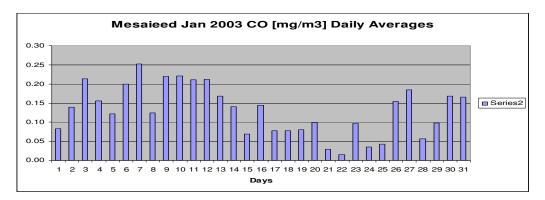


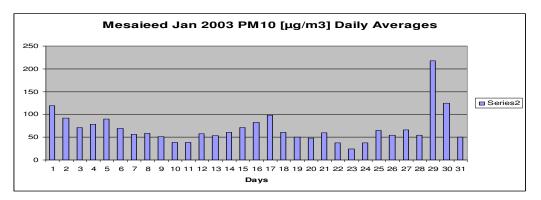


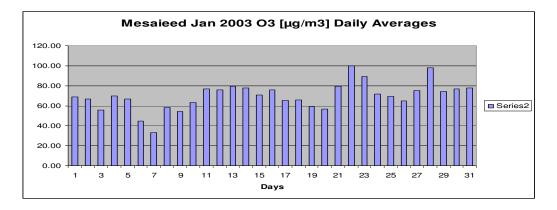
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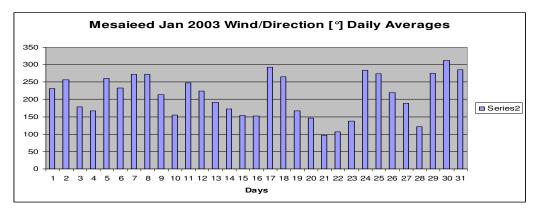


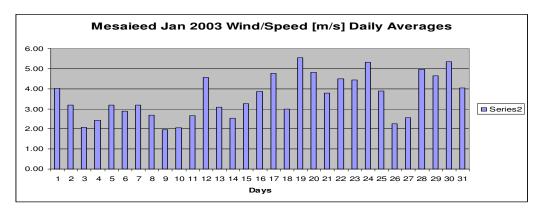




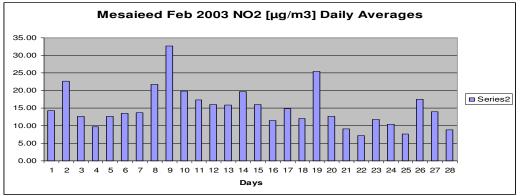


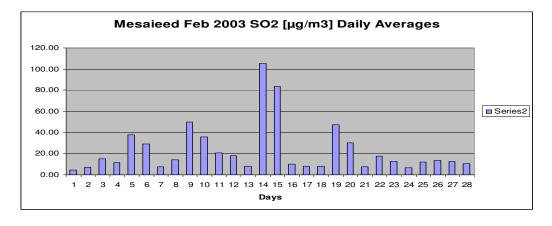


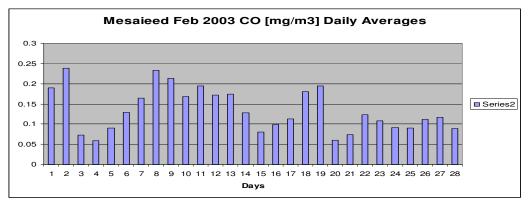


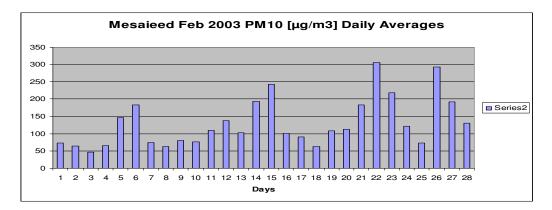


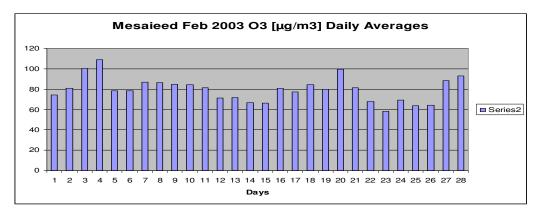
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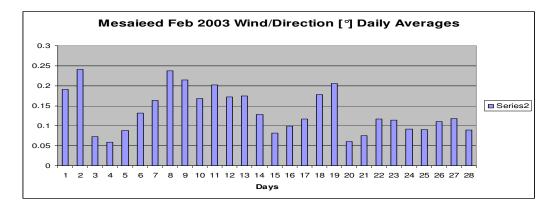


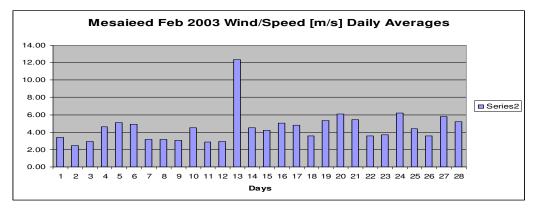




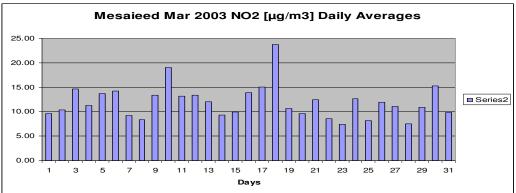


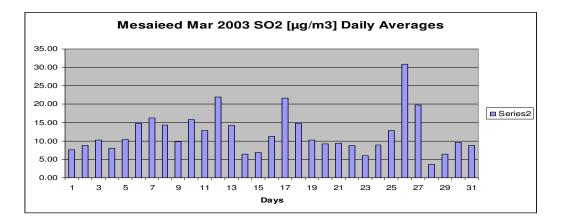


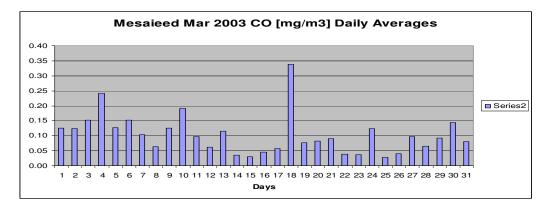


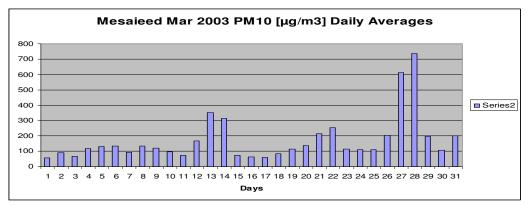


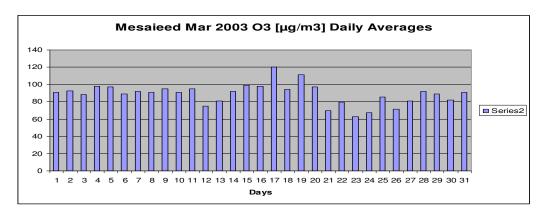
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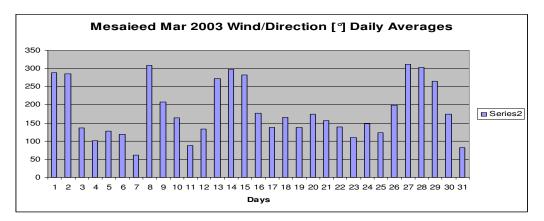


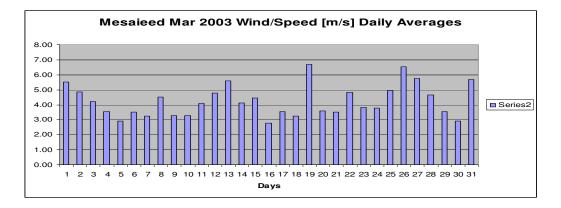




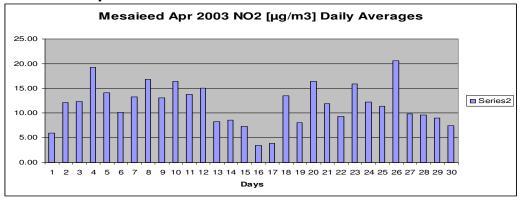


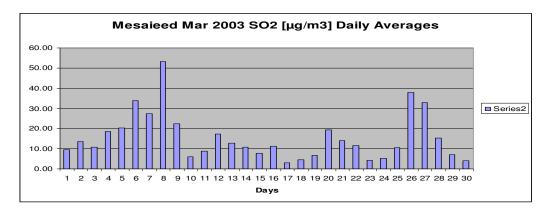


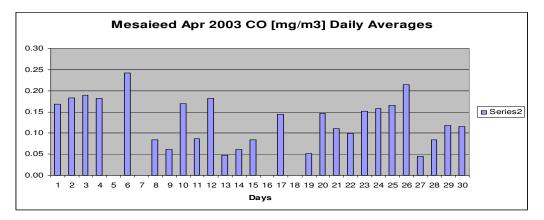


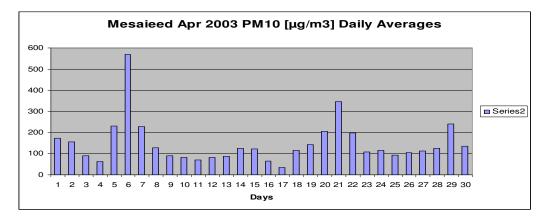


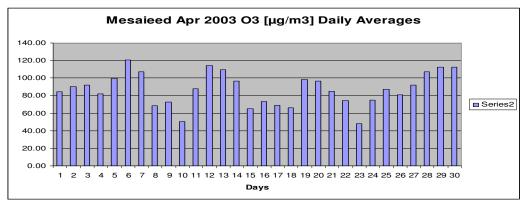
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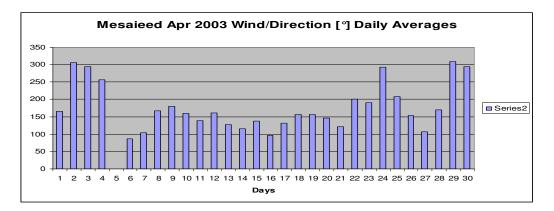


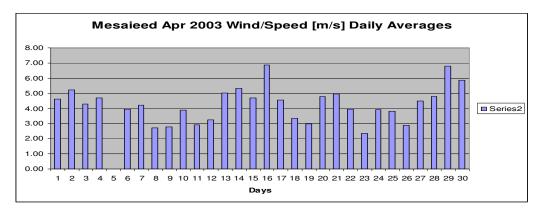




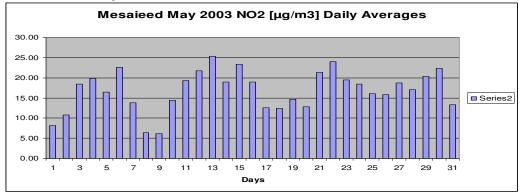


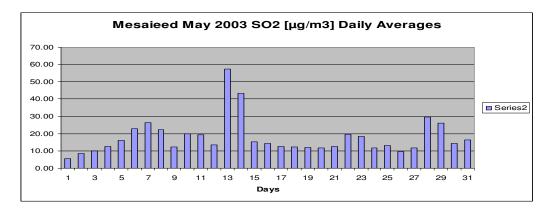


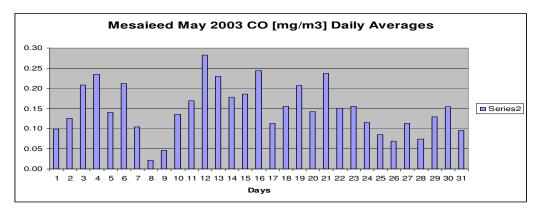


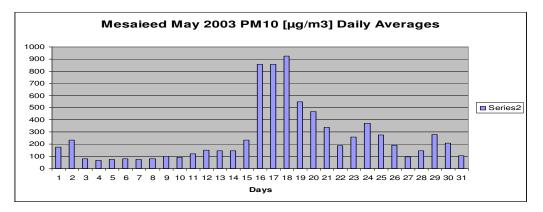


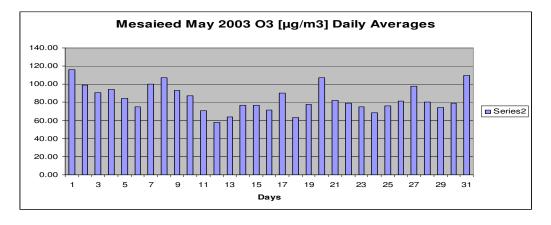
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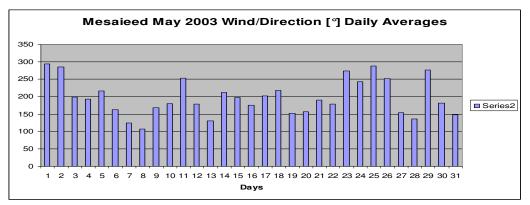


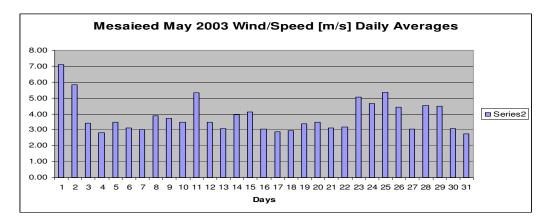




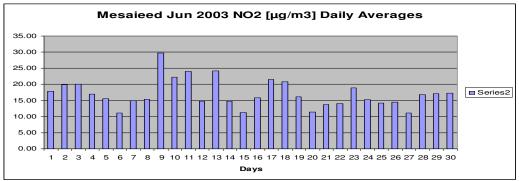


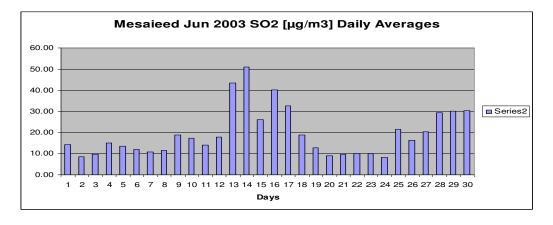


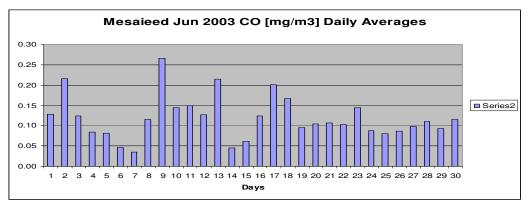


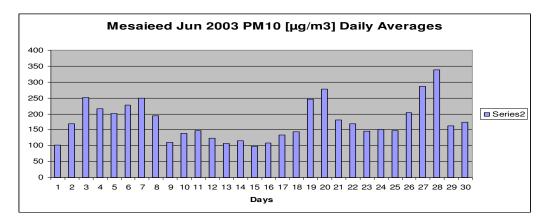


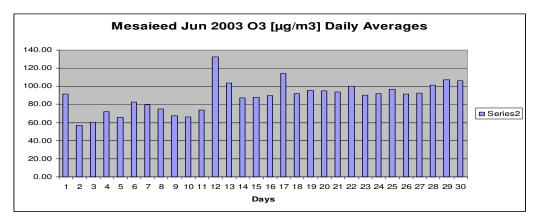
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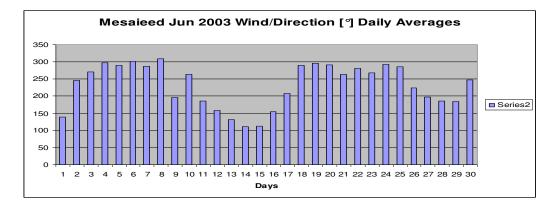


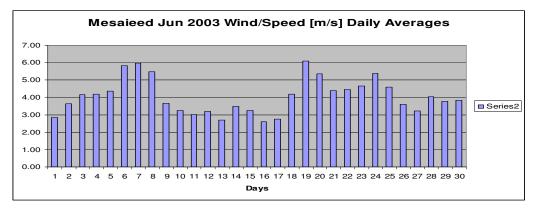




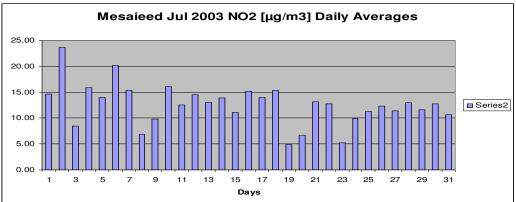


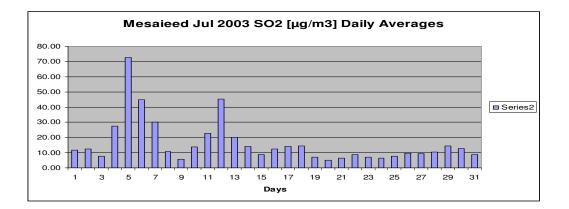


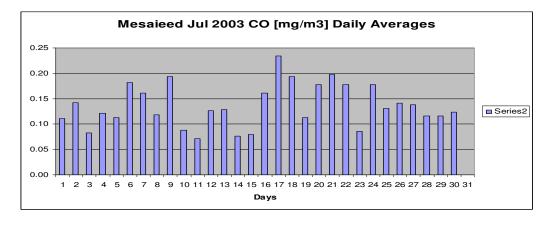


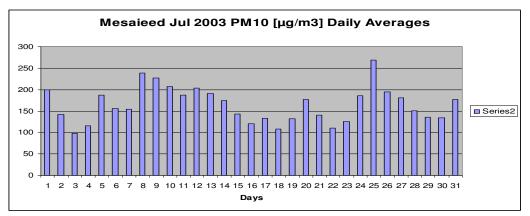


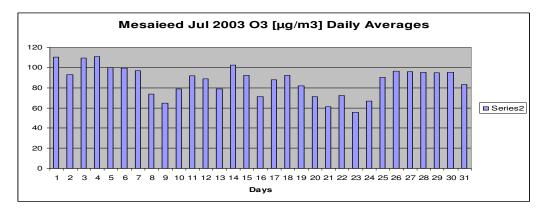
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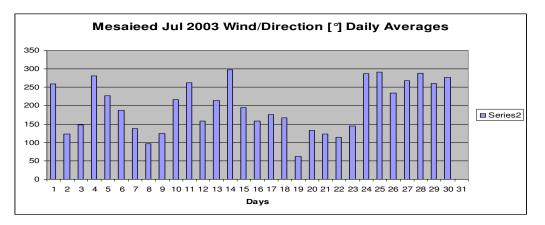


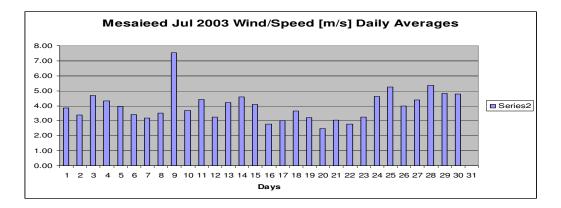




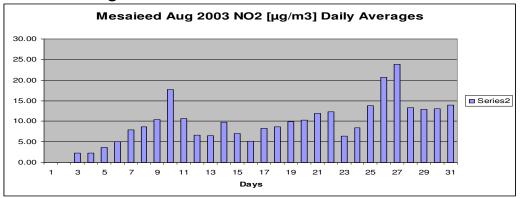


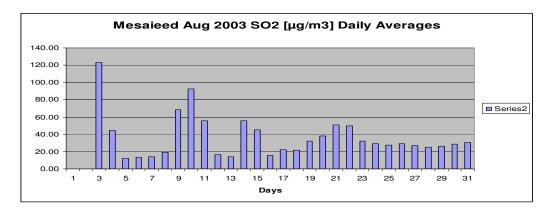


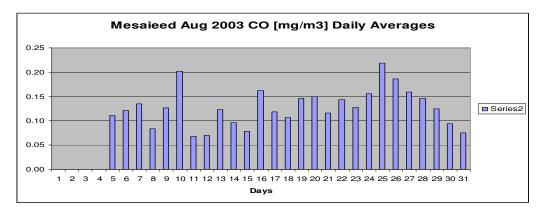


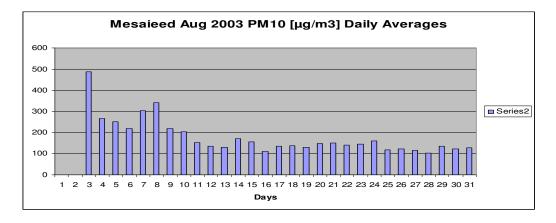


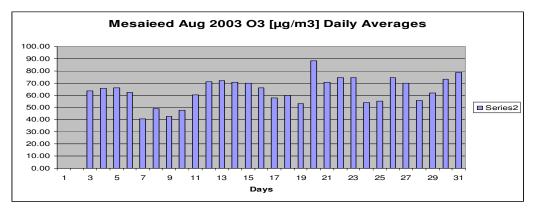
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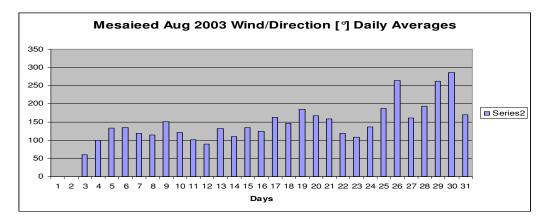


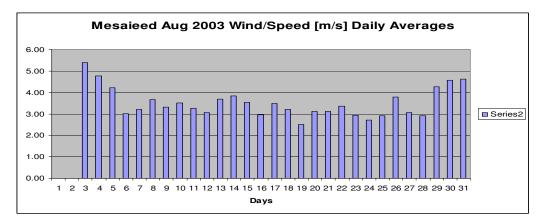




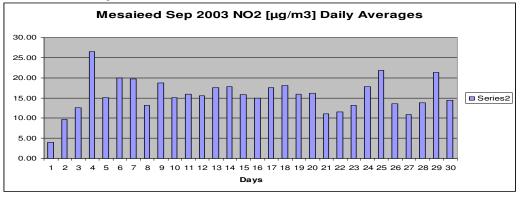


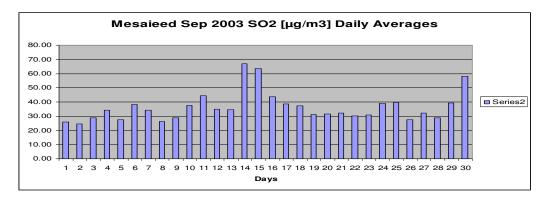


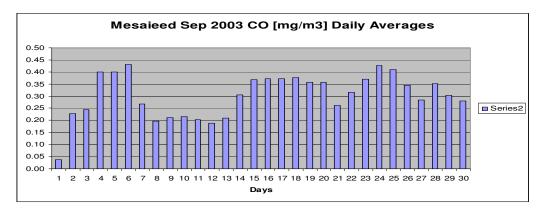


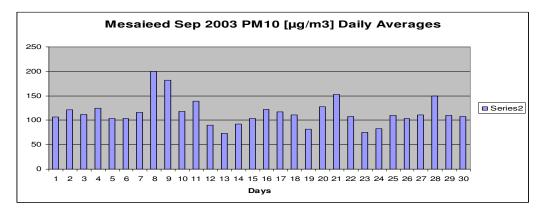


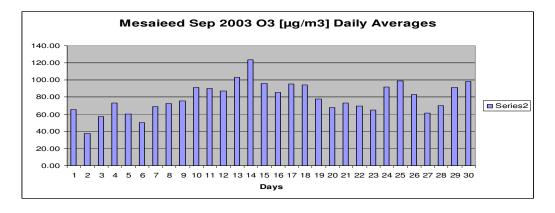
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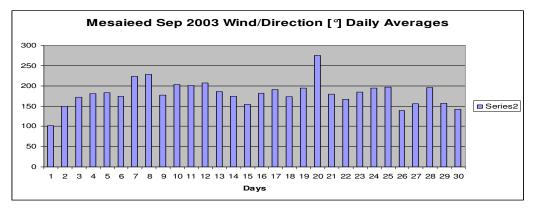


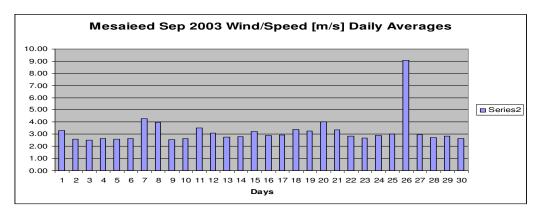




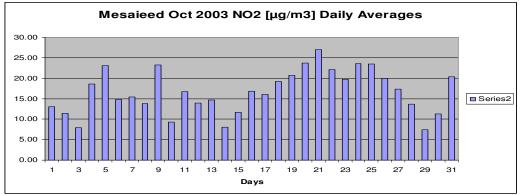


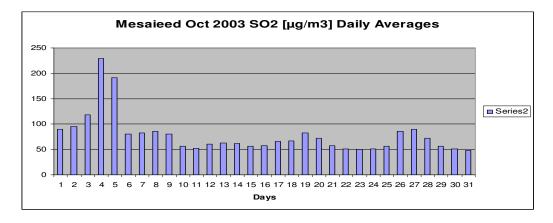


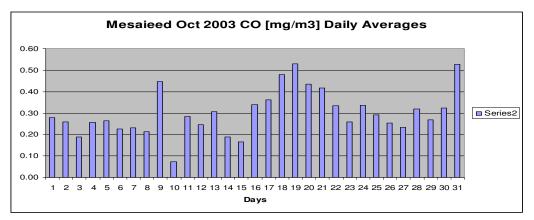


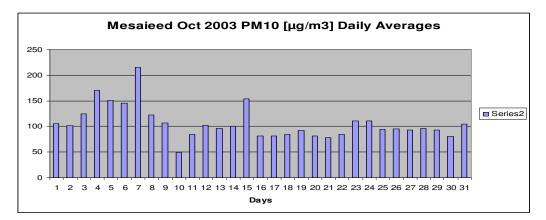


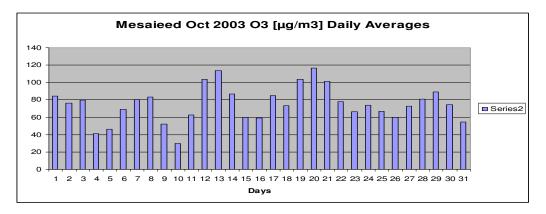
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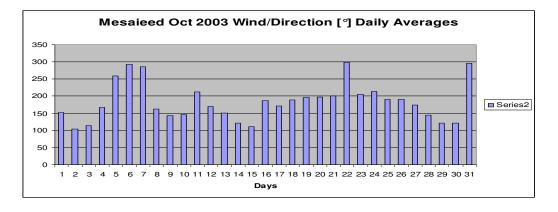


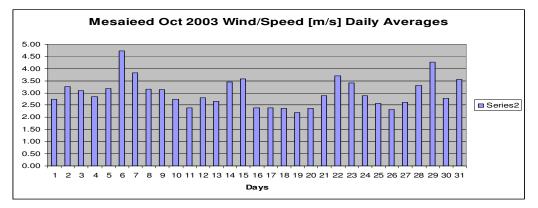




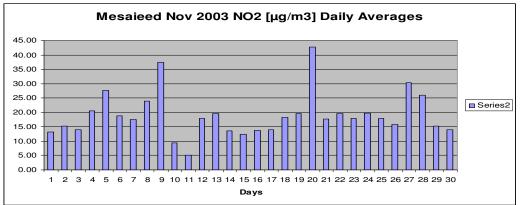


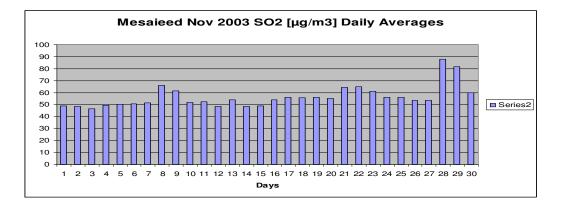


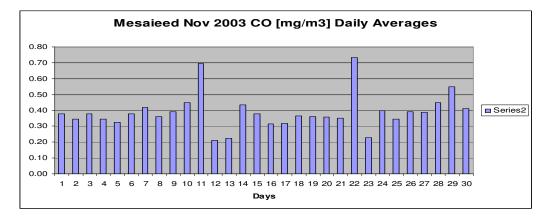


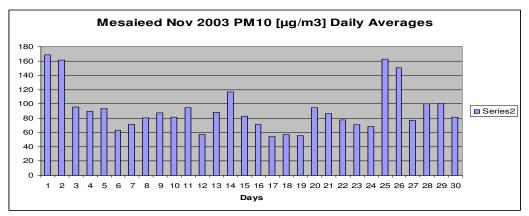


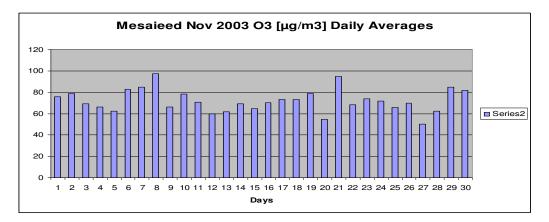
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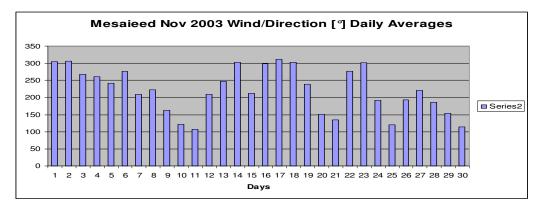


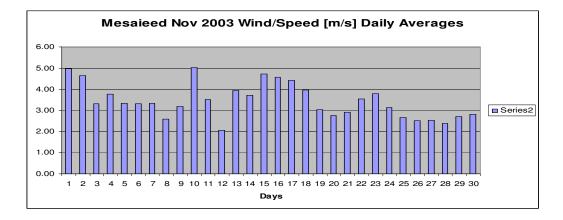




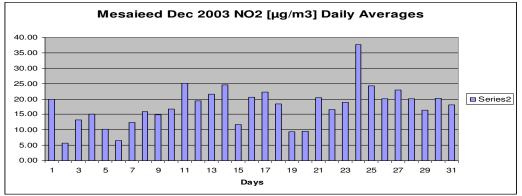


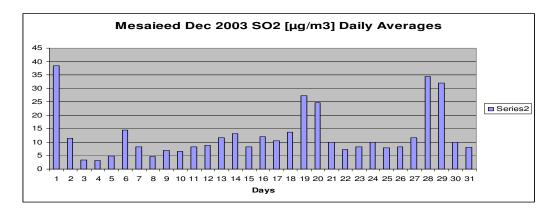


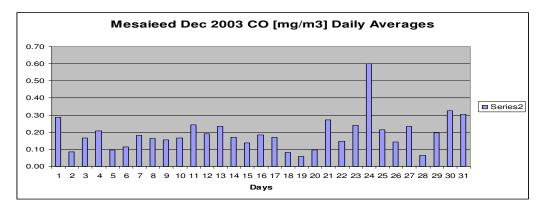


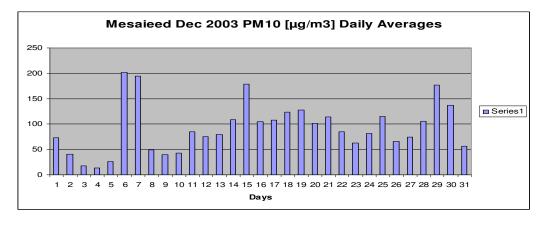


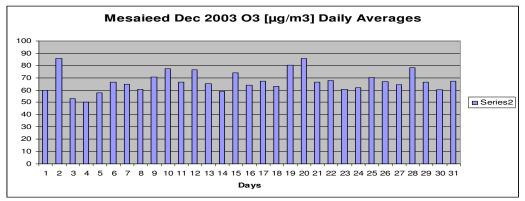
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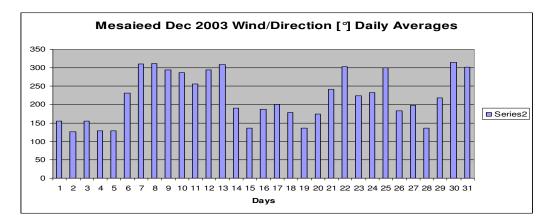


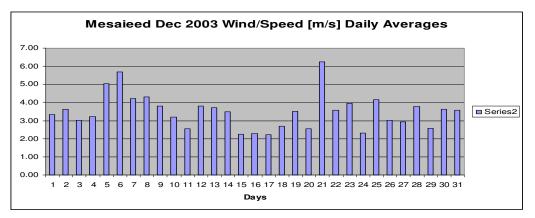






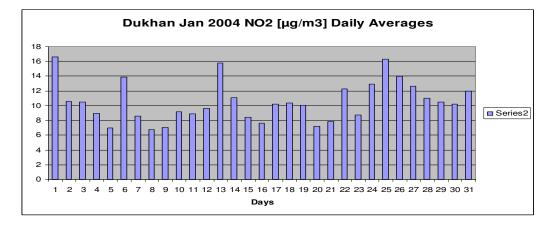


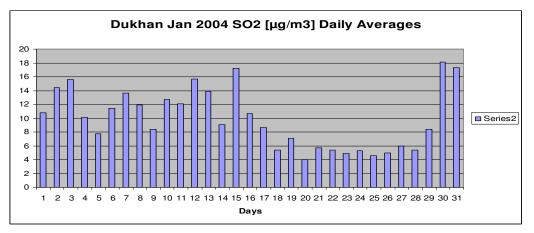


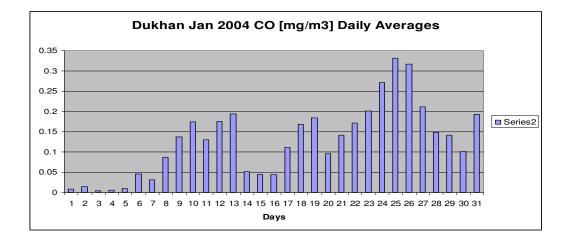


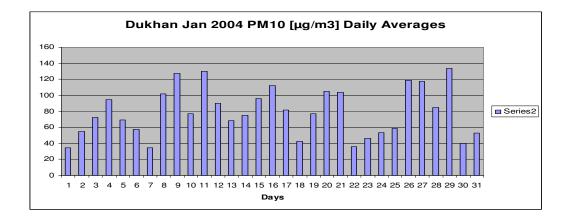
# 2.15 DUKHAN GRAPHS (24-Hour Averages of Data) / 2004

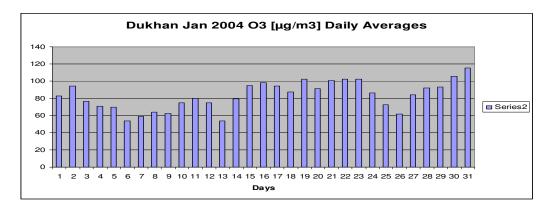
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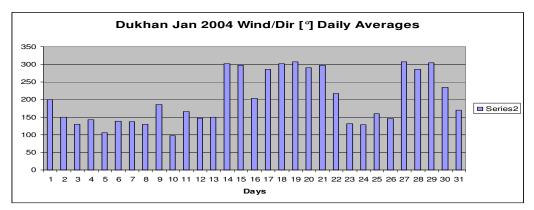


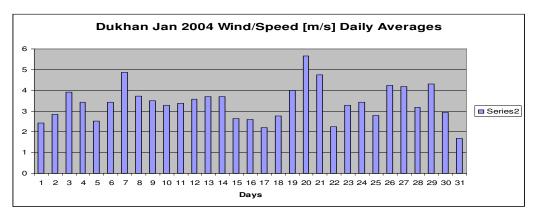




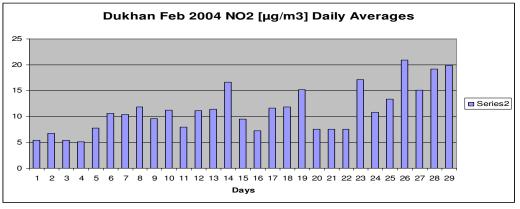


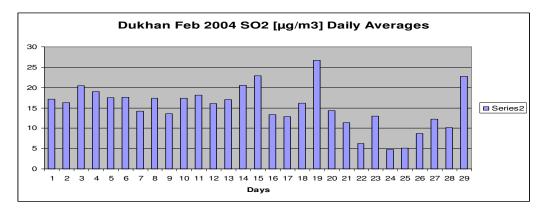


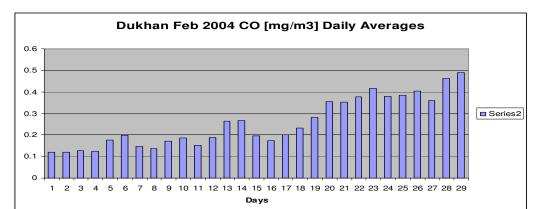


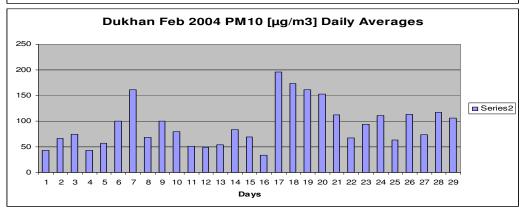


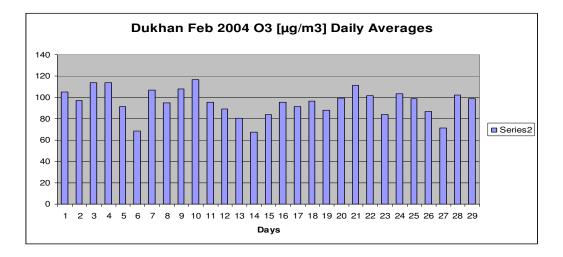
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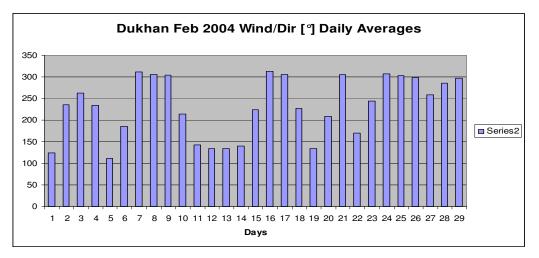


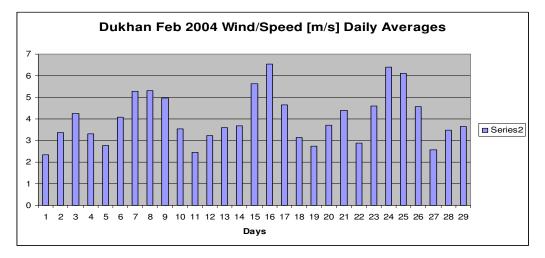




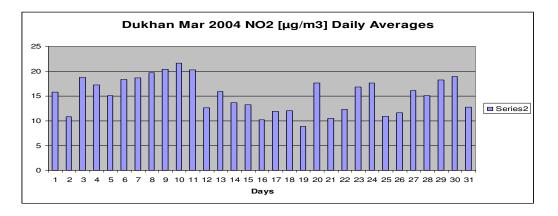


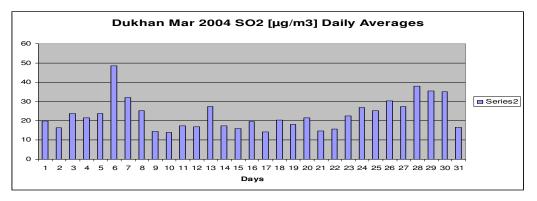


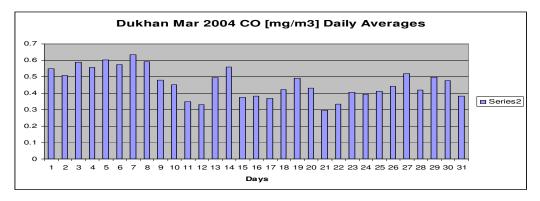


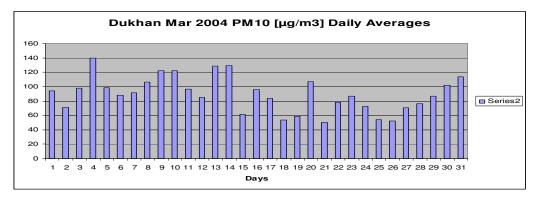


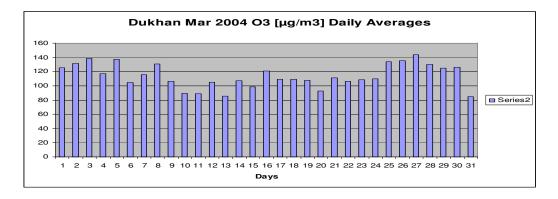
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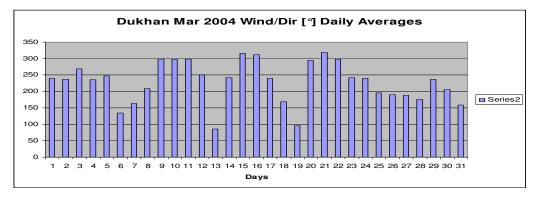


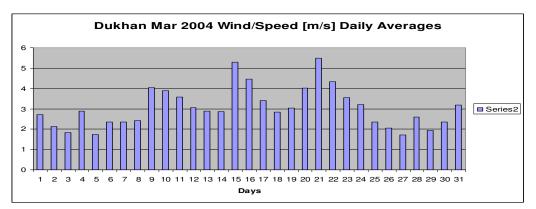




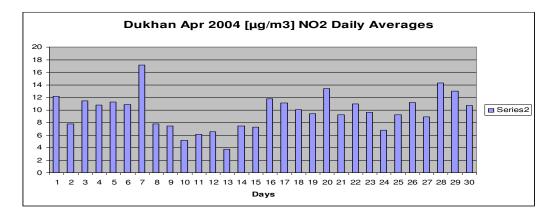


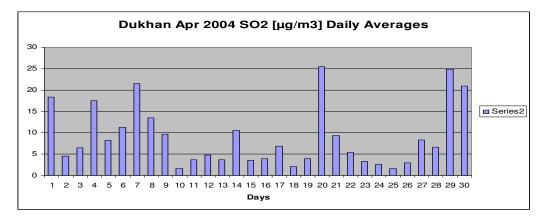


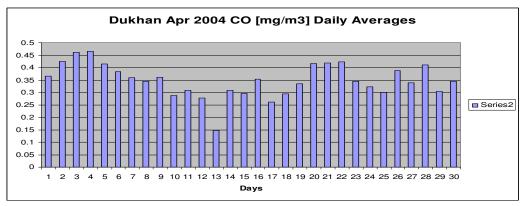


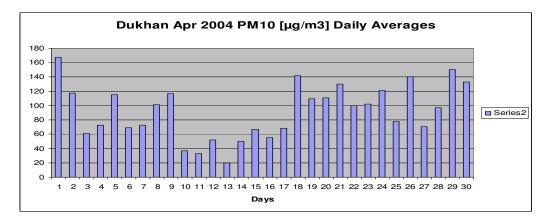


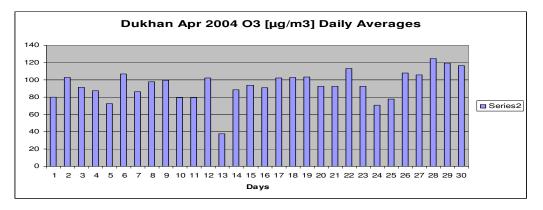
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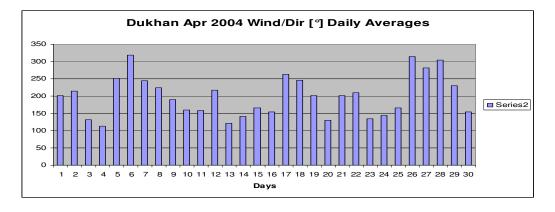


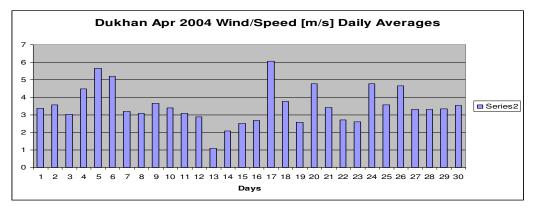




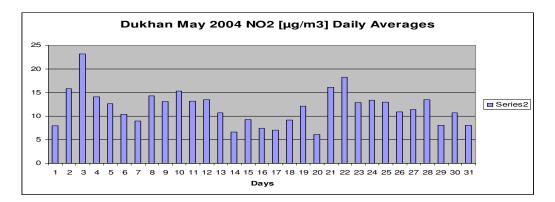


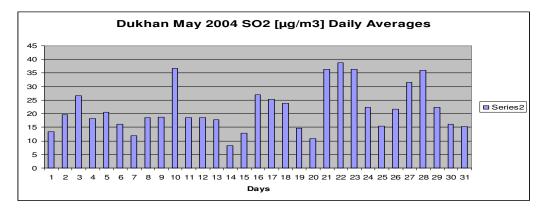


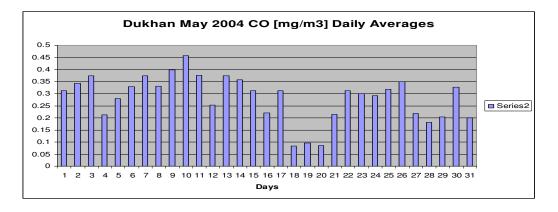


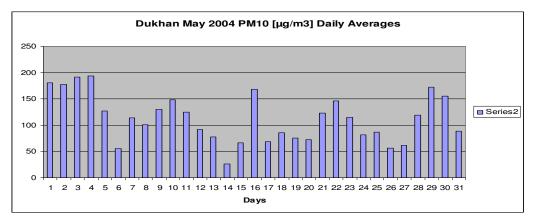


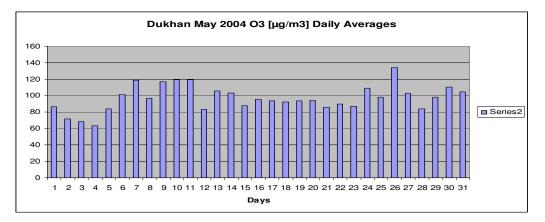
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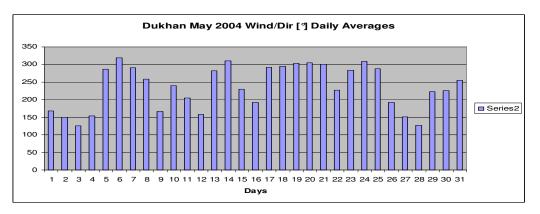


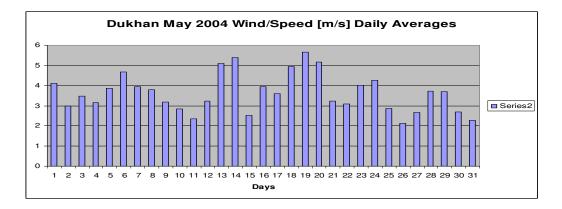




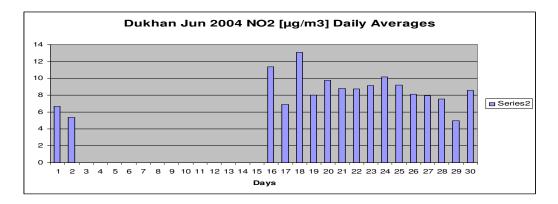


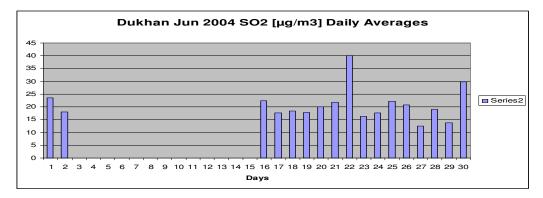


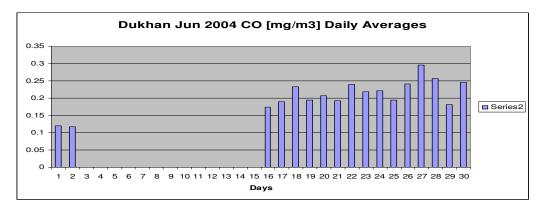


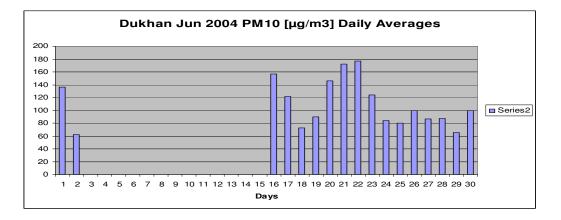


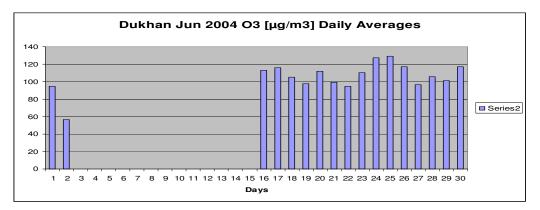
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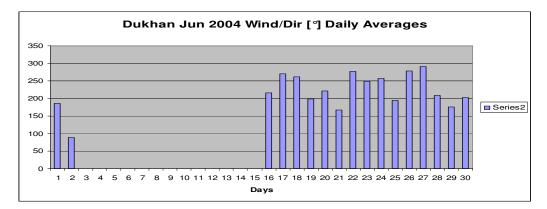


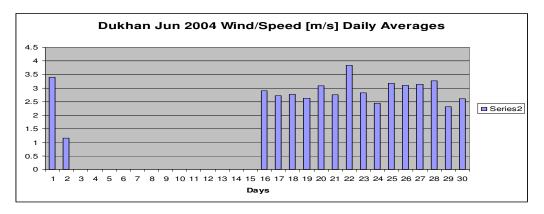




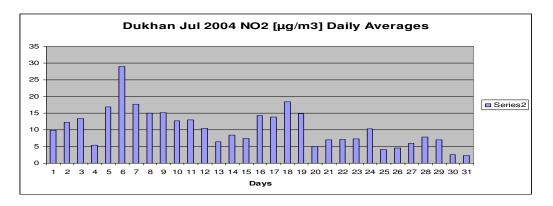


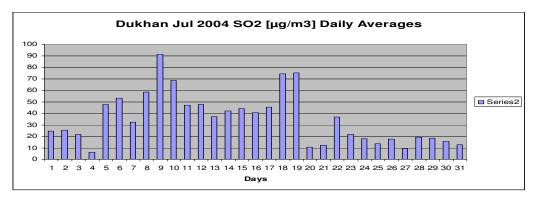


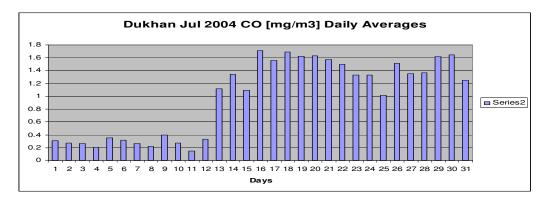


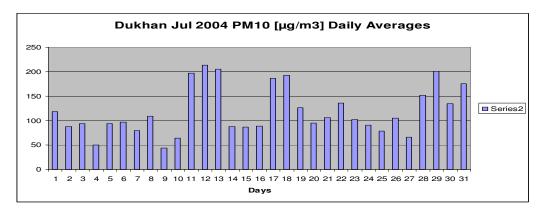


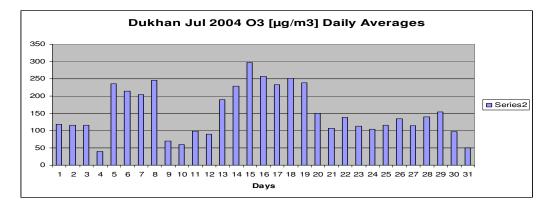
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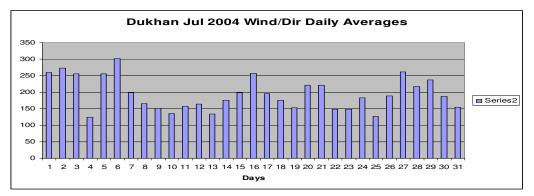


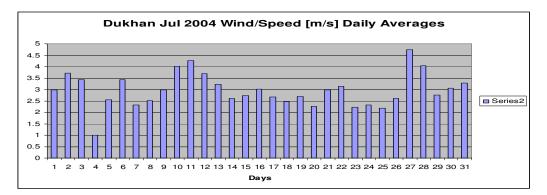




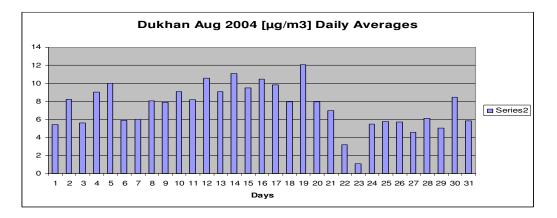


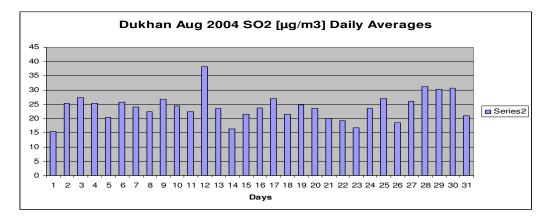


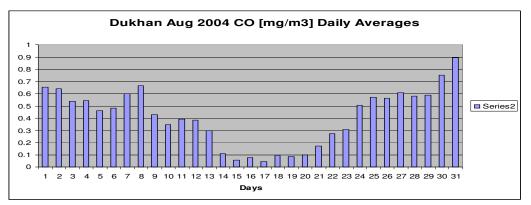


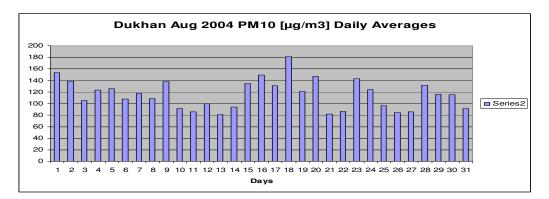


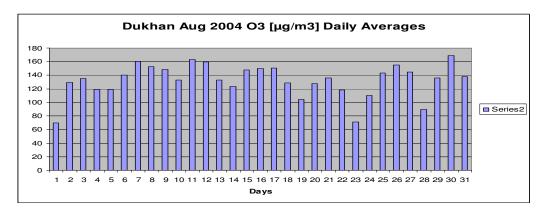
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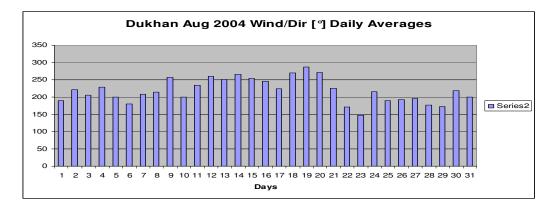


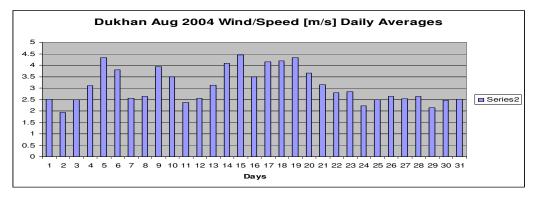




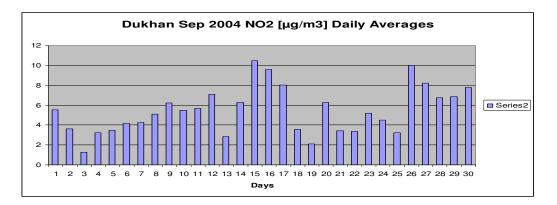


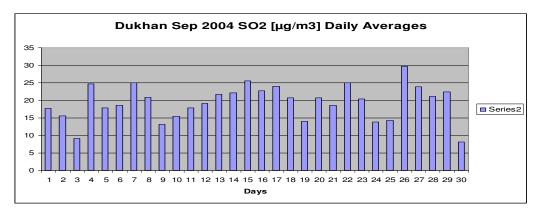


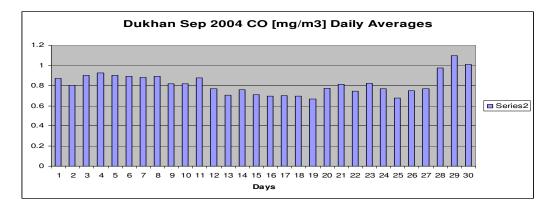


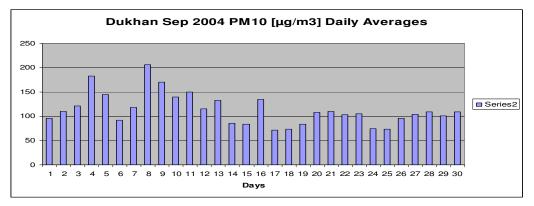


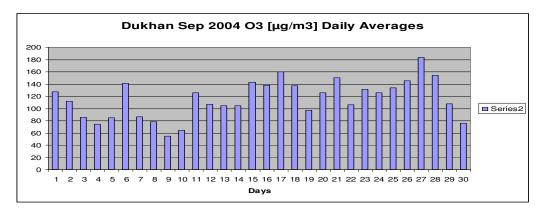
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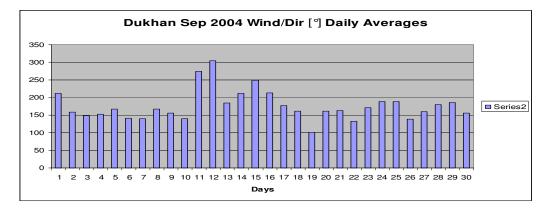


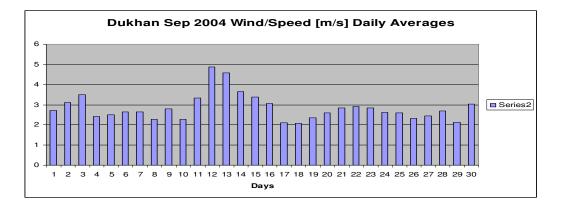




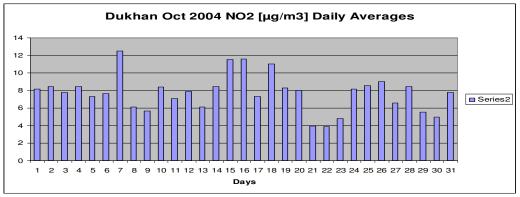


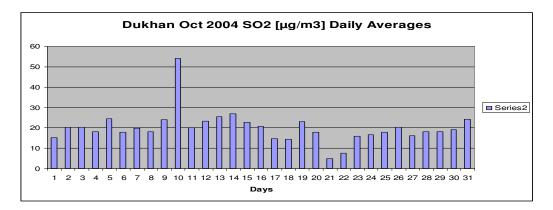


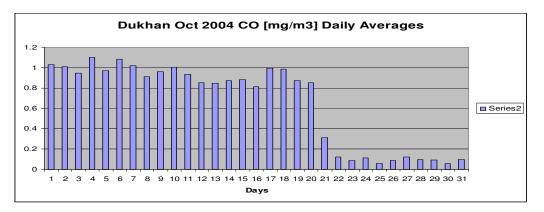


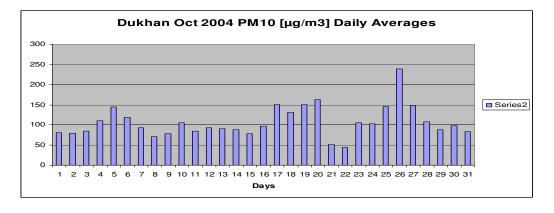


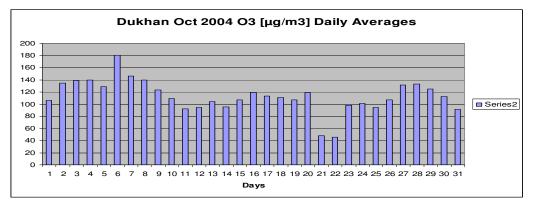
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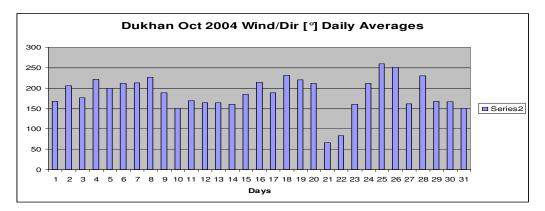


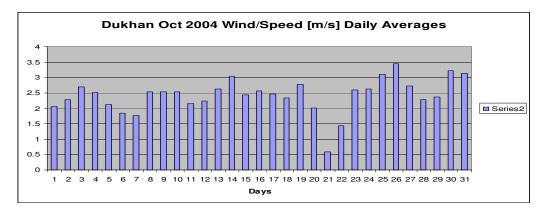




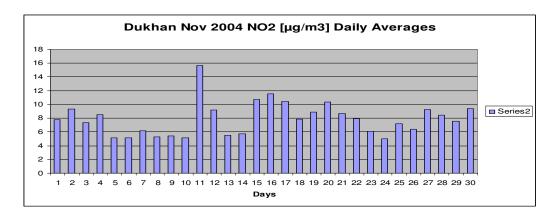


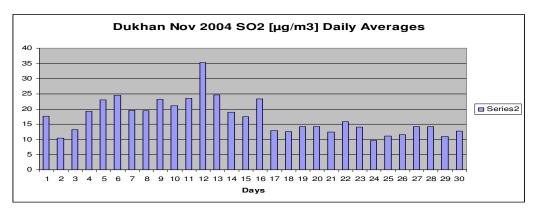


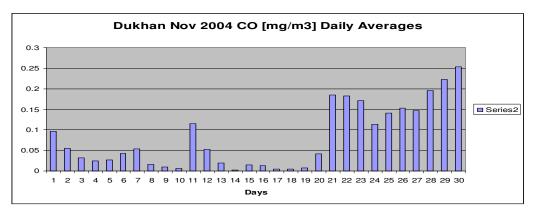


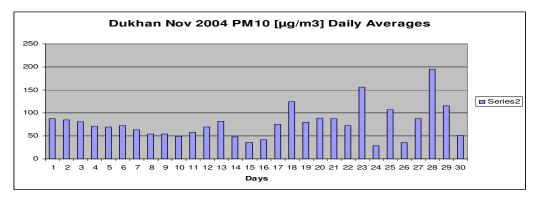


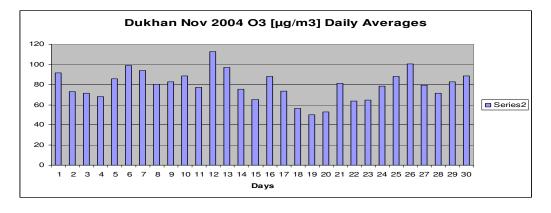
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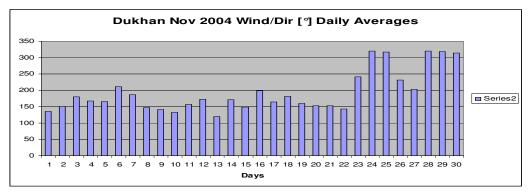


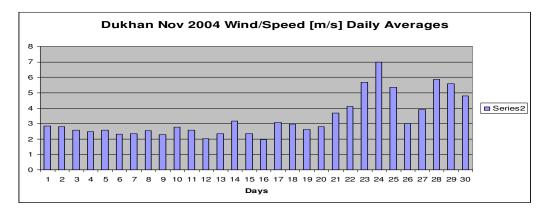




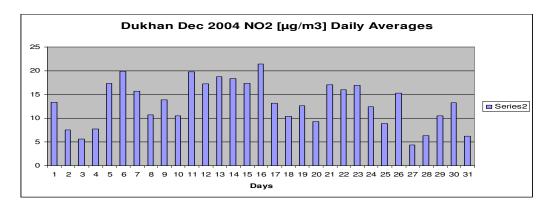


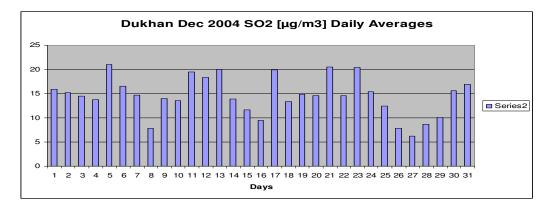


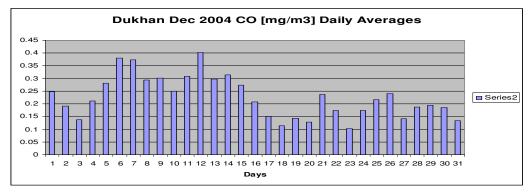


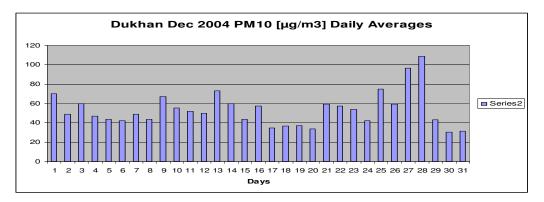


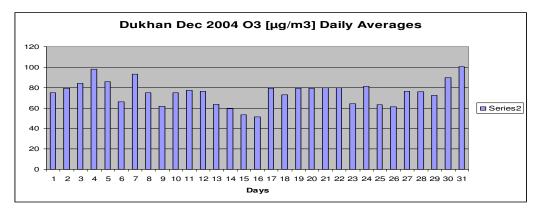
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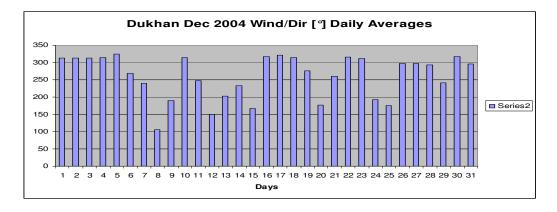


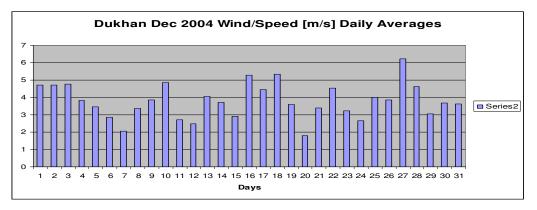






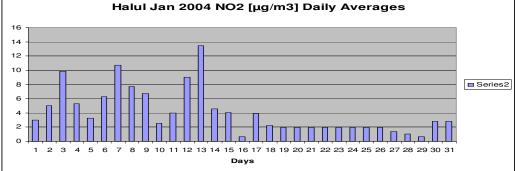


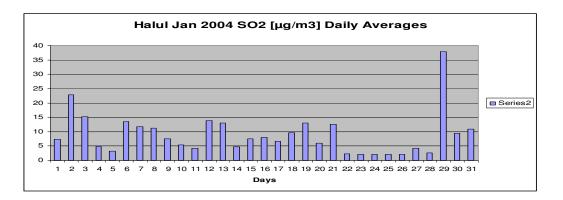


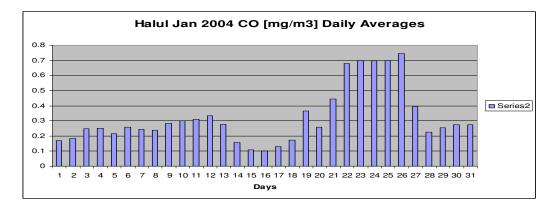


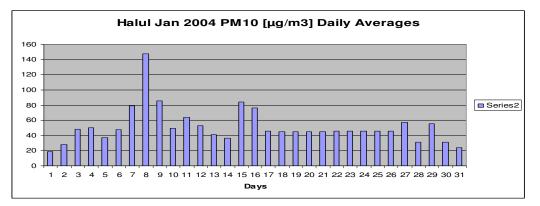
## 2.16 HALUL GRAPHS (24-Hour Averages of Data) / 2004

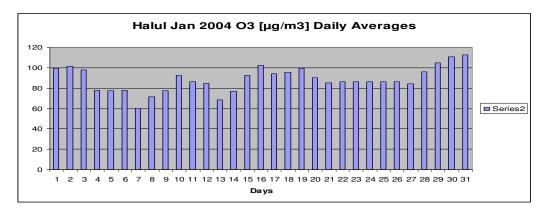


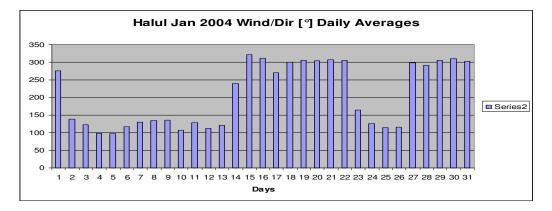


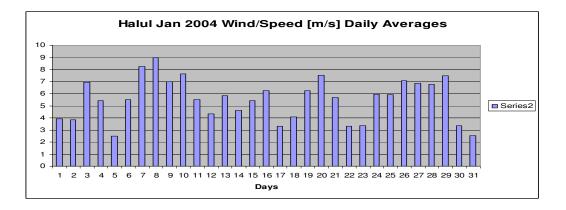




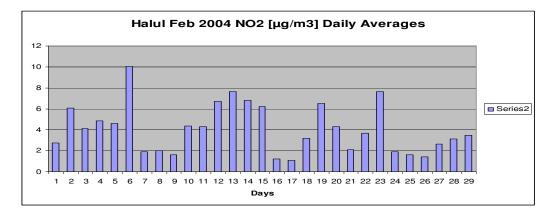


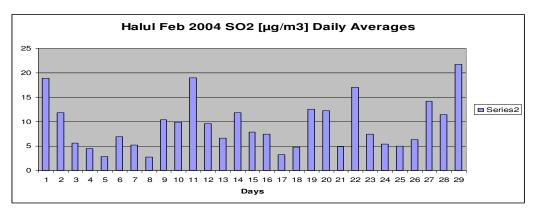


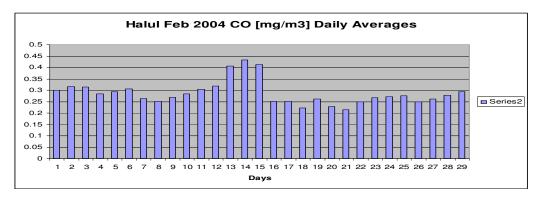


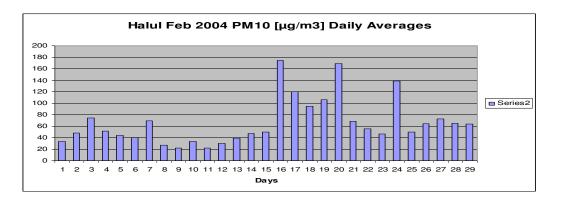


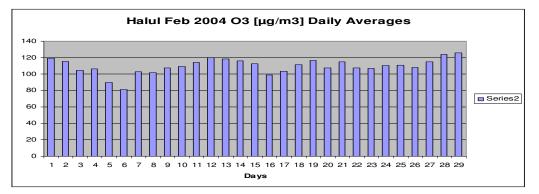
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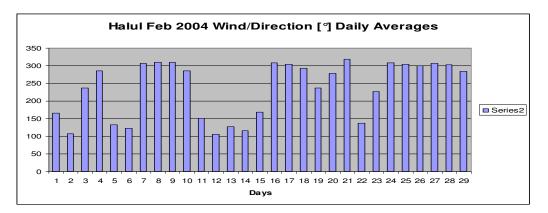


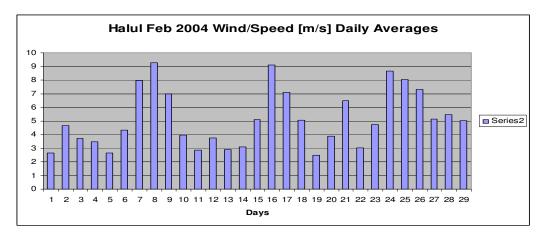




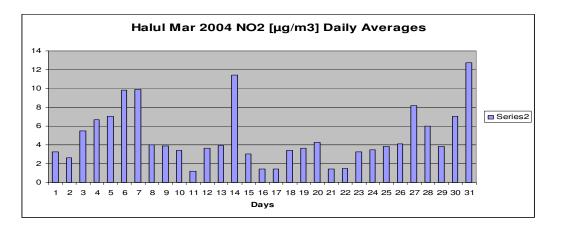


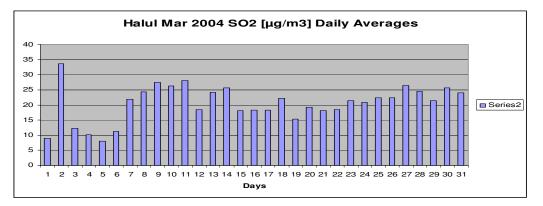


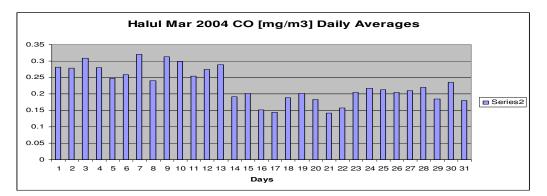


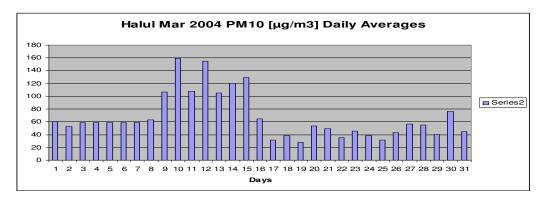


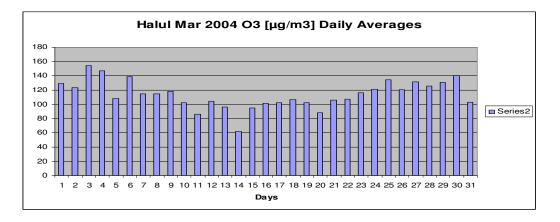
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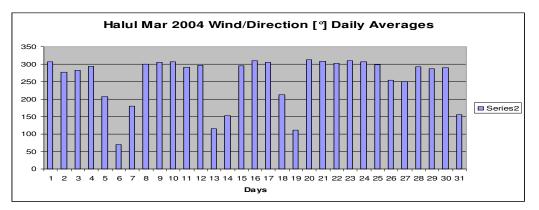


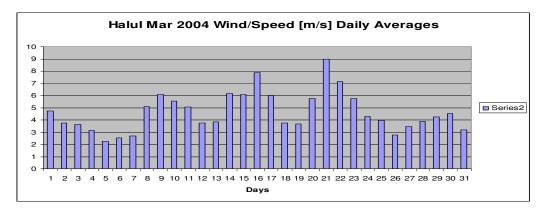




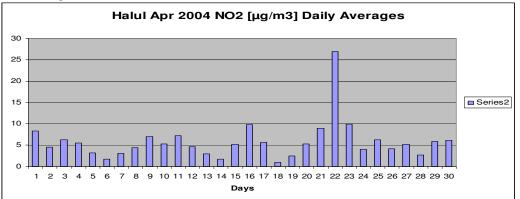


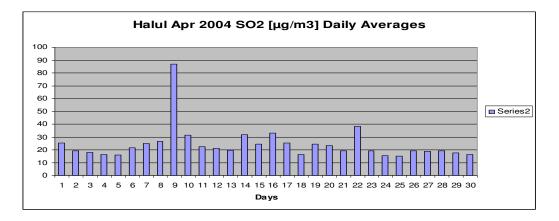


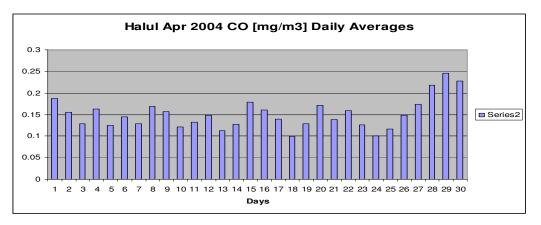


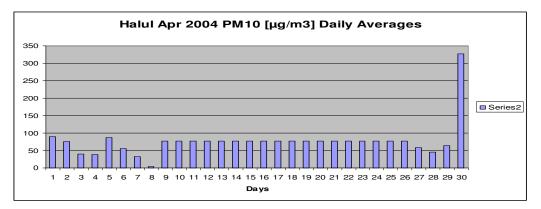


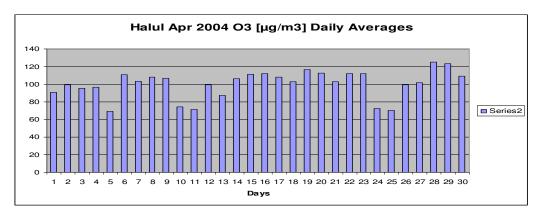
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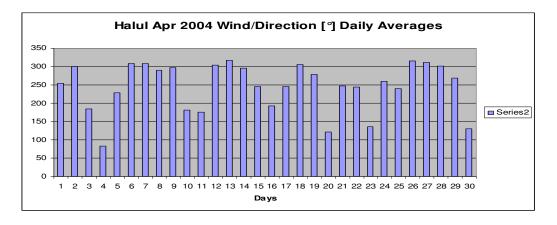


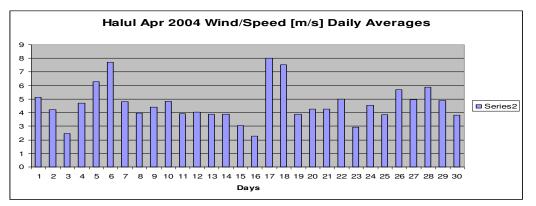




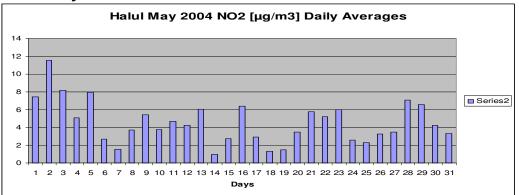


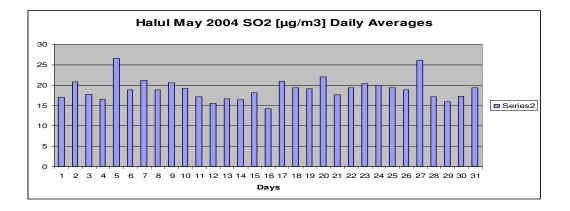


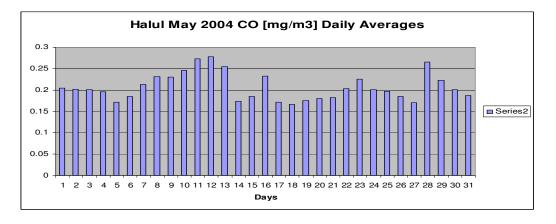


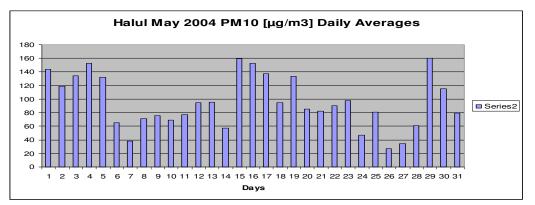


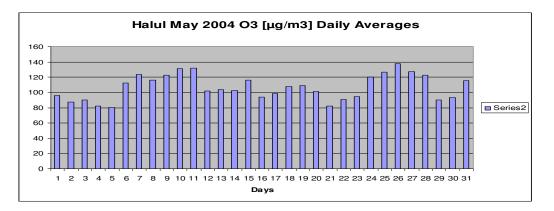
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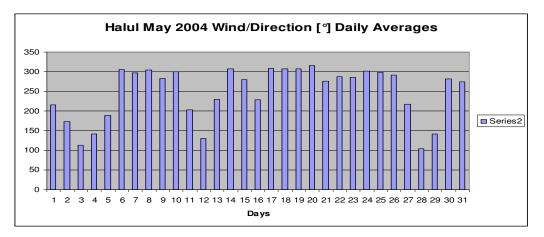


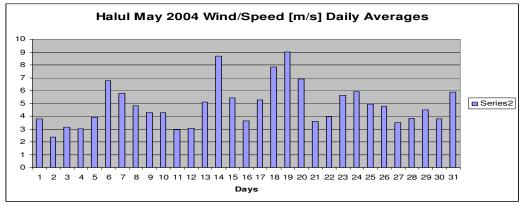




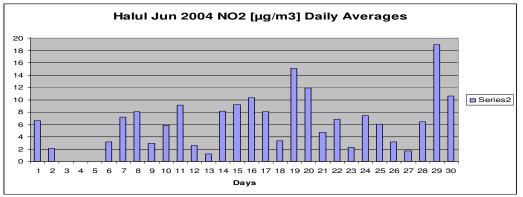


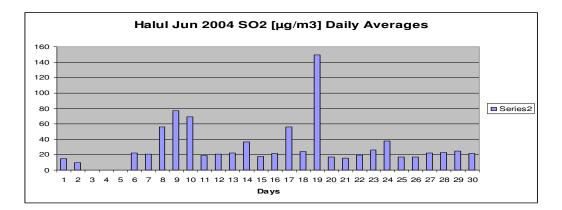


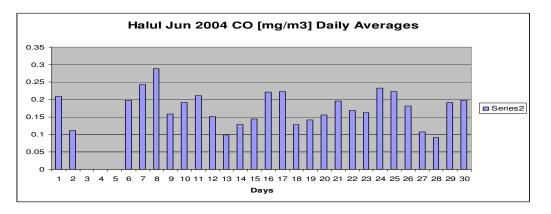


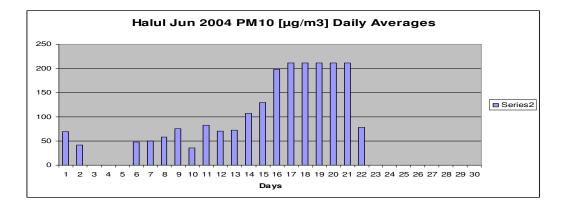


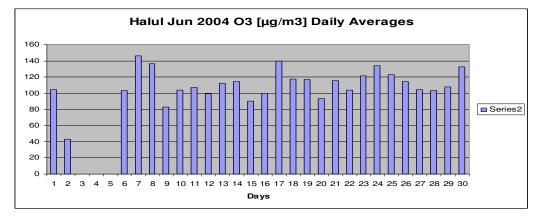


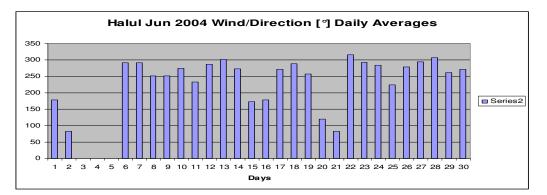


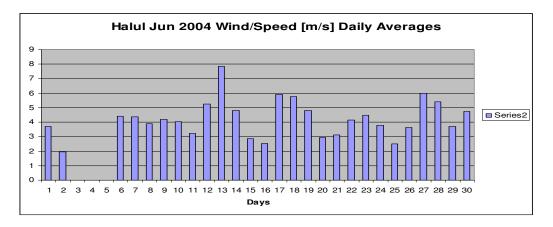




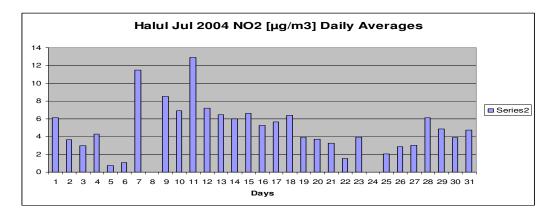


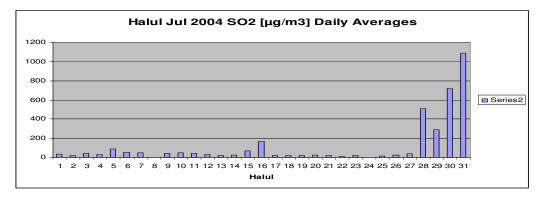


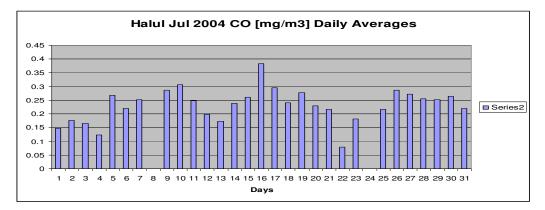


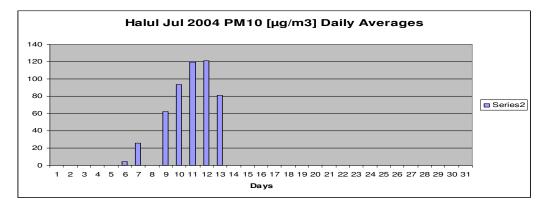


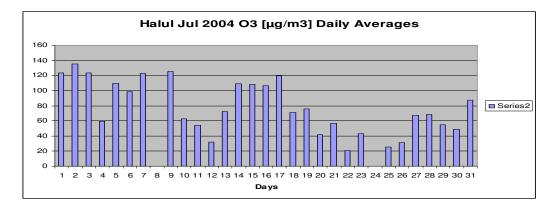
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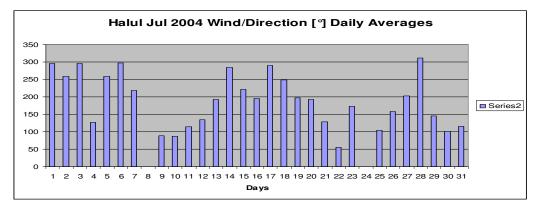


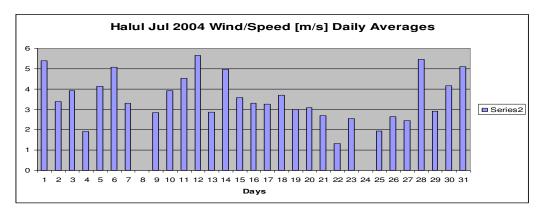




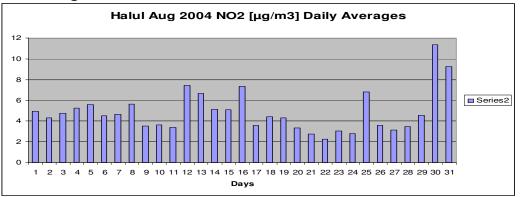


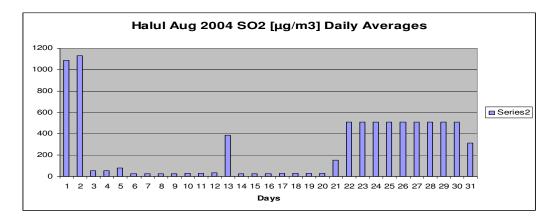


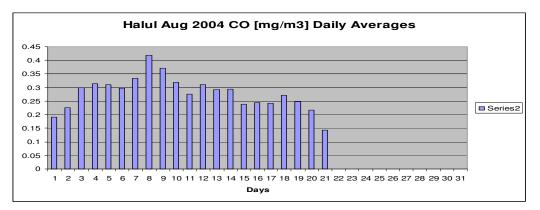


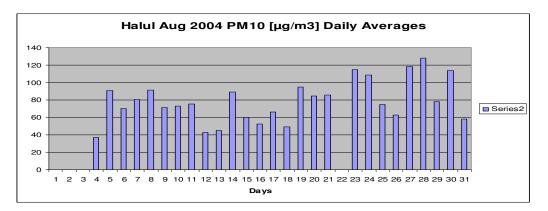


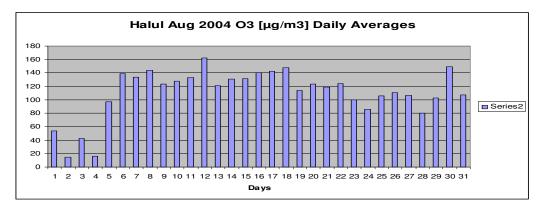
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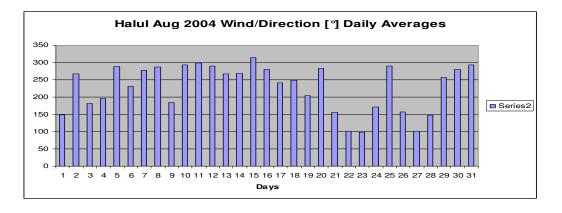


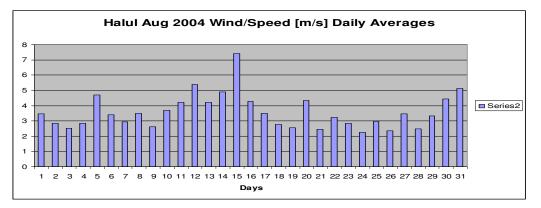




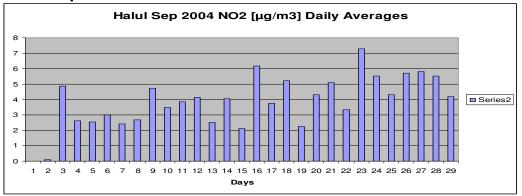


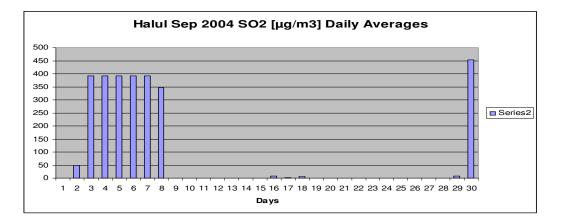


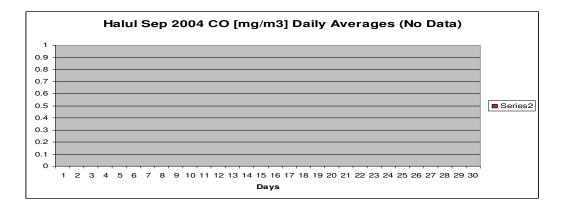


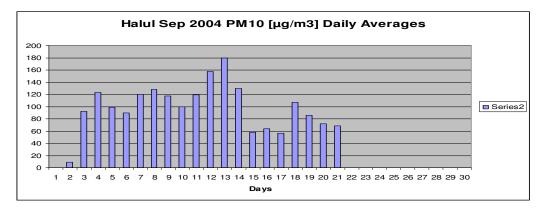


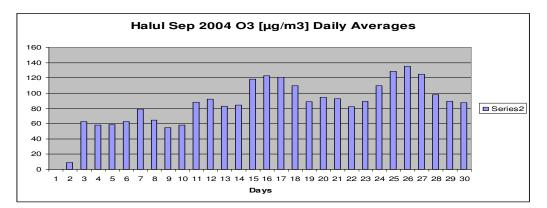
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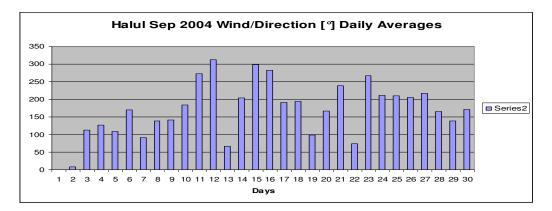


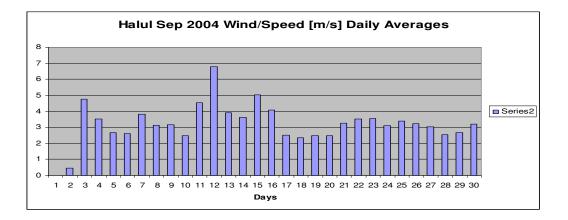




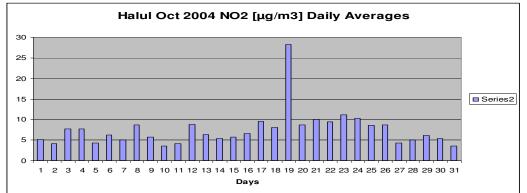


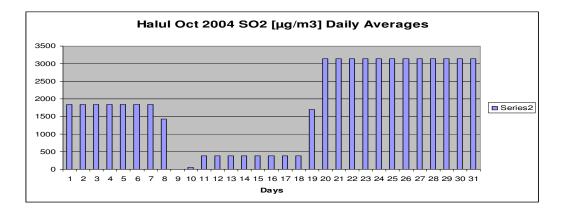


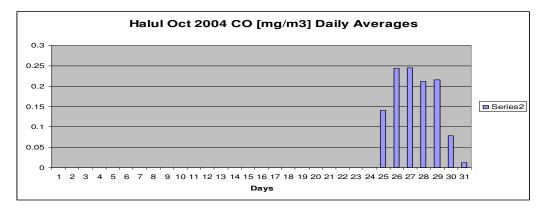


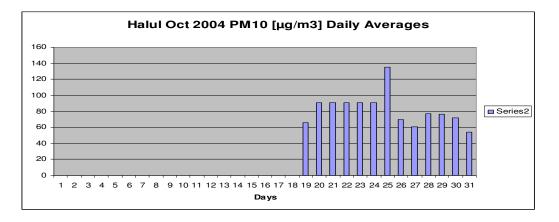


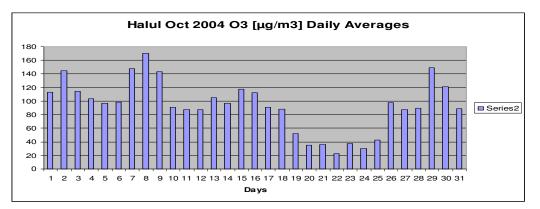
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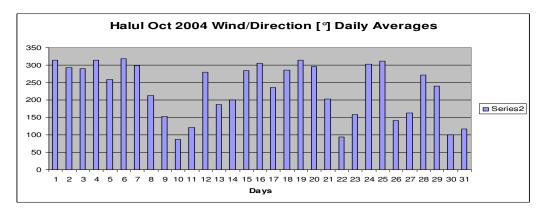


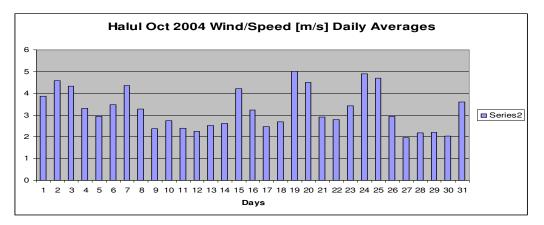




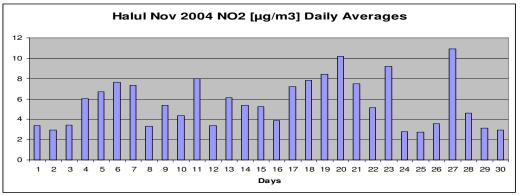


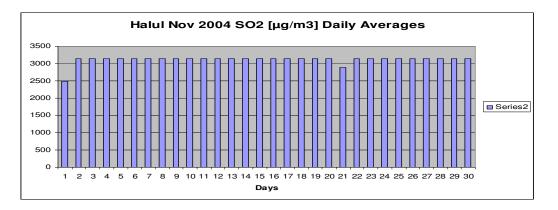


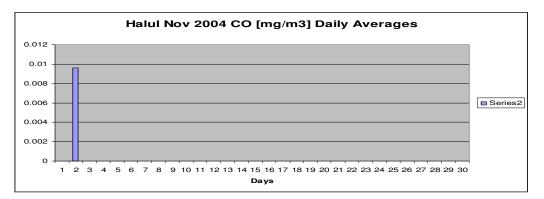


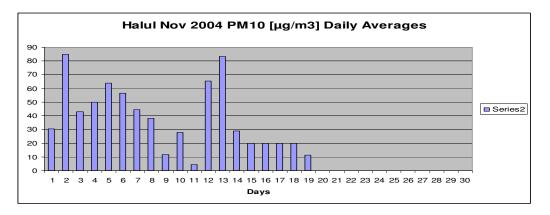


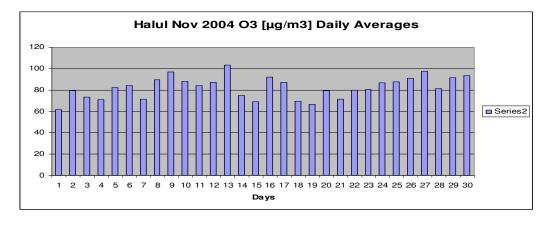
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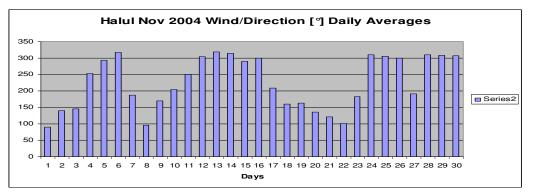


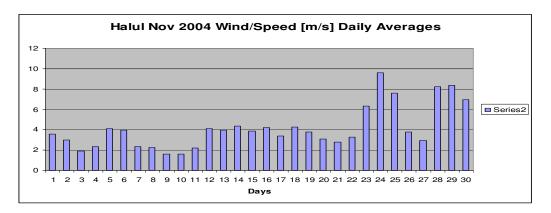




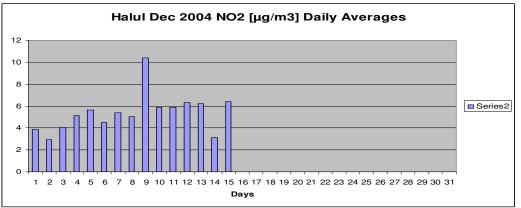


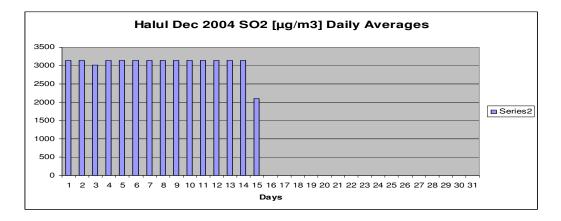


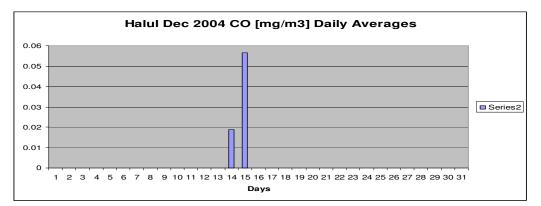


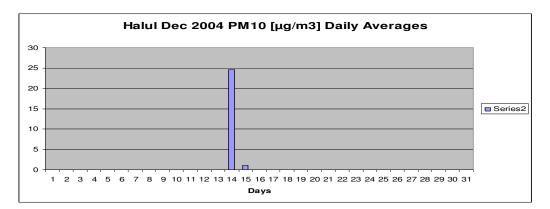


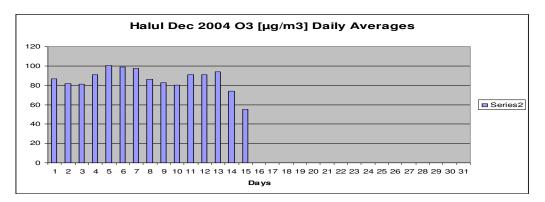
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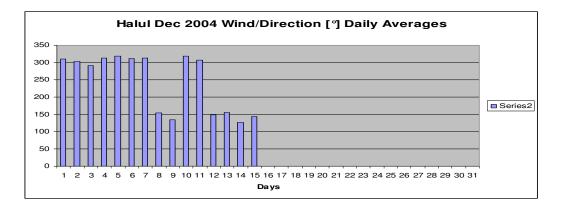


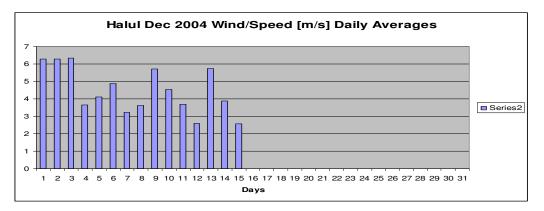




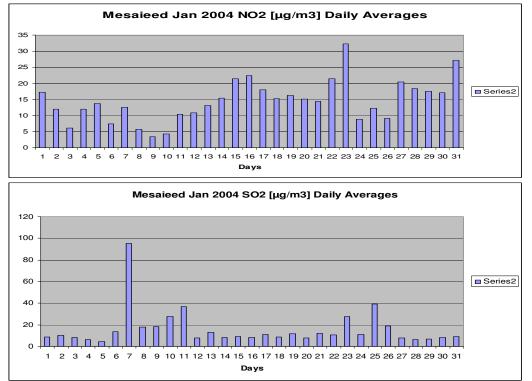




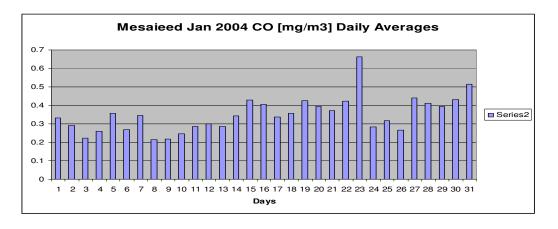


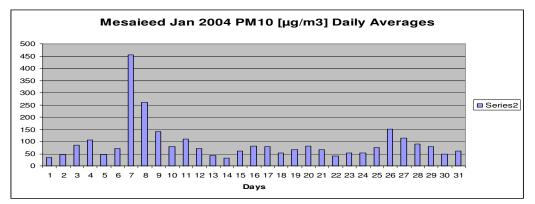


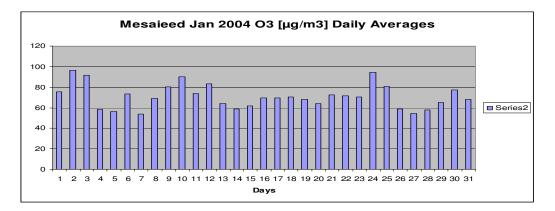
# 2.17 MESAIEED GRAPHS (24-Hour Averages of Data) / 2004

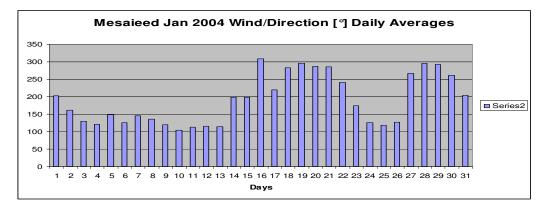


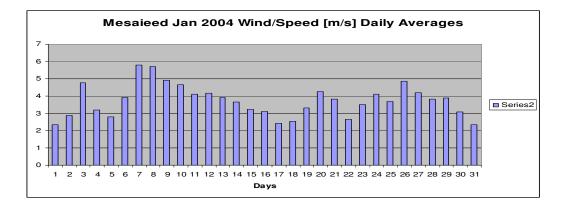
#### Mesaieed Jan 2004



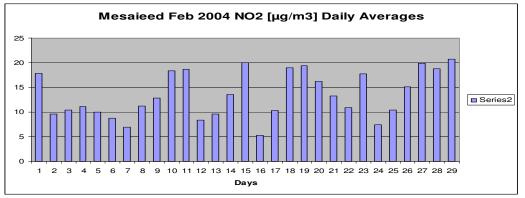


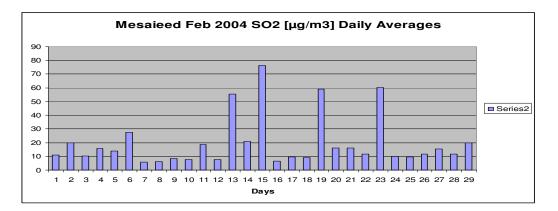


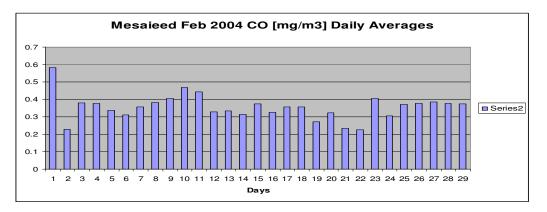


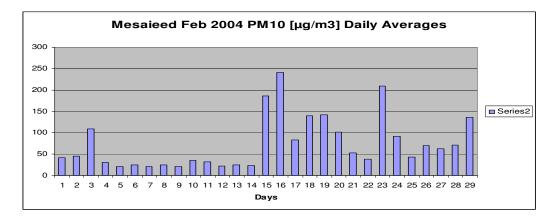


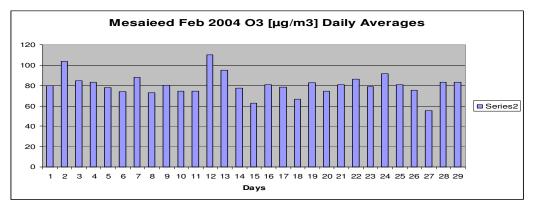
#### **Mesaieed Feb 2004**

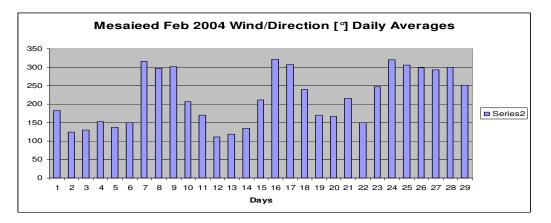


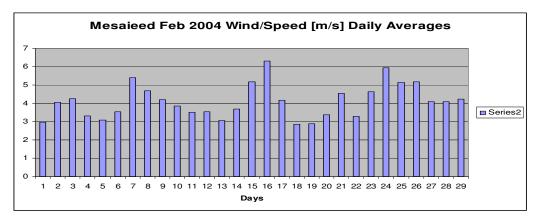




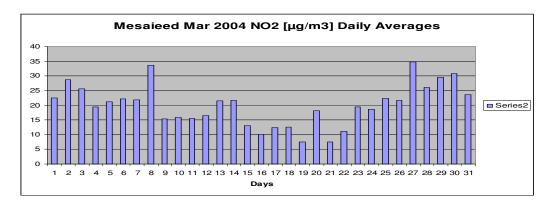


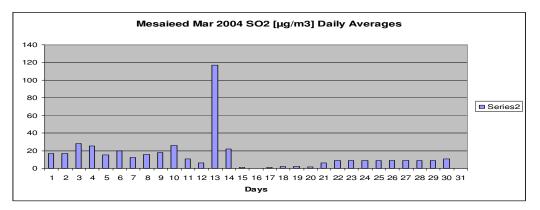


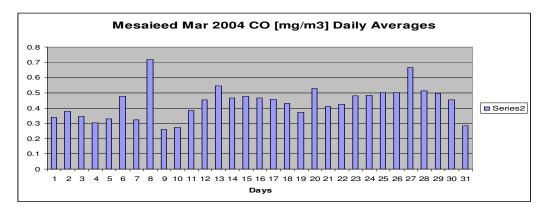


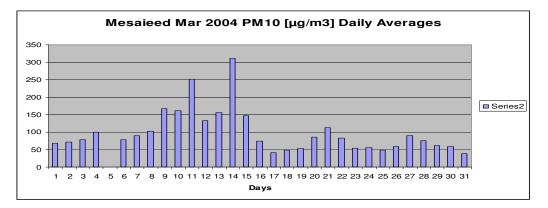


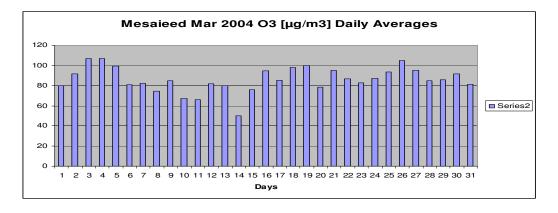
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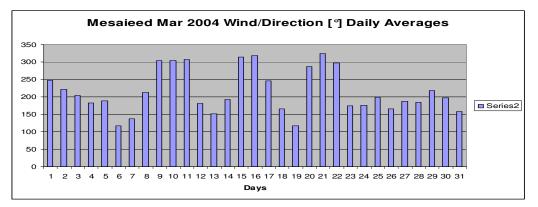


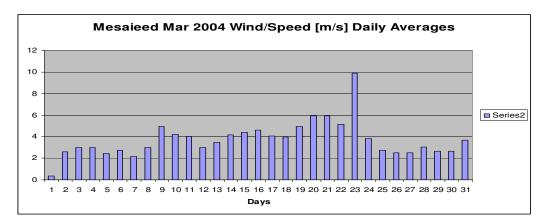




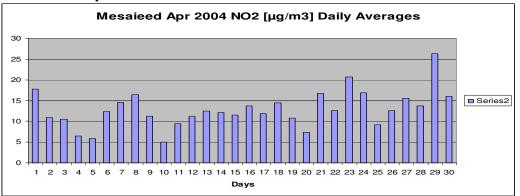


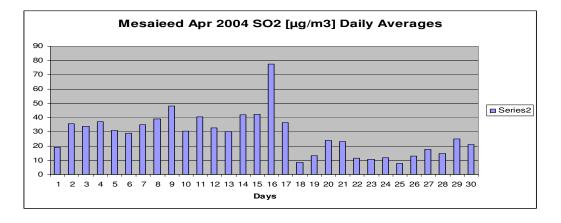


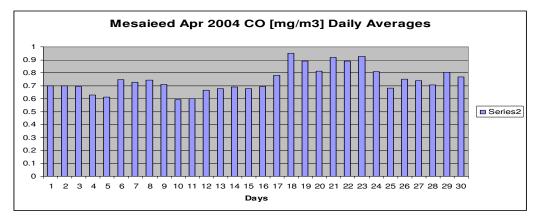


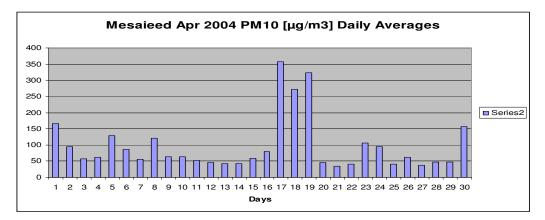


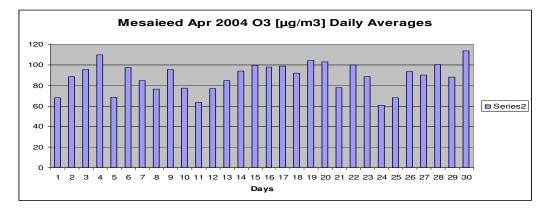
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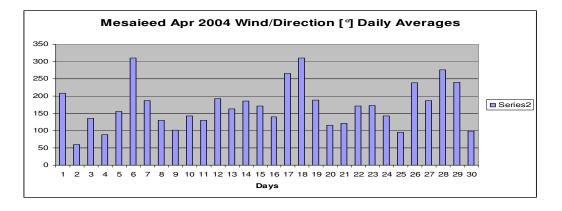


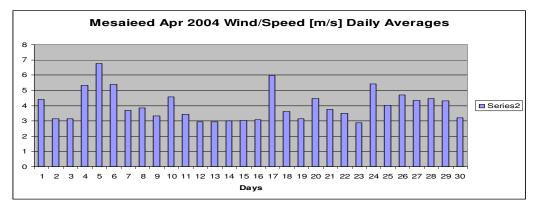




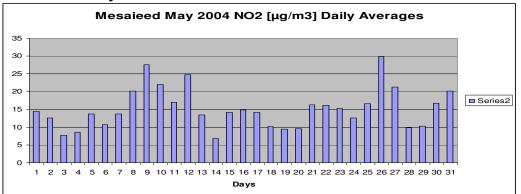


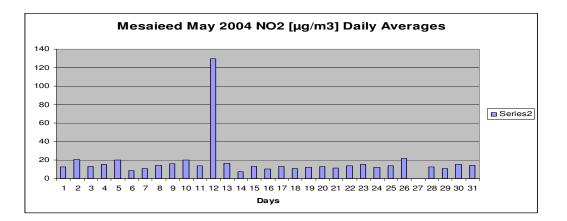


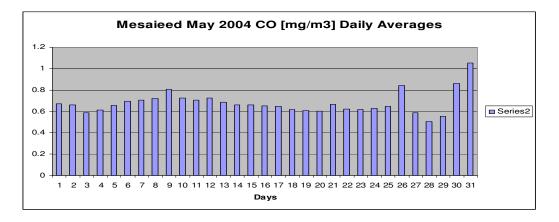


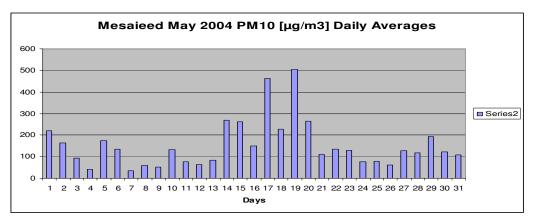


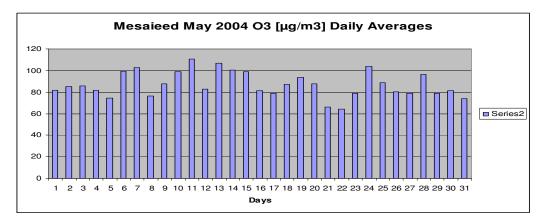
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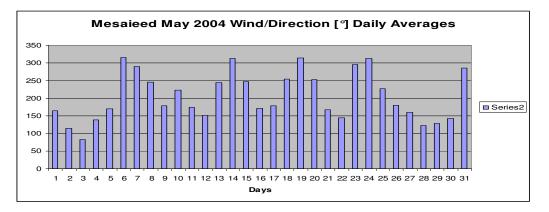


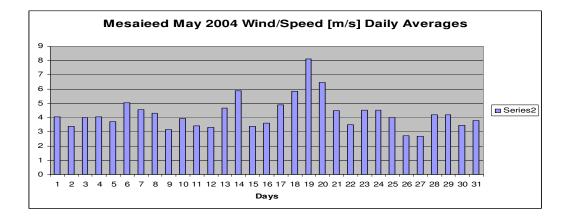




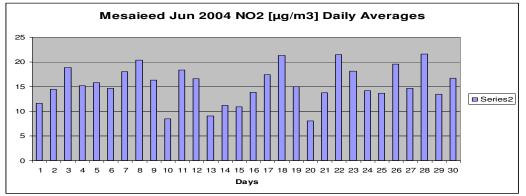


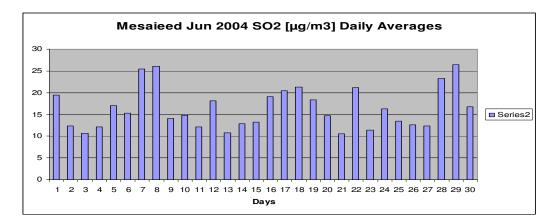


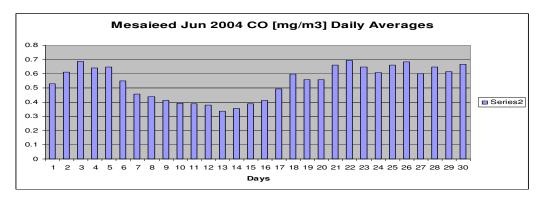


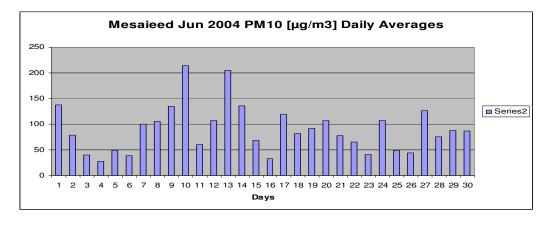


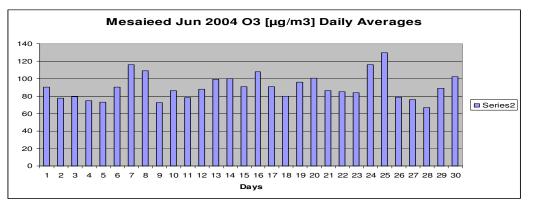
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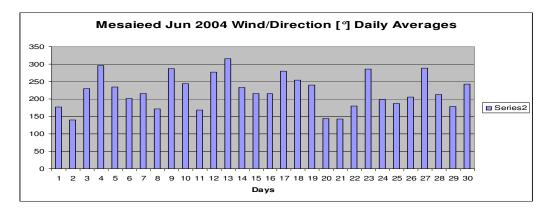


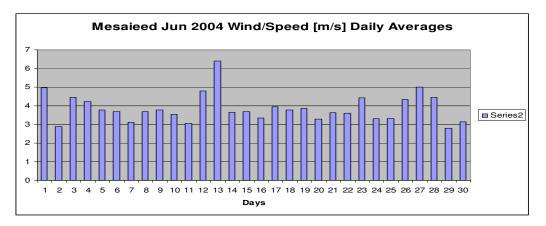




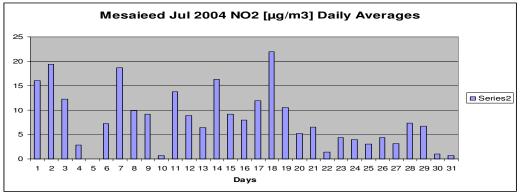


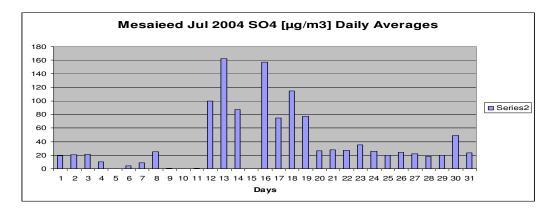


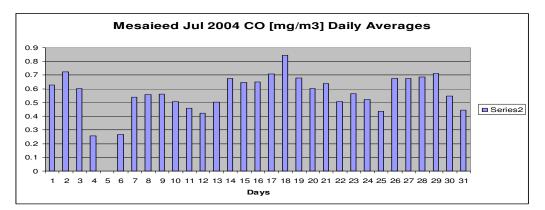


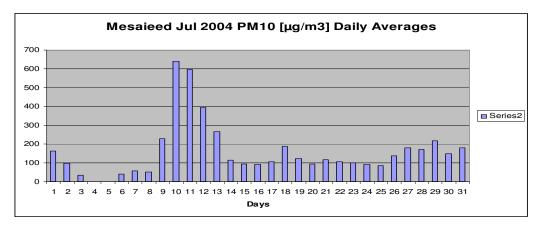


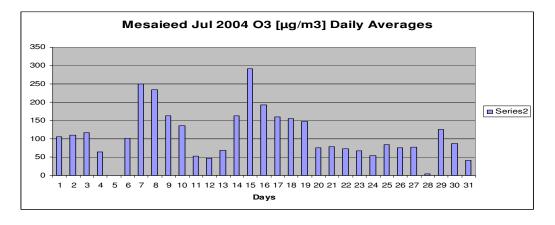
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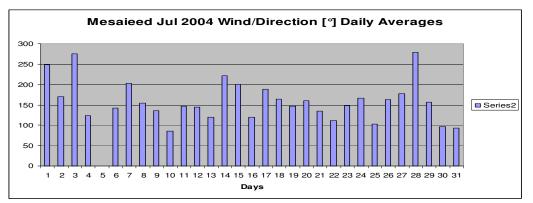


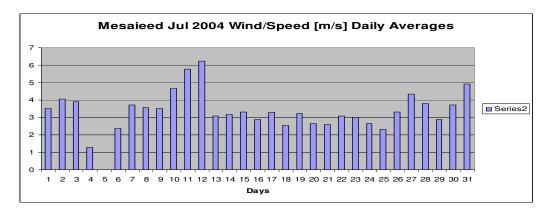




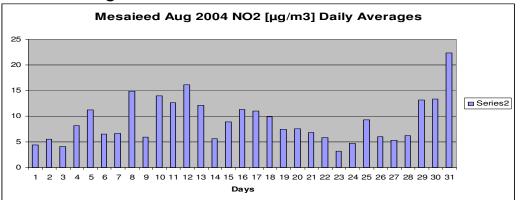


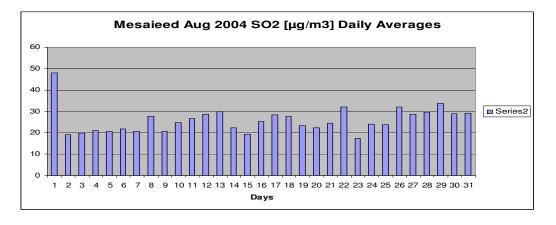


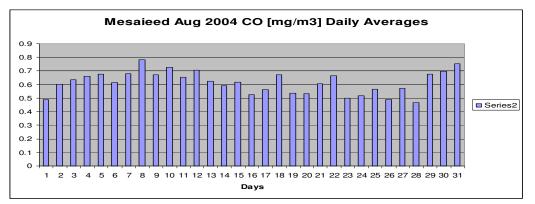


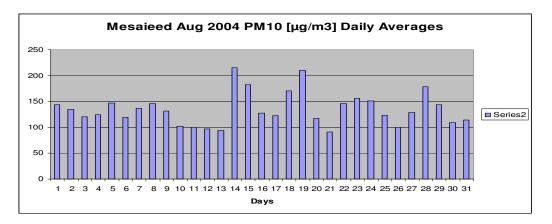


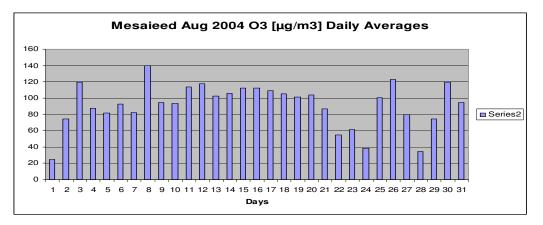
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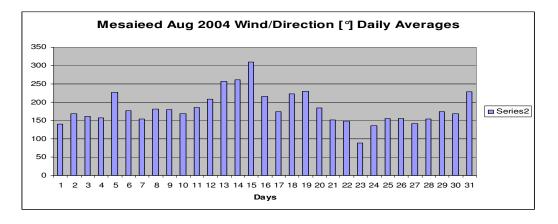


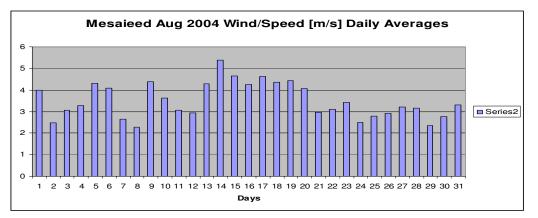




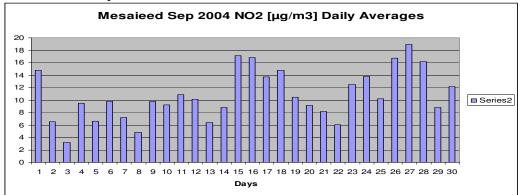


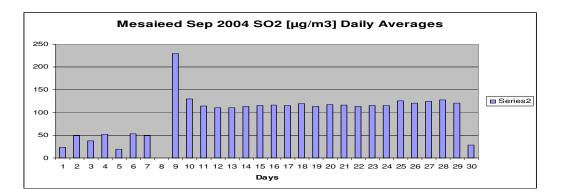


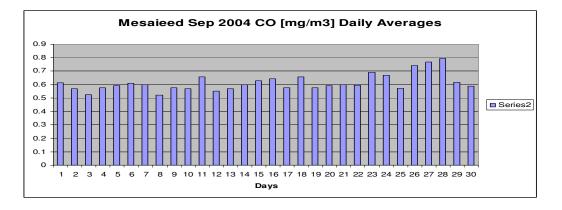


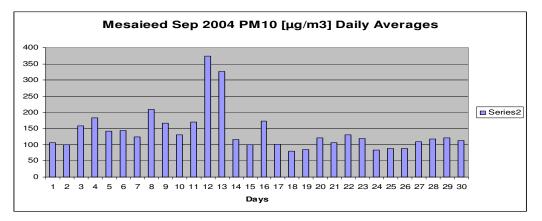


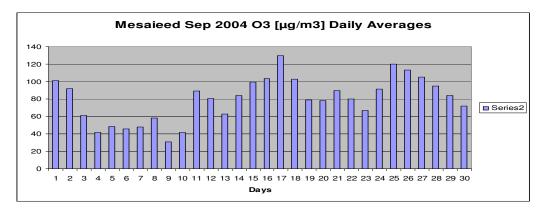
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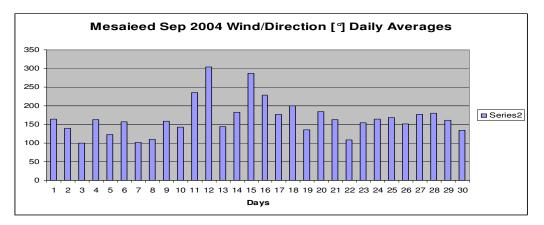


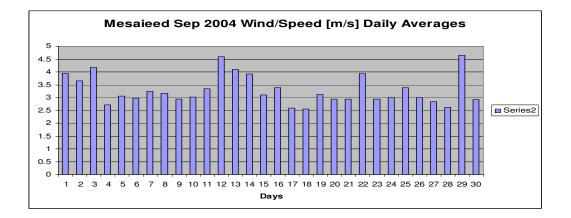




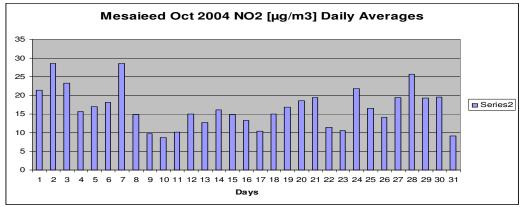


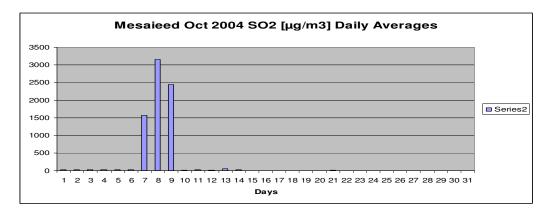


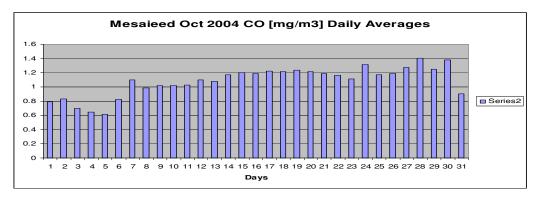


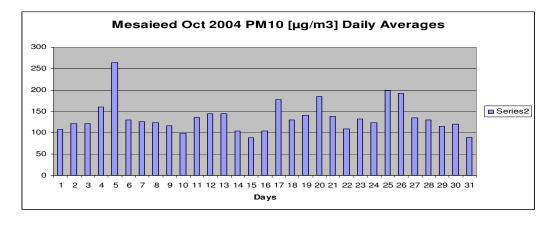


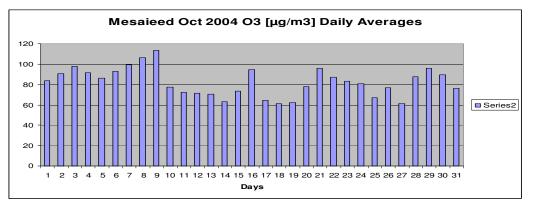
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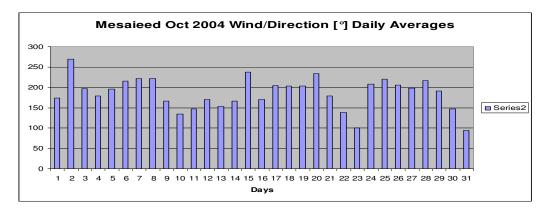


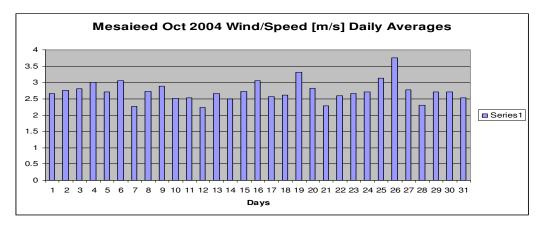




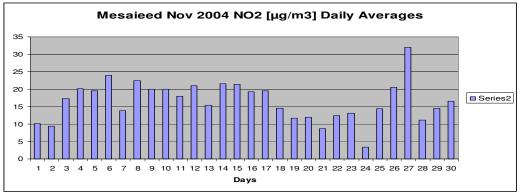


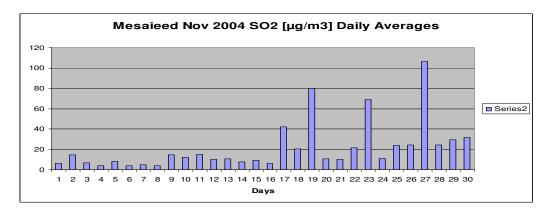


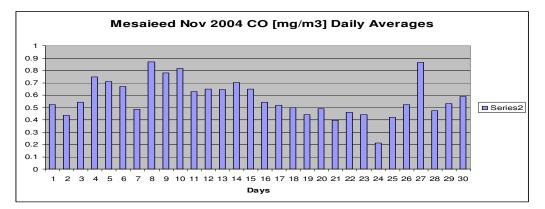


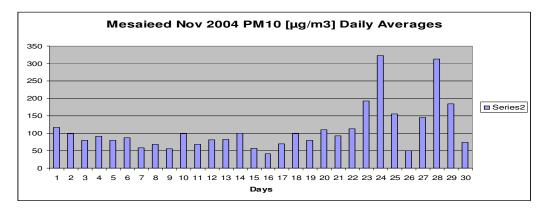


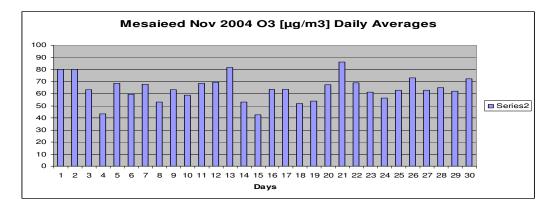
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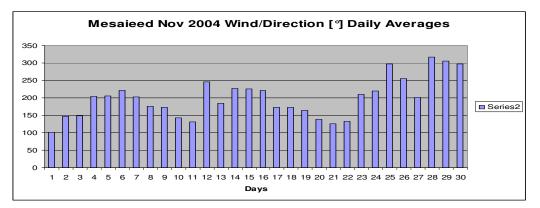


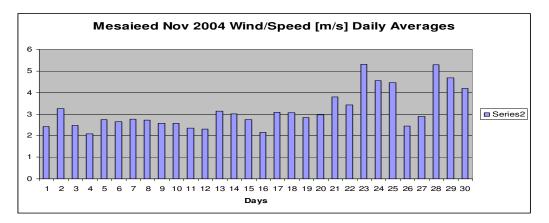




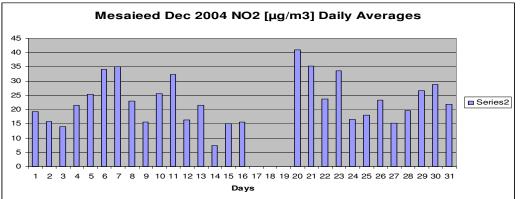


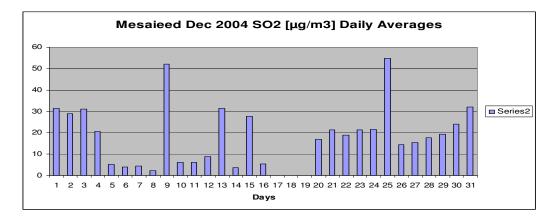


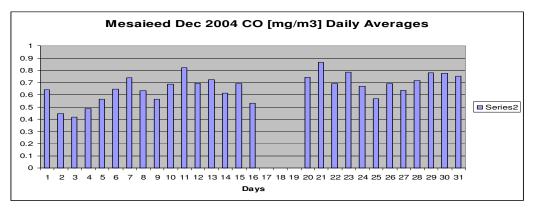


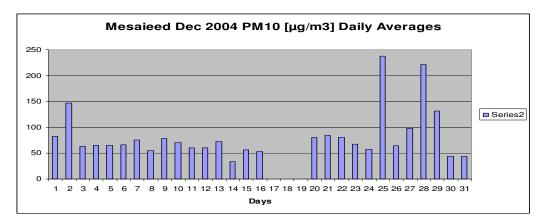


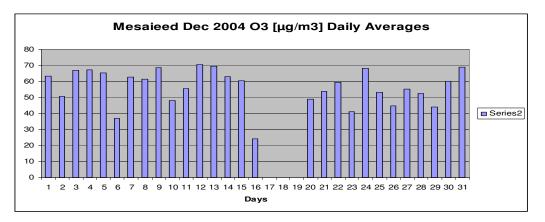
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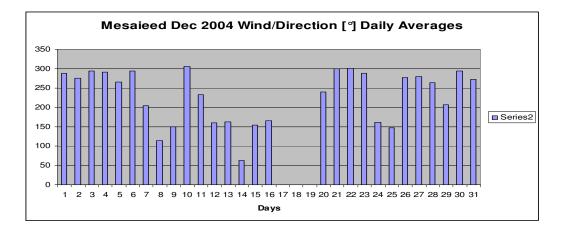


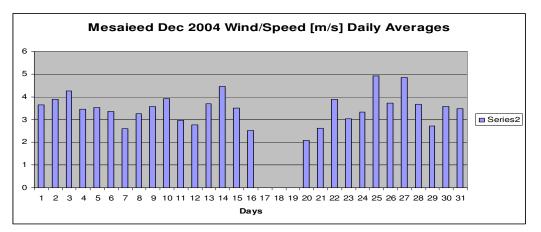




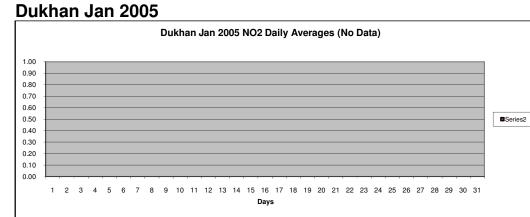


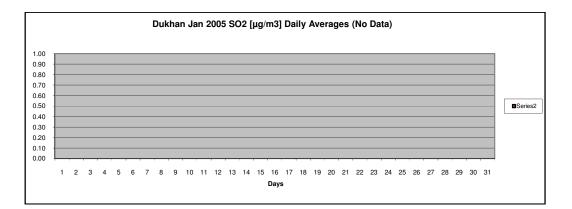


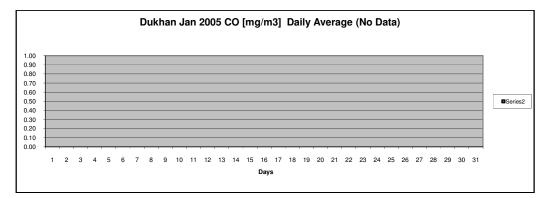


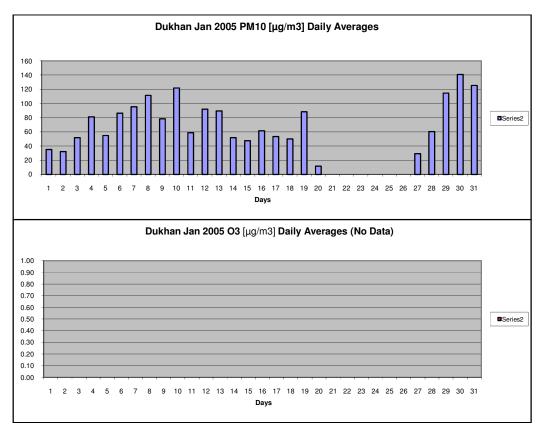


# 2.18 DUKHAN GRAPHS (24-Hour Averages of Data) / 2005

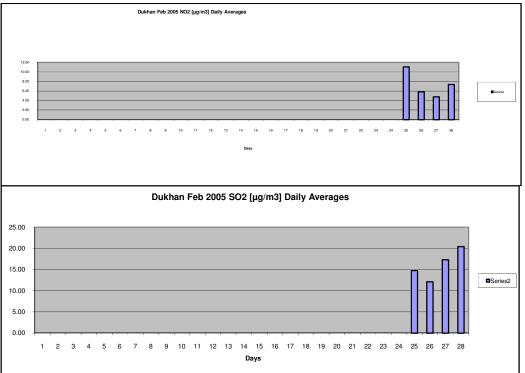


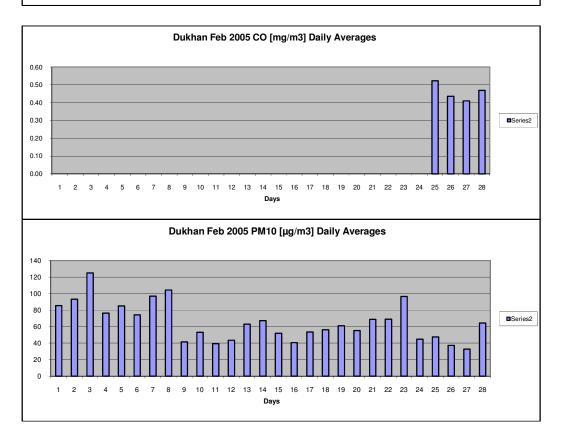


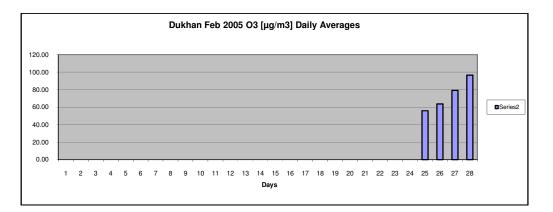




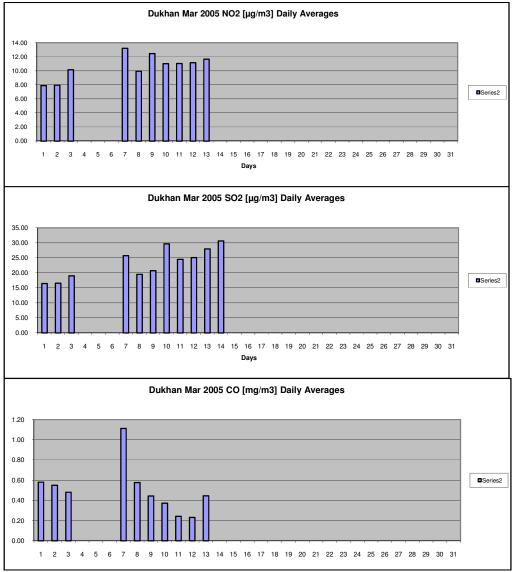
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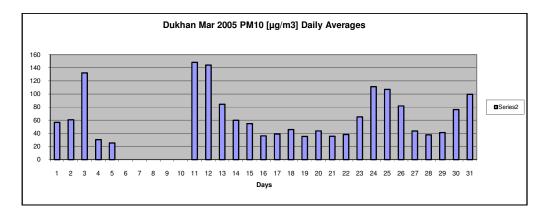


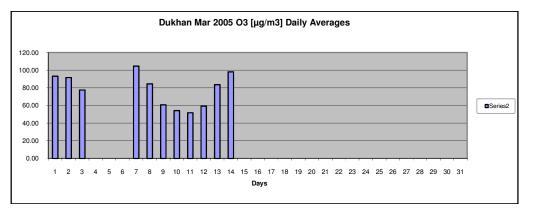




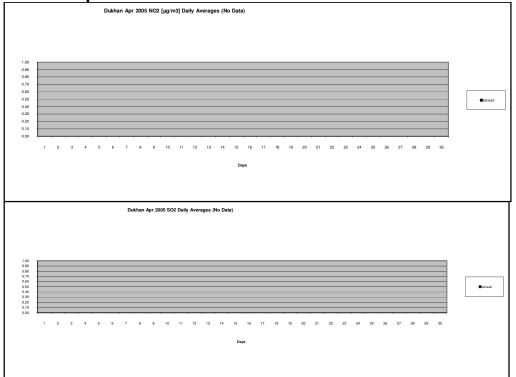
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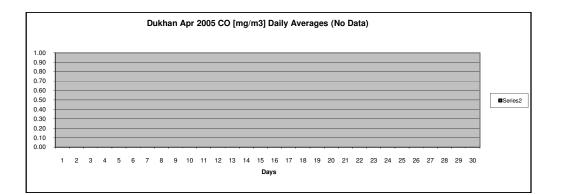


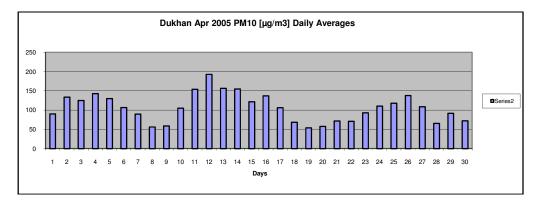


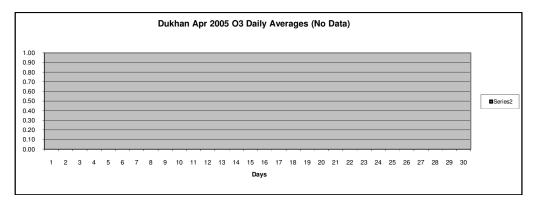


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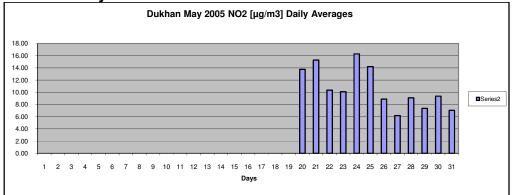


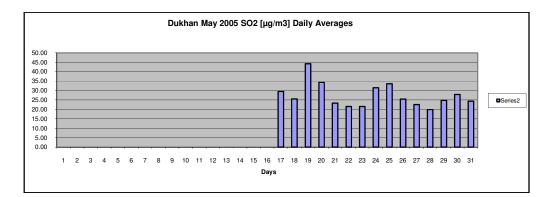


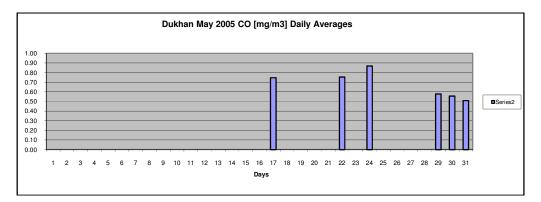


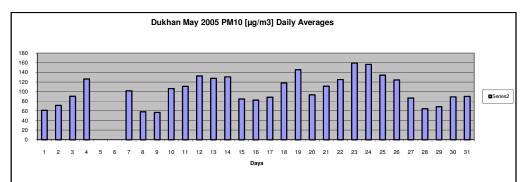


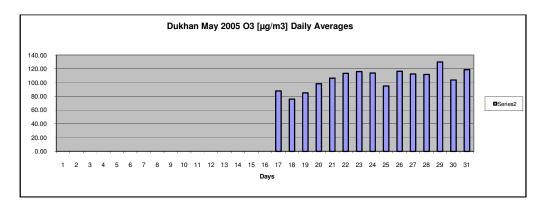
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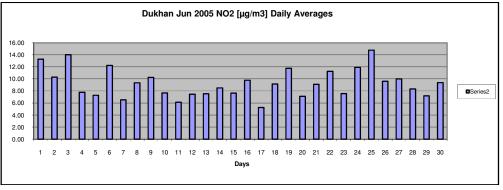


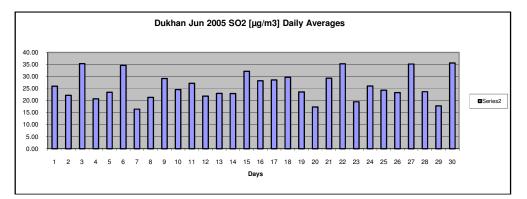


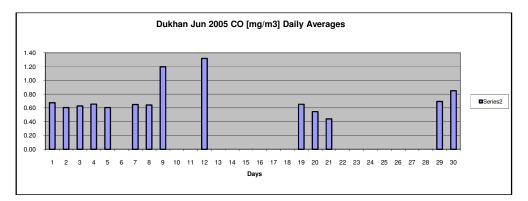


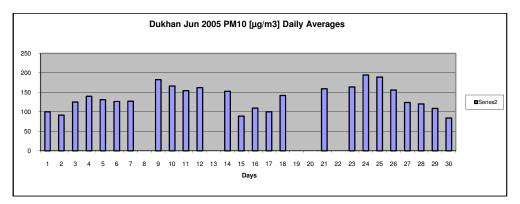


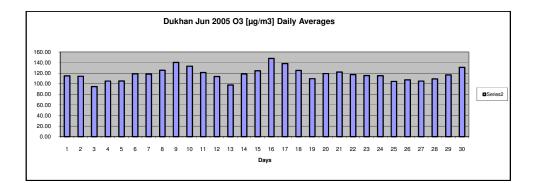
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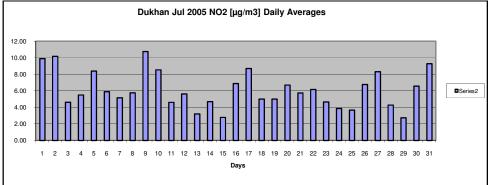


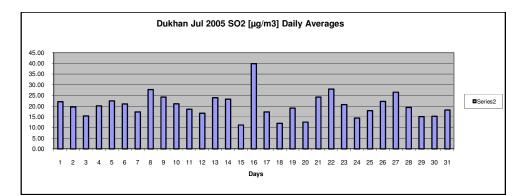


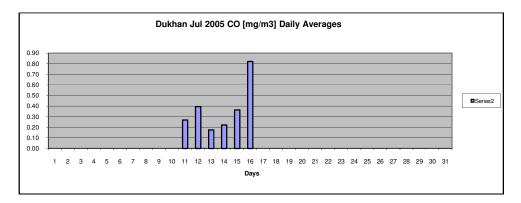


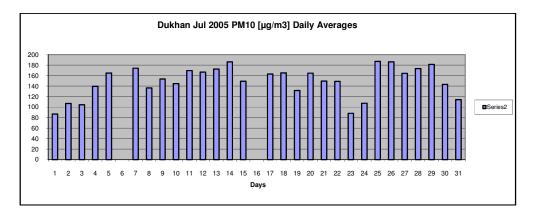


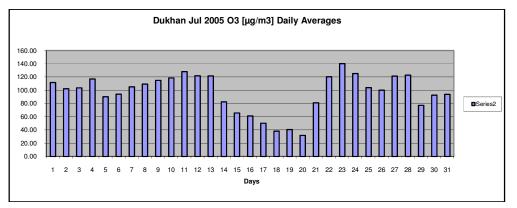
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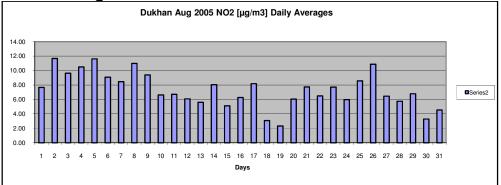


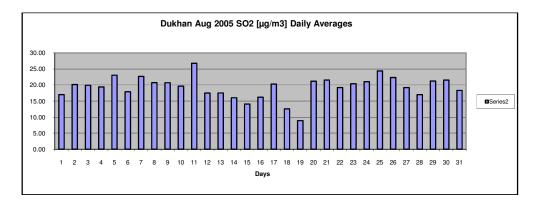


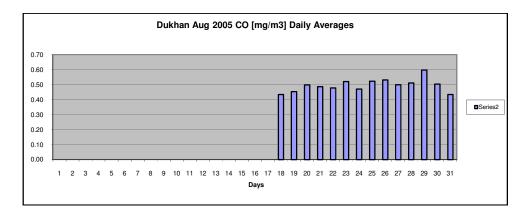


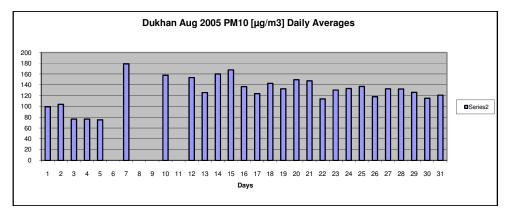


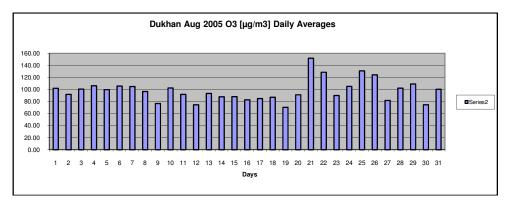
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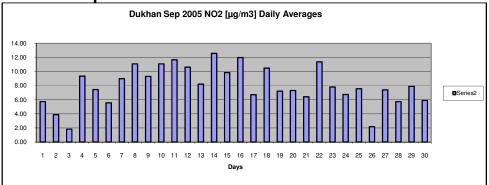


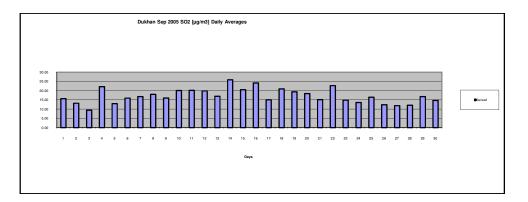


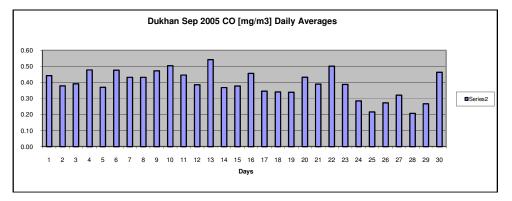


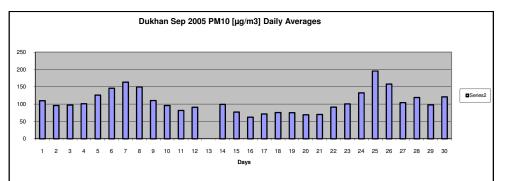


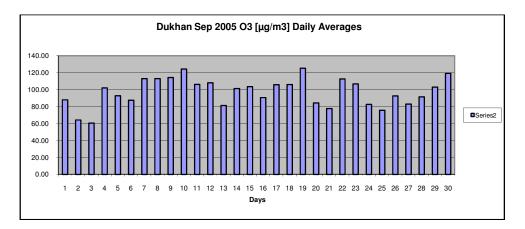
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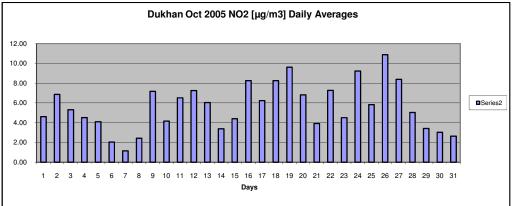


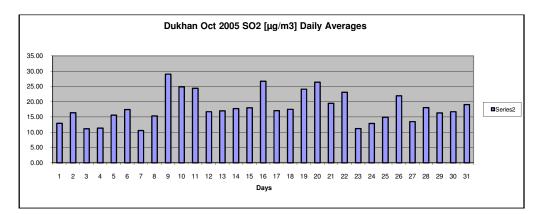


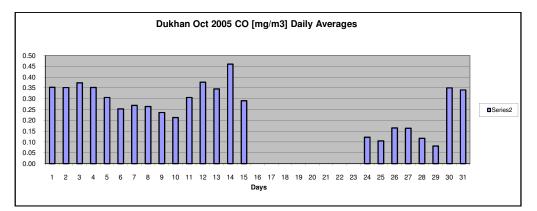


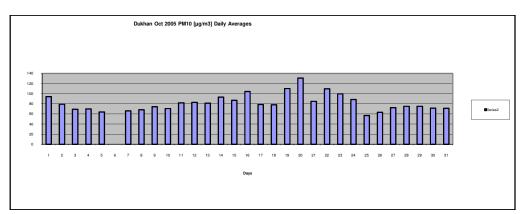


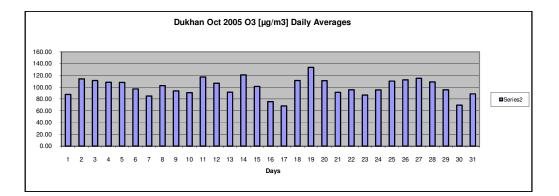
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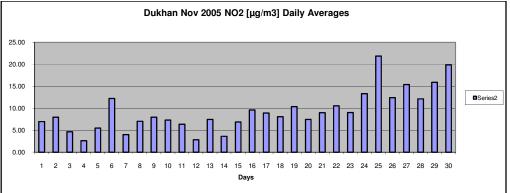


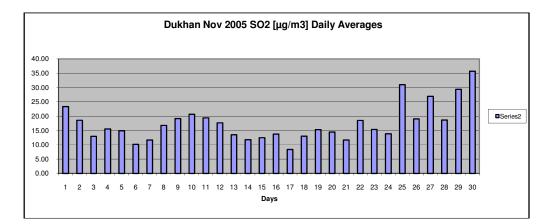


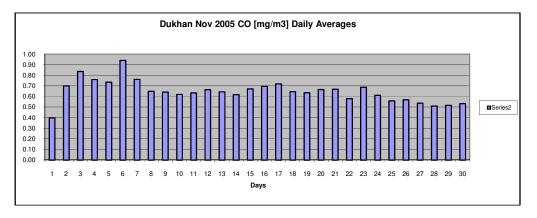


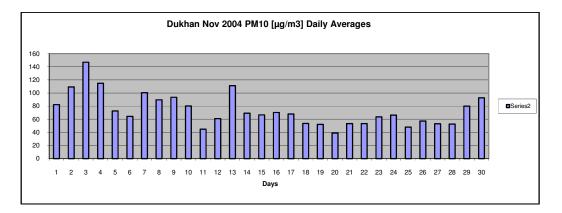


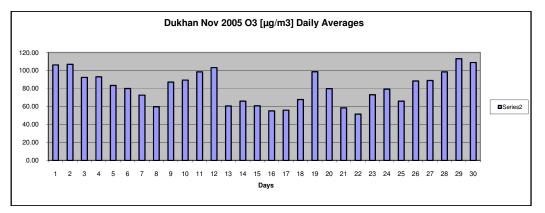
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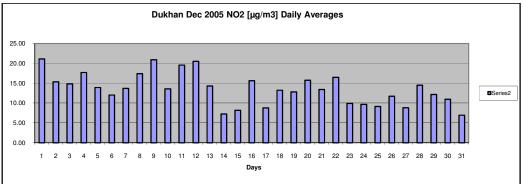


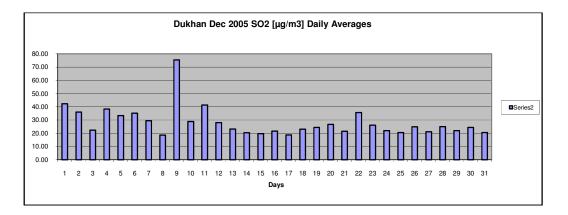


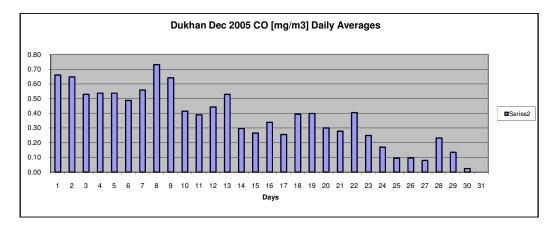


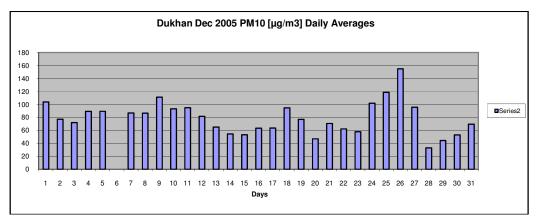


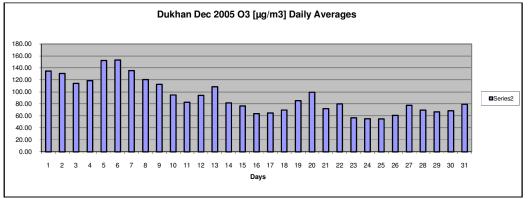
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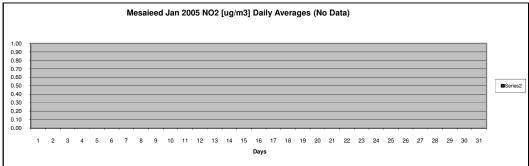


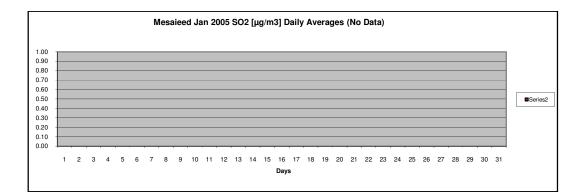


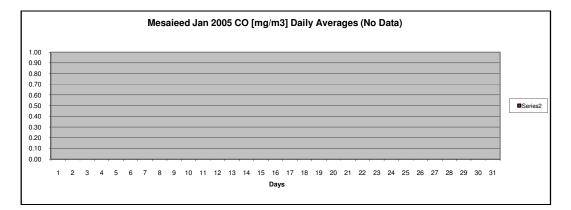


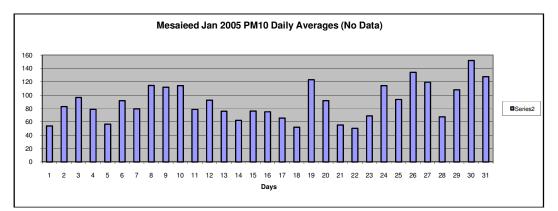
### 2.19 MESAIEED GRAPHS (24-Hour Averages of Data) / 2005

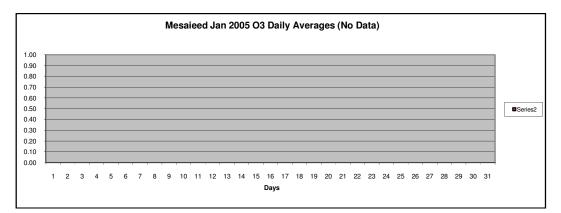
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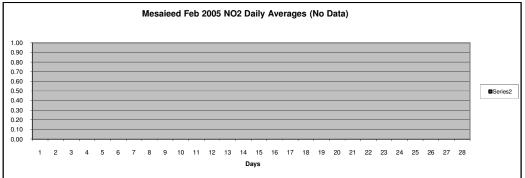


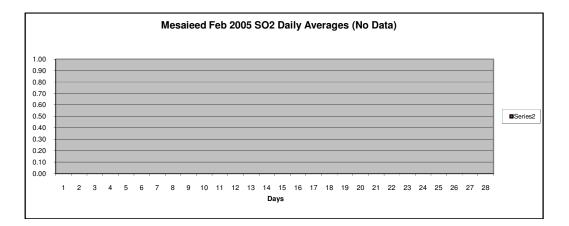


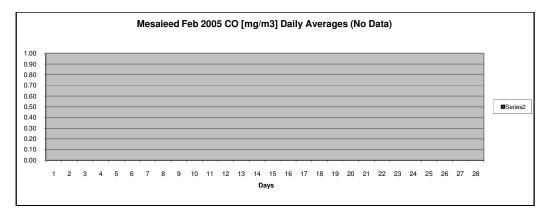


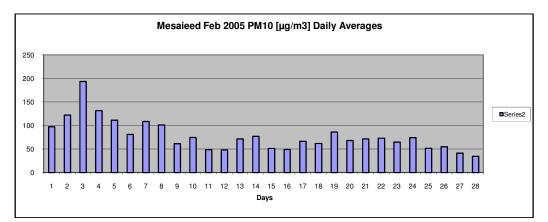


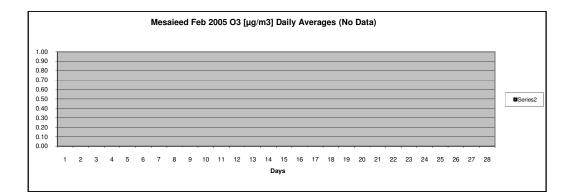
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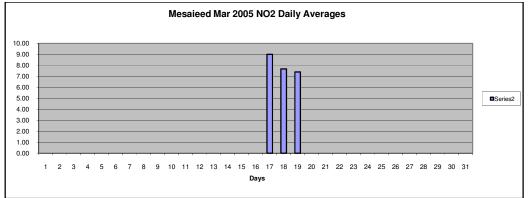


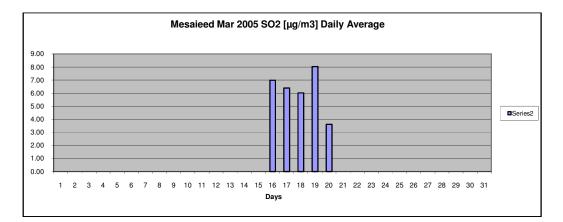


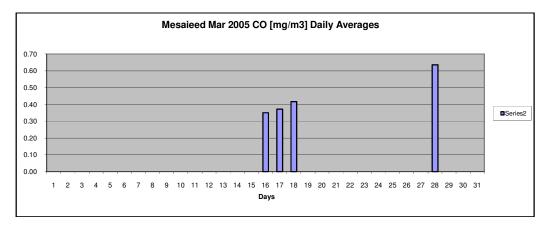


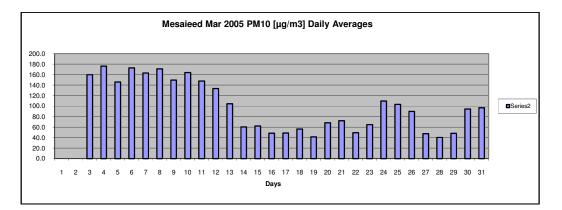


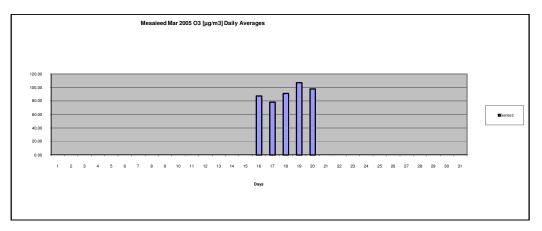
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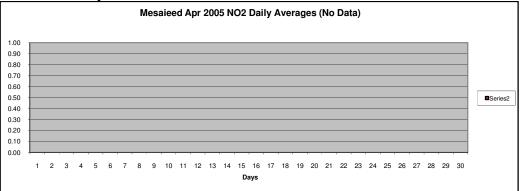


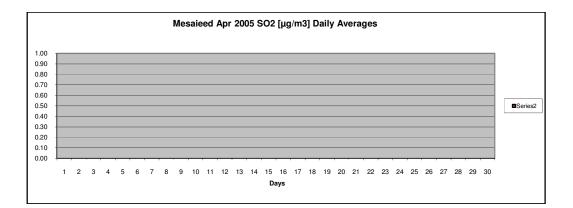


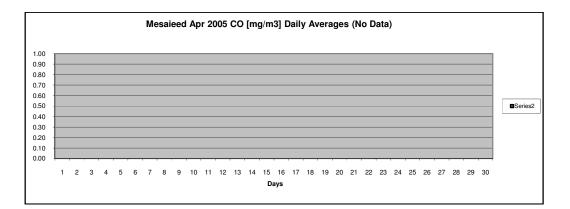


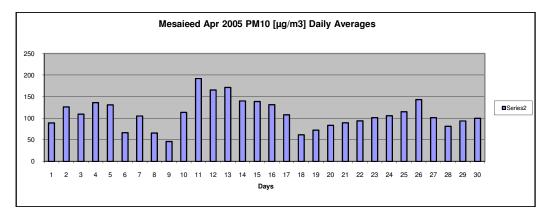


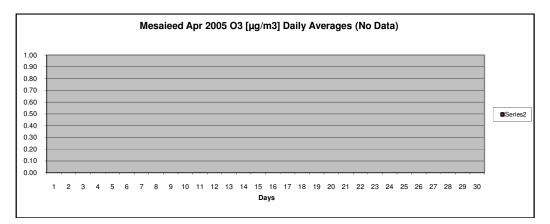
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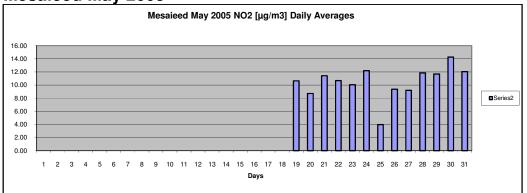


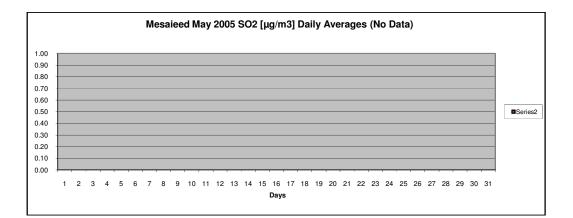


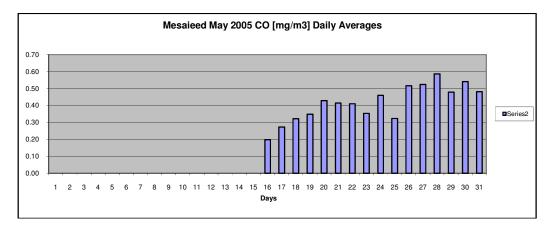


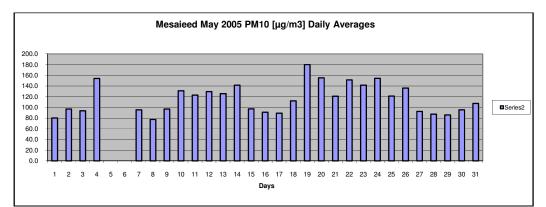


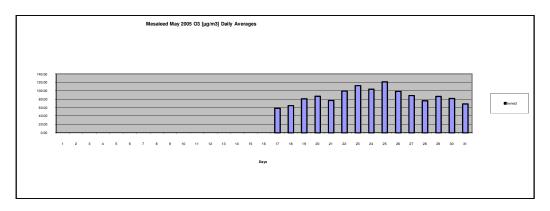
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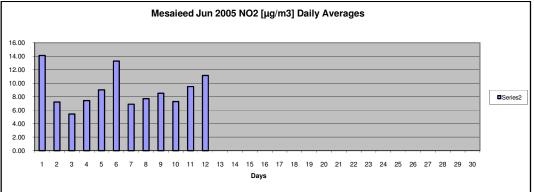


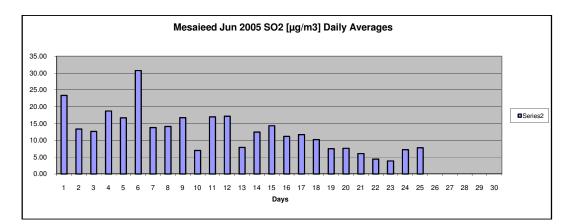


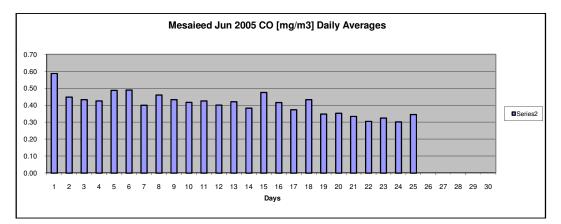


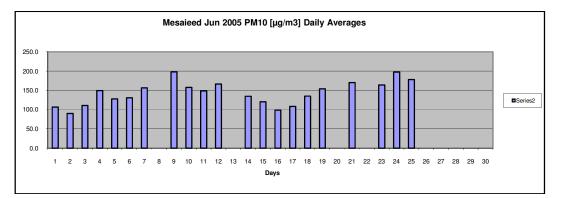


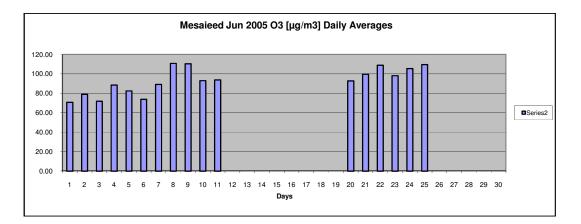
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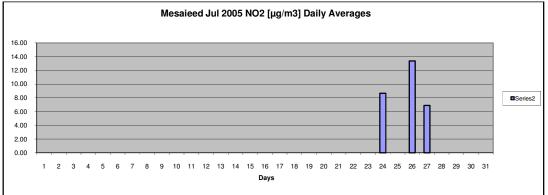


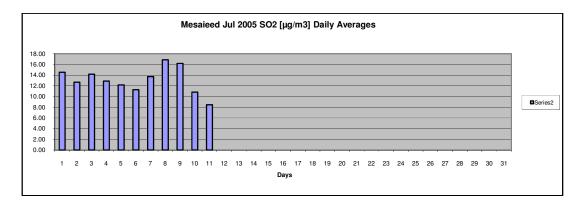


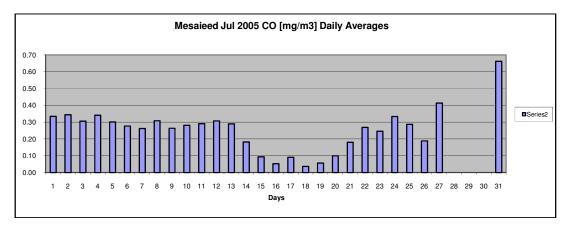


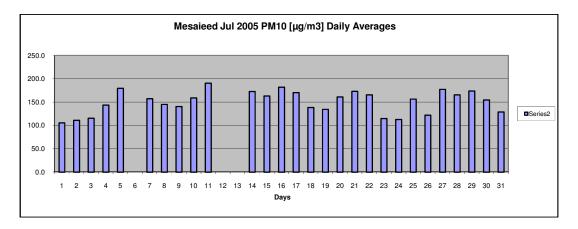


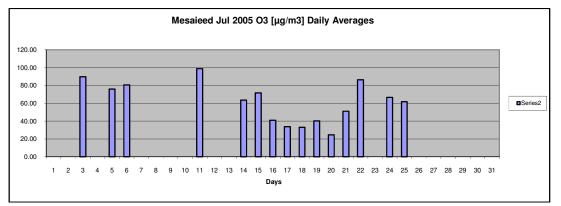
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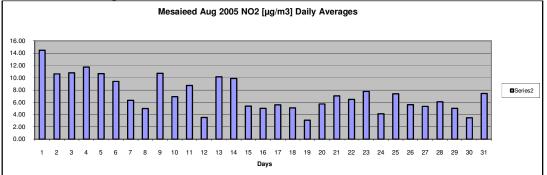


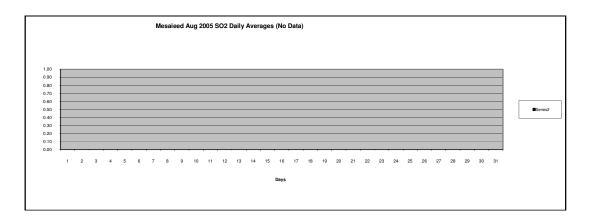


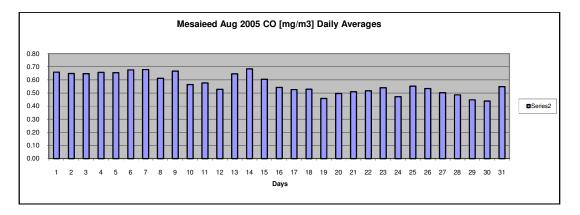


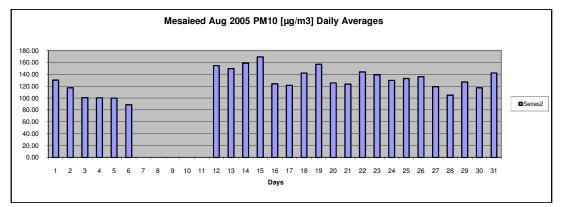


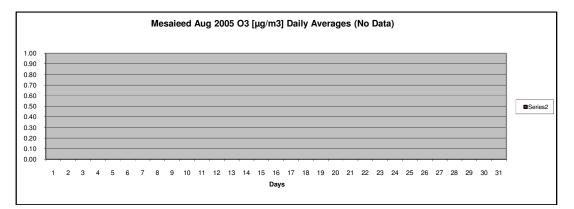
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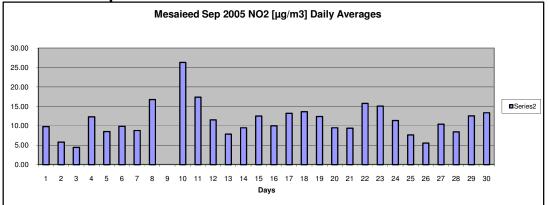


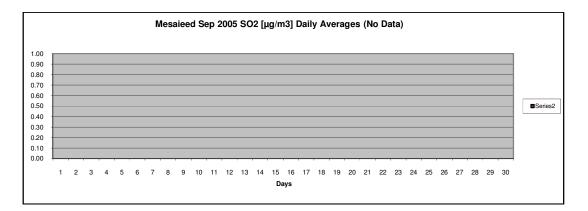


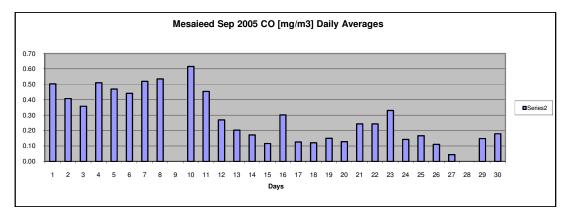


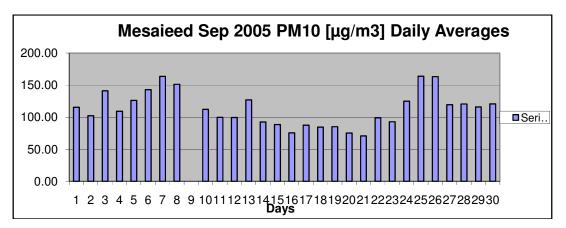


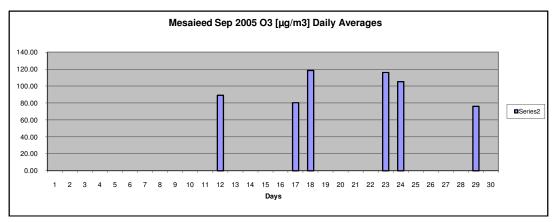
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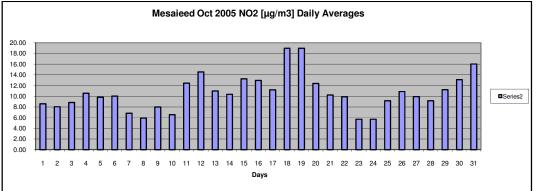


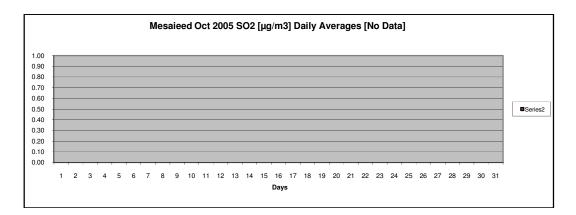


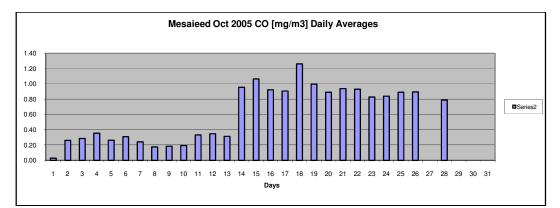


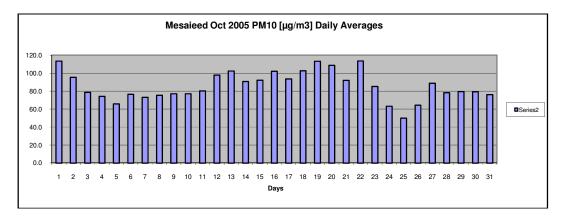


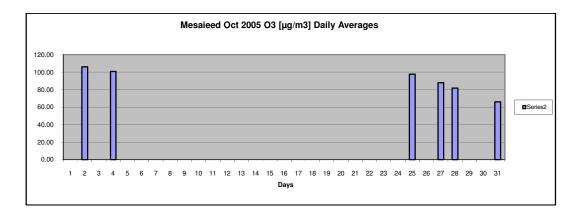
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#### **Mesaieed Nov 2005**

