ANALYSIS OF NO_X, NO AND NO_2 AMBIENT LEVELS AS A FUNCTION OF METEOROLOGICAL PARAMETERS IN DHAHRAN, SAUDI ARABIA

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ABSTRACT

NO_x, NO and NO_2 concentrations, and meteorological parameters, temperature, wind speed, relative humidity and pressure were measured simultaneously and continuously in Dhahran (Saudi Arabia) during three months in summertime. The hourly and daily NO_x, NO and NO_2 average concentrations were investigated as a function of the meteorological parameters. NO_x, NO, and NO_2 were found to have a common source and to be highly influenced by traffic emission and meteorological conditions, and the trend of NO showed a higher concentration during weekdays than weekends. NO_x has significant positive correlation coefficients with NO and NO_2, respectively. Similarly, NO_2 also has a positive correlation coefficient with NO. The temperature and wind speed showed negative correlation coefficients while relative humidity showed positive correlation coefficient with NO_x, NO and NO_2. On the other hand, NO_2 was found to exceed international air quality standards, which indicates the existence of a possible NO_2 air pollution problem in Dhahran.

Keywords: NO_x, NO, NO_2, traffic emission, meteorological parameters.

1 INTRODUCTION

Nitrogen oxides (NO_x) are one of the main pollutants in urban areas. They are very reactive and play an important role in air pollution chemistry [1]–[3]. Their concentrations in ambient air are the result of processes of accumulation, dispersion, transformation and removal [4]. In general, NO_x concentrations vary rapidly in urban areas over the course of the day with a typical residence time of about few days [5].

The main source of NO_x in urban areas is from traffic emission [6]–[10], which depends on vehicle type and size, fuel used and the manner of driving [11].

NO_x may further lead to the formation of other harmful pollutants such as ozone (O_3), acid rain, and photochemical smog through photochemical reactions [12]. Also, they may react with other compounds available in the atmosphere to form small particles that can be harmful to human health [13]. It was found that nitrogen dioxide (NO_2) has a certain positive correlation with a number of cancer cases in Saudi Arabia [14].

Many regulatory environmental agencies around the world set safe limits for NO_2 concentration in ambient air. Usually two safe limits are established for this purpose; one for long-term exposure averaged over one year, and the second is for short-term exposure averaged over one hour. The US Environmental Protection Agency (US EPA) sets the safe limit of 53 ppb averaged over one-year and 100 ppb averaged over one hour [15]. The European Directorate-General for Environment (DG Environment) sets even a tighter safe limit for long-term exposure of 20 ppb averaged over one year, while setting the same safe limit for short-term exposure of 100 ppb but not to be exceeded more than eighteen occasions each year [16]. The World Health Organization (WHO) sets similar safe limits to that of the European environmental legislation for universal use [17].

To the best of our knowledge, this paper is the first study of NO_x concentrations in ambient air in Dhahran, Saudi Arabia. Dhahran is one of the major cities in Saudi Arabia and is the host of Saudi ARAMCO, which is the largest oil company in the world. Ghawar oil field,

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which is the largest conventional oil field in the world, is located at a distance of about 85 km from Dhahran. In addition, Dhahran is located at 5 km and 25 km from two big cities Khobar and Dammam. Furthermore, Dhahran is about 100 km from Jubail, the biggest industrial city in Saudi Arabia and a host of many different chemical and industrial plants. The high number of vehicles per capita, the dense road network and the almost total absence of urban public transportation also is a feature of Dhahran. It was found that cars produce the quadruple of NO_x emissions than the large buses in city driving conditions according to a report from the Norwegian Centre for Transport Research [18].

In this paper, hourly and daily NO_x, NO and NO_2 average concentrations are investigated as a function of the meteorological parameters (temperature, wind speed, relative humidity and pressure) in Dhahran from 07 May to 30 July 2015.

2 METHODOLOGY

2.1 Study area and monitoring site

The location of Dhahran with the monitoring site and its surroundings are shown in Fig. 1. Dhahran is located on the western coast of the Arabian Gulf with an elevation of about 45 m above sea level and at a latitude of 26.24° north and a longitude of 50.04° east. Dhahran is one of the important cities in Saudi Arabia with about 100,000 inhabitants and is part of Dammam metropolitan area, which includes the nearby cities of Dammam and Khobar. Dammam metropolitan area has an estimated population of about 4 million inhabitants (census of 2012). The climate of Dhahran is characterized by warm and humid summers, and little rainfall with an annual average of about 10 mm. In summer, temperatures can rise to more than 40 °C coupled with humidity as high as 85%. Winds usually blow from north to south in the beginning of the summer and can last for up to six months, bringing dust storms.

The monitoring site is located at King Fahd University of Petroleum and Minerals campus in Dhahran. The campus is surrounded by three major high ways, number 80, 613, and 615, which makes it an excellent location to study the contribution of traffic emission to NO_x concentrations in the area. The monitoring site is at a distance of about 1.8 km from highway 613.

2.2 Instrumentation and data analysis

NO_x, NO, and NO_2 concentrations are measured using nitrogen oxides analyzer model EC9841 from Ecotech with detection range from 0 to 20 ppm and detection limit of less than 0.5 ppb. The EC9841 nitrogen oxides analyzer uses gas-phase chemiluminescence detection. It consists mainly of NO_2-to-NO converter, reaction cell, photomultiplier tube (PMT), and processing electronics.

Air samples are collected from the roof of a 10-m high building and are drawn through Teflon pipes to the instrument sample inlet, which is located in the ground floor of the laboratory. The monitoring site is the tallest building in the vicinity and hence setting up the sample air collector at a roof of the building clears off the possibility of air mass flow being obstructed by either another tall building or trees. In addition to the analyzer internal filter, a 5-micron filter is installed in the sample air collector to prevent tiny sand particle from getting into the analyzer. The 5-micron inlet filter is necessary to meet US EPA requirements.

A portable weather station model Orion from Columbia Weather Systems that allows accurate and stable measurements is deployed near the sample collector on the top of the

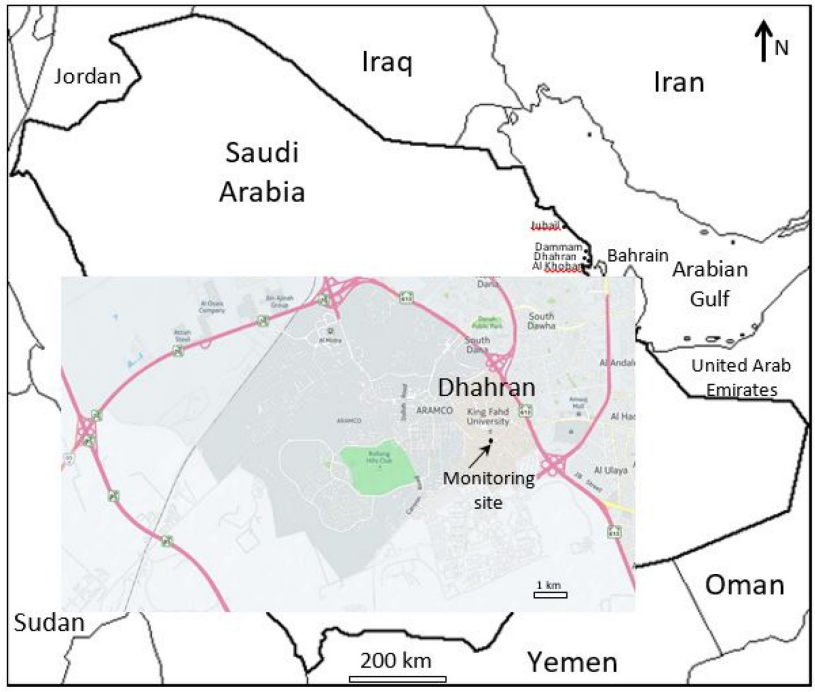

Figure 1: The location of Dhahran in the Arabian Peninsula with the monitoring site and its surroundings.

building to measure the meteorological parameters (temperature, wind speed, relative humidity and pressure). A wireless connection is used to transfer data from the weather station at the top of the building to the PC in the laboratory.

NO_x, NO, and NO_2 concentrations along with meteorological parameters are recorded simultaneously every second and continuously day and night for the period of 85 days during summer 2015 from 07 May to 30 July. To ensure data integrity, periodic calibration and quality control checks of NO_x analyzer are performed in line with the US EPA recommendation on quality assurance and quality control. LabVIEW code is used to synchronize the two devices and to automate the process of data acquisition.

Hourly and daily NO_x, NO, and NO_2 average concentrations and meteorological parameters are computed from the raw data using Mathematica program. Time series plotting is used to visualize the variation of NO_x, NO, and NO_2 concentrations and meteorological parameters. Statistical analysis is performed using MINITAB software.

3 RESULTS AND DISCUSSION

The average daily variation of NO_x, NO and NO_2 concentrations at the monitoring site over the study period are shown in Fig. 2. In the early morning, around 5:00 am, NO concentration starts increasing and reach its maximum level during morning rush hours around 8:00 am, when the human activities and traffic flow are at their highest level and ozone at its lowest level. After 8:00 am, NO concentration starts decreasing and this decrease continues until

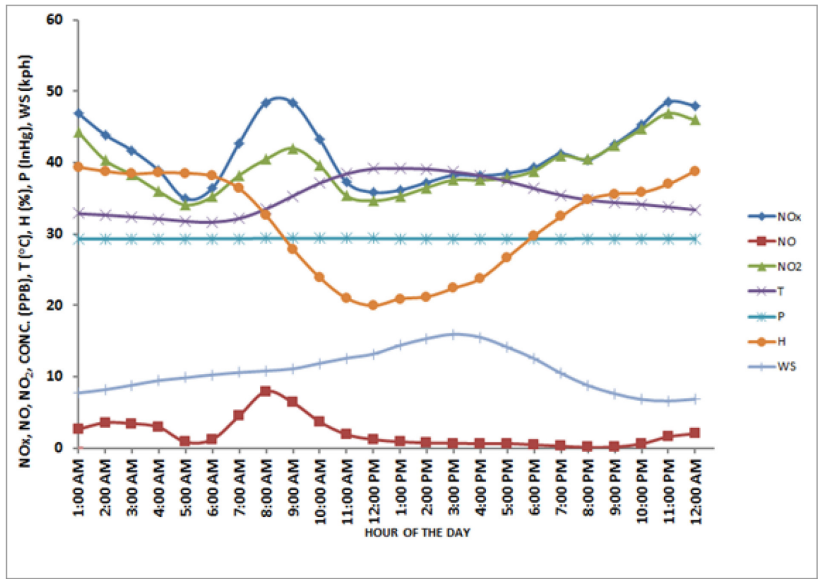

Figure 2: Average daily variation of NO_x, NO and NO_2 concentrations as a function of meteorological parameters: temperature (T), wind speed (WS), relative humidity (H) and pressure (P).

around 9:00 pm. After that, NO concentration starts rising, but without reaching the maximum level reached in the morning. This variation in NO concentration may be explained by an interplay between traffic flow and ozone levels. The more traffic flow the more NO emitted and the more ozone available the more NO removed a fact that is supported by the following reaction:

$$NO + O_3 \rightarrow NO_2 + O_2. \quad (1)$$

Although the traffic flow is almost similar at the morning and afternoon rush hours, around 8:00 am and 3:00 pm, respectively, NO concentration is significantly higher in the morning. This can be explained by the low ozone level available in the morning.

It is well known that ozone level in early morning is low and increases considerably at midday, attains its maximum in the afternoon and decreases during night [19]. There is a strong correlation between ozone and ultraviolet flux from solar radiation, with maximum level of ozone attained about 1 to 2 hours after UV flux maximum [1]. Mainly, the solar radiation catalyzes the production of ozone from NO_2 according to the following reaction:

$$NO_2 + O_2 + h\nu\ (\lambda < 424\ nm) \rightarrow NO + O_3. \quad (2)$$

To lesser extent, the solar radiation can catalyze the production of ozone from volatile organic compounds (VOCs) and NO_x [7], [20].

NO_2 concentration shown in Fig. 2 also starts increasing around 5:00 am and attains its maximum around 9:00 am; one hour after NO concentration reaches its maximum. The delay between the NO and NO_2 measured maxima confirms that NO_2 is partially produced from

the primary direct contaminant NO through the oxidation chemical reaction (1), which is the main reaction that contributes to the production of the indirect secondary contaminant NO_2 in the roadside air [8]. The same behavior is observed in the city of Tianjin in China where the morning maximum of NO_2 appears 1 to 2 hours after the NO maximum [1]. This behavior is also observed in the metropolitan area of Porto Alegre in Brazil with a delay of about 2 hours between the two maxima [6]. This delay can be explained by the fact that the rate of NO emission from car engines is higher than the rate of reaction (1).

Unlike NO, the concentration of NO_2 increases during afternoon hours and reaches its maximum level at about 11:00 pm. NO_2 is mainly produced via reaction (1) and is removed by breaking the molecule by UV radiation according to reaction (2). NO_2 can also be diluted by diffusion or by vertical mixing due to heat convection. It should be noted that the traffic flow in Dhahran continues until about 12:00 am. Hence, the increase in NO_2 is probably due to accumulation effect of NO_2 since, during night, no UV radiation is available to remove NO_2 and the vertical mixing is low [12]. The consequence of this low vertical mixing of the air is that the ozone formed during the afternoon is trapped in a layer with an average minimum height of about 100 m close to the surface during the relatively cool night [1]. This accumulated aged ozone will react with fresh NO emitted during night to produce NO_2. Hence, NO_2 concentration continues increasing according to reaction (1) despite the probable decrease in ozone production during night due to the absence of solar radiation.

Also observed in Fig. 2 are three small NO_2 peaks at around 3:00 pm, 7:00 pm, and 11:00 pm. Spikes in traffic flow can explain the presence of these peaks. Furthermore, NO_2 concentration is much higher than NO concentration, which indicates that NO_2 is more abundant because of its longer lifetime in the atmosphere than the more reactive NO. Although, the emission of NO_x into the atmosphere is mainly in the form of NO, which is later oxidized according to reaction (1) to form NO_2. In fact, 95% of NO_x is estimated to be emitted as NO [12]. In the morning, even though there is a low concentration of ozone in the atmosphere to convert NO to NO_2, the high NO_2 concentration is probably due to accumulation effect.

Between midnight and 4:00 am, NO concentration is almost constant while NO_2 concentration decreases significantly reaching its lowest levels around 5:00 am. The NO behavior can be attributed to the fact that in the early morning, the traffic flow is uniformly low and ozone is at its lowest levels minimizing the conversion of NO to NO_2. Since no ultraviolet radiation available during the early mornings, the decrease in NO_2 could be attributed to diffusion and dispersion of NO_2.

The daily average variation of NO_2 concentration over the study period is shown in Fig. 3. Also shown in the figure, the overall measured average of NO_2 concentration during the study period along with the maximum annual exposure limit set by US EPA. The overall average concentration of NO_2 for the whole period of measurements of 41.19 ppb is below the maximum annual exposure limit of 53 ppb propounded by US EPA but higher than the European standard of 20 ppb.

The minimum concentration of 15.6 ppb measured on the weekend day of Saturday (May 16) coincides with the end of classes' period in schools and colleges in Dhahran. This can explain the low traffic flow and hence low emission of NO. The maximum concentration of 94.7 ppb measured on Thursday (July 16) coincides with the day before the holiday of "Eid Al Fitr". Commonly, during this day shopping and other activities that lead to high traffic flow and hence high emission of NO are observed. In addition to the day before the holiday, the annual safe limit according to US EPA is exceeded in 12 other days and all of these days are weekdays. This behavior could be linked to higher traffic flow with supporting meteorological conditions.

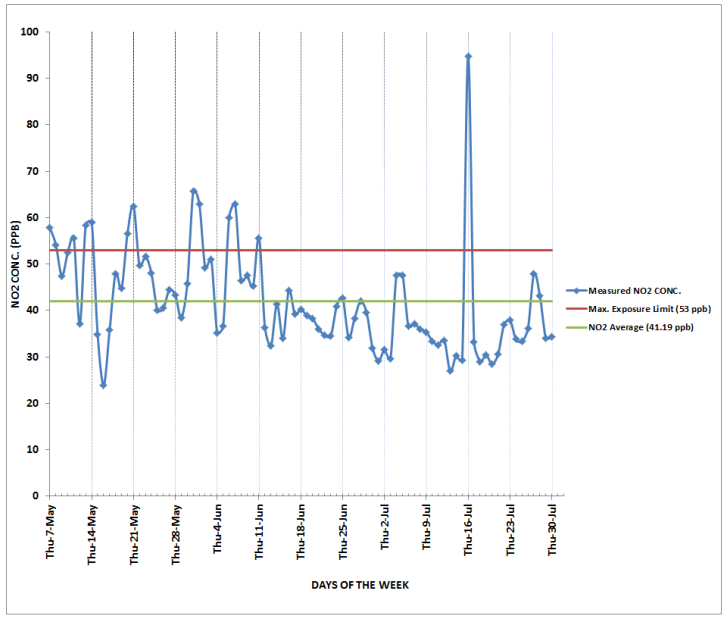

Figure 3: Daily average variation of NO_2 concentration during the study period.

A trend of higher NO_2 levels is observed during the first half of the study period compared to the second half. This behavior can be explained by temperature effect [1]. As it can be seen in Fig. 1, a trend of lower temperatures is observed during the first half of the study period compared to higher temperatures during the second half. In general, higher temperatures lead to lower NO_2 levels since higher temperatures cause more vertical mixing and smaller reaction rate of reaction (1).

The daily variation of NO_2 concentration for all measurements as a function of hour of the day is shown in Fig. 4. It can be observed that the maximum hourly permissible limit of 100 ppb of both US EPA and the European standard is exceeded in eighteen occurrences within the whole measurement period of 85 days. As mentioned before, the safe limit for short-term exposure of the European environmental policy should not be exceeded more than 18 occasions each year. However, in Dhahran, it is observed that this safe limit is exceeded in eighteen occasions in only 85 days, which indicates the existence of possible NO_2 air pollution problem.

Fig. 5 shows the average weekly variation of NO_x, NO, and NO_2 concentrations for the period of measurements. It should be noted that the weekend days in Saudi Arabia are Fridays and Saturdays during which there is a slight decrease in NO concentration and no noticeable decrease in NO_2 concentration compared to the weekdays. The expected decrease in the traffic flow during the weekend is not big enough to cause a significant decrease in NO concentration that leads to noticeable decrease in NO_2 concentration. The relatively high average of NO and NO_2 concentration measured on Thursdays is due to the exceptionally high NO_2 concentration measured on Thursday, 16th of July before holiday day. Therefore, weekend-weekday effect for NO_x concentrations in Dhahran during the study period from 07

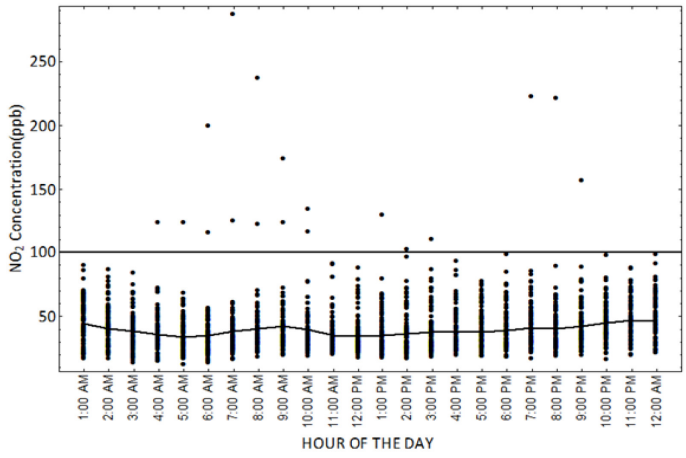

Figure 4: Daily variation of NO_2 concentration for all measurements as a function of hour of the day. The straight line at 100 ppb indicates the hourly safe limit. The other line connects the averages of hours.

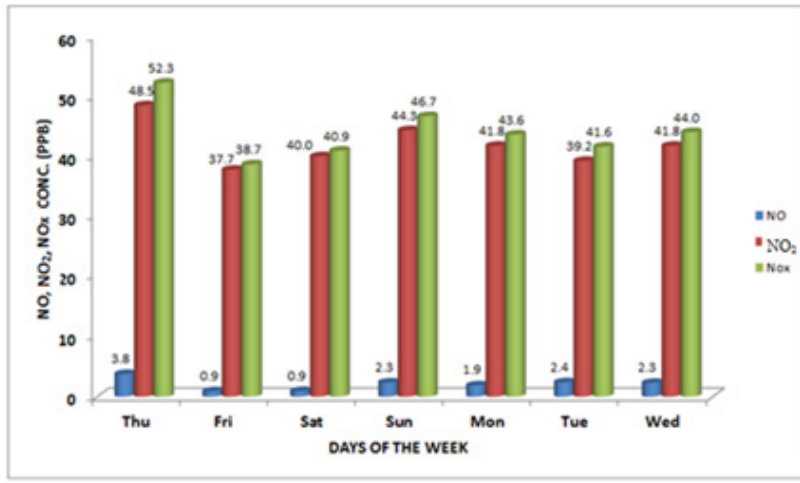

Figure 5: Average weekly variation of NO_x, NO, and NO_2 concentrations for the period of measurements.

May to 30 July is not significant. It should be noted that the mechanism for the weekend behavior observed in many cities, until now is not well understood [1], [19], [21].

Table 1 shows the correlation coefficients between hourly NO, NO_2 and NO_x concentrations and the measured meteorological parameters. NO, NO_2 and NO_x concentrations are found to have positive correlation coefficients with each other. NO_x has significant correlation coefficients of 0.578 and 0.889 with NO and NO_2, respectively. Similarly, NO_2 also has a positive correlation coefficient of 0.141 with NO. These results confirm that these pollutants have a common source and their concentrations depend on traffic emission.

Table 1: Pearson correlation coefficients between hourly average NO, NO_2 and NO_x concentrations and the meteorological parameters: temperature (T), wind speed (WS) and relative humidity (H).

	NO_2	NO	NO_x	T	WS	H
	1					
NO	0.141	1				
NO_x	0.889	0.578	1			
T	–0.319	–0.341	–0.410	1		
WS	–0.672	–0.154	–0.624	0.798	1	
H	0.455	0.162	0.449	–0.963	–0.864	1

Negative correlation coefficients of –0.341, –0.319, and –0.410 are observed between ambient air temperature and NO, NO_2, and NO_x, respectively. The increase of the temperature near the surface, mainly during summer and during daytime, enhances the vertical mixing, resulting in minimizing the concentrations of the nitrogen oxides in the lower atmosphere [1]. The analysis also shows that NO, NO_2, and NO_x have negative correlation coefficients of –0.154, –0.672, and –0.624 with wind speed, respectively. This can be explained by the fact that the high wind speed improves the dispersion and mixing of these atmospheric pollutants emitted from localized sources such as car engines, thereby minimizing their cumulative concentrations in the atmosphere. This result is consistent with those of several studies in which wind speed shows an inverse correlation with NOx concentrations. It was observed that low wind speeds might increase the influence of local emission sources [6], [22]. Furthermore, Table 1 shows that relative humidity has positive correlation coefficients of 0.162, 0.455, and 0.449 with NO, NO_2, and NO_x, respectively. This result is similar to those reported in other studies [23], [24]. This behavior is in line with the fact that the relative humidity falls when the temperature rises [25]. Pressure is almost constant and its effect can be assumed negligible.

4 CONCLUSIONS

The study showed that the urban air of Dhahran is strongly affected by traffic emission and photochemistry. It was found that the concentrations of NO_x, NO, and NO_2 are linked with one another, which indicates that they have a common source. It was also found that NO_x, NO, and NO_2 concentrations are affected by traffic emission and meteorological conditions. The ambient air temperature and wind speed have negative correlation coefficients with NO_x, NO, and NO_2 concentrations, whereas relative humidity is found to have positive correlation coefficient.

On the other hand, it was found that the average concentration of NO_2 for the full period of measurements of 41.19 ppb was below the maximum annual exposure limit of 53 ppb propounded by US EPA but higher than the European standard of 20 ppb. In addition, it was found that 13 days exceeded the maximum annual exposure limit of 53 ppb. Furthermore, it was found that the maximum hourly exposure limit of 100 ppb of both US EPA and the European standard is exceeded in eighteen occurrences in only 85 days, which indicates the existence of possible NO_2 air pollution problem.

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REFERENCES

[1] Han, S., et al., Analysis of the relationship between O_3, NO and NO_2 in Tianjin, China. *Aerosol and Air Quality Research*, **11**, pp. 128–139, 2011.

[2] Richter, A., Burrows, J.P., Nuss, H., Granier, C. & Niemeier, U., Increase in tropospheric nitrogen dioxide over China observed from space. *Nature*, **437**, pp. 129–132, 2005.

[3] Wang, X. & Mauzerall, D.L., Evaluating impacts of air pollution in China on public health: Implications for future air pollution and energy policies. *Atmospheric Environment*, **40**, pp. 1706–1721, 2006.

[4] Mazzeo, N.A., Venegas, L.E. & Choren, H., Analysis of NO, NO_2, O_3 and NO_x concentrations measured at a green area of Buenos Aires City during wintertime. *Atmospheric Environment*, **39**, pp. 3055–3068, 2005.

[5] Andrews, J.E., Brimblecombe, P., Jickells, T.D., Liss, P.S. & Reid, B., *An introduction to Environmental Chemistry*, 2nd ed, Blackwell Publishing: Malden, MA, 2004.

[6] Agudelo-Castaneda, D.M., Teixeira, E.C. & Pereira, F.N., Time-series analysis of surface ozone and nitrogen oxides concentrations in an urban area at Brazil. *Atmospheric Pollution Research*, **5**, pp. 411–420, 2014.

[7] Carslaw, D.C., Evidence of an increasing NO_2/NO_x emissions ratio from road traffic emissions. *Atmospheric Environment*, **39**, pp. 4793–4802, 2005.

[8] Itano, Y., Yamagami, M. & Ohara, T., Estimation of primary NO_2/NO_x emission ratio from road vehicles using ambient monitoring data. *Studies in Atmospheric Science*, **1**, pp. 1–7, 2014.

[9] Kurtenbach, R., Kleffmann, J., Niedojadlo, A. & Wiesen, P., Primary NO_2 emissions and their impact on air quality in traffic environment in Germany. *Environmental Sciences Europe*, **24**, pp. 1–8, 2012.

[10] Zhao, L., Xie, Y., Wang, J. & Xu, X., A performance assessment and adjustment program for air quality monitoring networks in Shanghai. *Atmos Environ*, **122**, pp. 382–392, 2015.

[11] Clapp, L.J. & Jenkin, M.E., Analysis of the relationship between ambient levels of O_3, NO_2 and NO as a function of NO_x in the UK. *Atmospheric Environment*, **35**, pp. 6391–6405, 2001.

[12] Notario, A., et al., Analysis of NO, NO_2, NO_x, O_3 and oxidant ($OX = O_3 + NO_2$) levels measured in a metropolitan area in the southwest of Iberian Peninsula. *Atmospheric Research*, **104–105**, pp. 217–226, 2012.

[13] Kampa, M. & Castanas, E., Human health effects of air pollution. *Environmental Pollution*, **151**, pp. 362–367, 2008.

[14] Al-Ahmadi, K. & Al-Zahrani, A., NO_2 and cancer incidence in Saudi Arabia. *Int J Environ Res Public Health*, **10**, pp. 5844–5862, 2013.

[15] US Environmental Protection Agency (US EPA), *EPA's Final Report on the Environment*, US Environmental Protection Agency: Washington, DC, 2008.

[16] Directorate-General for Environment (DG ENV), Directive 2008/50/EC of Directorate-General for Environment on Ambient Air Quality and Cleaner Air for Europe, 2016.

[17] World Health Organization (WHO), *Guidelines for Air Quality*, WHO: Geneva, 2000.

[18] TØI, Norwegian Centre for Transport Research Reports 1405/2015 and 1407/2015, Oslo, 2015.
[19] Adame, J.A., Hernández-Ceballos, M.Á., Sorribas, M., Lozano, A. & De la Morena, B.A., Weekend-weekday effect assessment for O_3, NO_x, CO and PM10 in Andalusia, Spain (2003-2008). *Aerosol and Air Quality Research*, **14**, pp. 1862–1874, 2014.
[20] Finlayson-Pitts, B.J. & Pitts, J.N., Jr., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press: San Diego, CA, 2000.
[21] Marr, L.C. & Harley, RA., Modelling the effect of weekday/weekend differences in motor vehicle emissions on photochemical air pollution in central California. *Environ Sci Technol*, **36**, pp. 4099–4106, 2002.
[22] Jones, A.M., Harrison, R.M. & Baker, J., The wind speed dependence of the concentrations of airborne particulate matter and NO_x. *Atmospheric Environment*, **44**, pp. 1682–1690, 2010.
[23] Elminir, H.K., Dependence of urban air pollutants on meteorology. *Science of the Total Environment*, **350**, pp. 204–211, 2005.
[24] Mavroidis, I. & Ilia, M., Trends of NO_x, NO_2 and O_3 concentrations at three different types of air quality monitoring stations in Athens, Greece. *Atmospheric Environment*, **63**,
pp. 135–147, 2012.
[25] Wallace, J. & Kanaroglou, P., The effect of temperature inversions on ground-level nitrogen dioxide (NO_2) and fine particulate matter (PM2.5) using temperature profiles from the Atmospheric infrared sounder (AIRS). *Science of the Total Environment*, **407**, pp. 5085–5095, 2009.