

Temporal Analysis of Ozone and Nitrogen Oxides Fluctuations at Pasir Gudang, Malaysia

Norrimi Rosaida Awang^{1,a,*}, Nor Azam Ramli^{2,b}, Ahmad Shukri Yahaya^{3,c}

^{1,2,3}Clean Air Research Group, School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, MALAYSIA.

^anorrimirosaida@gmail.com, ^bceazam@usm.my, ^cshukri@usm.my

Keyword: Annual fluctuations, monthly fluctuations, time series plot, nitric oxide, nitrogen dioxide

Abstract. Ozone (O₃) and nitrogen oxides (NO_x) are closely related in the atmosphere. In ambient air, these pollutants always fluctuated depending on their emission sources and meteorological influences. The paper aims to gain insight understanding of the monthly temporal variation of O₃ and NO_x concentrations to enable proper control strategies against these pollutants. One-year monitoring records from 1st January to 31st December 2009 of O₃ and NO_x at Pasir Gudang, were obtained from Department of Environmental Malaysia. Temporal analysis of O₃ and NO_x concentration fluctuation during annual and monthly were assessed using time series and scatter plots. The annual variations of O₃ concentrations were negatively correlated with annual variation of NO and NO₂ concentrations. Results suggest that O₃ concentration are higher than NO and NO₂ especially in May 2009. However, zero exceedences were recorded in the studied period for all pollutants against the Malaysia Ambient Air Quality Guidelines.

Introduction

Ozone (O₃) and nitrogen oxides (NO_x) are important compounds in atmospheric chemistry. At the ground level, ozone is one of the significant air pollutants and always relates with degrading air quality especially in urban areas. High ozone levels can potentially affected human health, plant species, various natural materials, and manufactured goods [1]. Ground level O₃ is produced by series of chemical reaction of the main precursors (NO_x and VOC_s) that were anthropogenic emitted in the ambient air with ultraviolet radiation that act as catalyst to the reactions [2].

NO_x is produced when fuel is burned at high temperature and the primary sources of NO_x are any human activities, which associated with burning fuels. The main sources of NO_x came from fossil fuel combustion from either industrial and vehicular, biomass burning, microbial activity in soils, and lightning [2]. In the presence of sunlight, NO is generated by photolysis of NO₂ but it will oxidized by O₃ to regenerated NO₂ [1,3]. Photolysis of NO₂ created atom O that will react with molecule O₂ that already existed in the atmosphere to create O₃. The destruction of O₃ will happen when it is reacted with NO to produce NO₂. Ghazali [1] regarded the NO₂ photolysis and NO titrations are the main chemical reactions that controlling the formations and destruction of the ground level ozone. These reactions also directly influence by meteorological variability such as temperature, solar radiation, wind speed and direction as well as the availability of the precursors sources [2, 3, 4].

Reduction in NO_x emission will tremendously effected the O₃ concentration vice versa. As levels of O₃ and NO_x are inextricably linked, any changes in O₃ levels may indicated the effectiveness of local NO_x emissions control [3]. The selection of Pasir Gudang is made based on the growth of the area regarding the populations, traffic density, shipping and industrial activities. Majority of air pollution studies in Malaysia focusing in Klang Valley [1, 4, 5]. It is therefore necessary to gain insight into the O₃ and NO_x relationship in the atmosphere at Sourthern region of Peninsular Malaysia. The paper, the fluctuational behavior of ozone O₃ and NO_x were analyzed temporally during annual and monthly. The rest of the temporal analysis is reported elsewhere.

Site description

The dispersion and dilution of air pollution are directly influenced by local attribution such as meteorological condition as well as the location of the monitoring stations. The monitoring station was established at Sekolah Menengah Kebangsaan Pasir Gudang, Pasir Gudang (Fig. 1). Pasir Gudang was located at Johor, which is the southern state of Peninsular Malaysia. The monitoring station was established and operated by Department of Environmental, Malaysia to monitor any significant changes in the ambient air quality. Pasir Gudang is one of the Johor's districts infamous with Pasir Gudang's Port. The major industries that were governing Pasir Gudang economy were transportation and logistics, shipyard industries, petrochemical industries and oil palm storage and distribution. Pasir Gudang Port was the third busiest port in Malaysia after Klang Port and Penang Port. In 2010, Pasir Gudang Port handled about 28 million tons of cargo and received nearly 5000 international and local ships [6]. Malaysia Statistical Department (2010) reported that during 2010 census the number of Pasir Gudang populations is approximately 43,000 persons. The growth of the town indirectly degrading the air quality status at Pasir Gudang due increasing anthropogenic emissions. Climatically, Pasir Gudang as the rest of Johor state experienced tropical monsoon with uniform temperature throughout the year an average temperature is ranging from 24°C to 32°C [7].

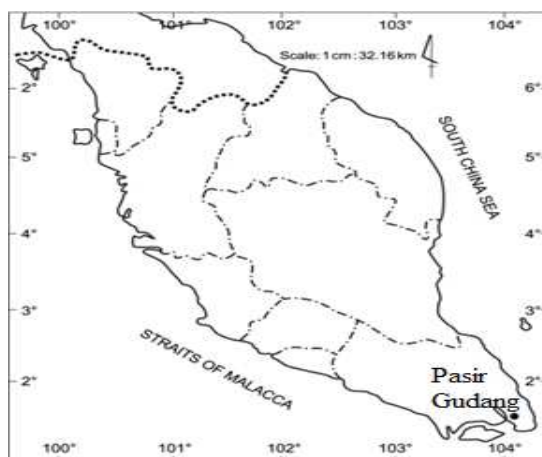


Fig 1 Location of Pasir Gudang (N01°28.225, E103°53.637) in Peninsular Malaysia

O₃ and NO_x monitoring records and measurement techniques

One year hourly continuously monitoring records of O₃, NO, and NO₂ were obtained from Department of Environmental Malaysia (DoE) from 1st January to 31st December 2009. The record is regularly subjected to standard quality control processes and quality assurance procedures by the DoE [8], the quality controlled procedures were followed the international standards outlined by United State Environmental Protection Agency (USEPA) [11]. Hourly O₃ concentrations monitoring samples were collected using UV Absorption Ozone Analyzer Model 400A which is a microprocessor controlled analyzer [8] based on the Beer-Lambert law in order to measure law ranges of O₃ the ambient air or gaseous media [1]. Ambient O₃ molecule were detected based on internal electronic resonance of O₃ molecule using absorption of 254 nm UV light that were emitted from internal mercury lamp [9]. Samples of hourly and daily NO_x (NO, NO₂) concentrations were collected using chemiluminescent NO/NO₂/NO_x Analyzer Model 200A which is an EPA approved method. Ghazali [1] reported that, the analyzer were applying the chemiluminescent detection principle to detect the NO_x concentration in the ambient air coupled with microprocessor technology to enhance the pollutants monitoring ability. The usage of microprocessor technologies in the analyzer provides sensitivity, stability and ease to be use in a continuous monitoring environment [10].

Temporal analysis of annual and monthly fluctuations of O₃ and NO_x concentrations

It is unarguable that NO and NO₂ plays the most significant role in formations and destructions of O₃ at ground level [1,2, 3]. Fig. 2 showed the scatter plots of daily average of O₃ variations against NO and NO₂ concentrations. Since, NO₂ and NO concentrations acts as the precursors to O₃, it is expected that O₃ variations to be negatively correlated with variations in NO₂ and NO concentrations. Weak correlations coefficients (R^2) is obtained from O₃ and NO₂ (-0.364), while for the relationship between O₃ and NO is slightly higher at -0.424. During the photochemical reactions of O₃ formations, molecule of NO₂ is react with solar radiation produced atom of oxygen, which is later reacted with oxygen molecule producing O₃ molecule [1, 3]. Meanwhile, reactions between O₃ and NO will destroying O₃ and reproducing NO₂. The inter-conversion between O₃, NO₂ and NO is can be well illustrated by diurnal plot (24 hour), however, the result is presented elsewhere.

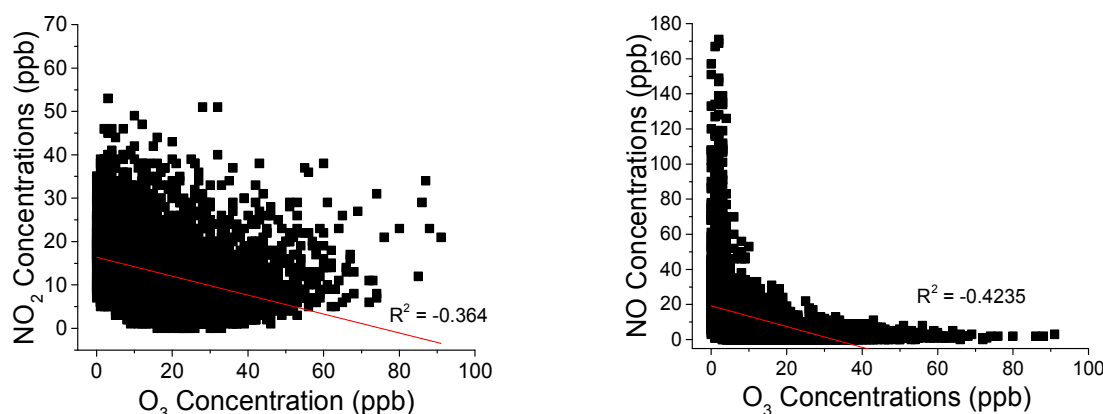


Fig 2 Scatter plots of O₃ variations against NO₂ and NO concentrations

Annual maximum concentrations of O₃, NO and NO₂ in Pasir Gudang are analyzed using time series plots as shown in Fig. 3. The results suggested that O₃, NO and NO₂ were fluctuated throughout the year and relatively high concentrations were observed during second and third quarter of the year (April- September). Figuratively, Pasir Gudang experienced more severe NO pollutions compared to O₃ and NO₂ pollutions. Han [3] reported that vehicular emissions is the main contributors towards NO pollution and it is reported by Ministry of Transport Malaysia [6] the total number of registered vehicle in Johor is approximately 2.7 million in year 2010. Noticeably, all pollutants were at minimal concentrations during the early and the end of the year compared to during the mid of the year. Several distinct peaks of O₃ concentrations were observed throughout the year especially during March to May, which is coincided with increasing trends in NO and NO₂ concentrations. However, these peaks concentrations not rise beyond MAAQG levels of 100 ppb for O₃ and 170 ppb for NO and NO₂ for 1-hor averaging period. The means of maximum concentrations of O₃, NO₂ and NO in Pasir Gudang in 2009 are 36.13 ppb, 24.80 ppb and 50.96, respectively.

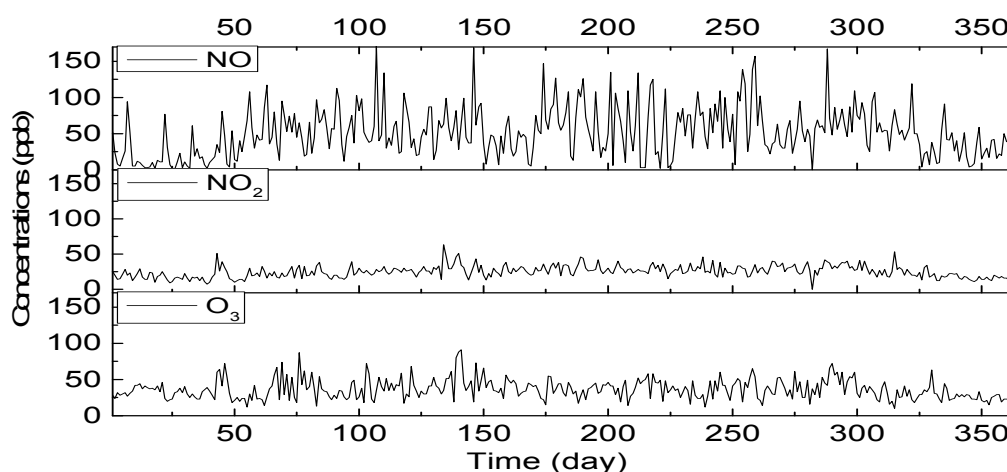


Fig 3 Time series plot of daily average O₃, NO, and NO₂ concentrations

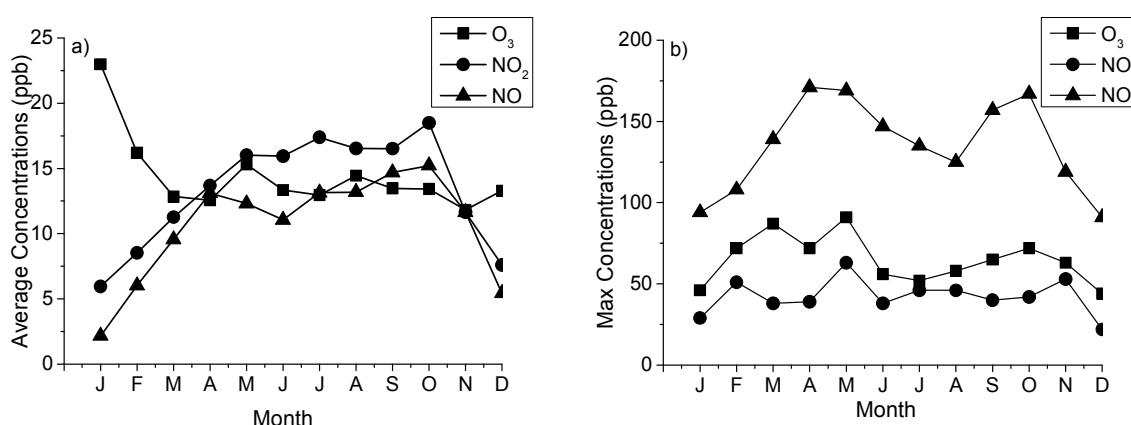


Fig 4 Monthly temporal variations concentrations of O₃, NO, and NO₂; a) average; b) maximum

Fig. 4 illustrated the plot of monthly average and maximum of O₃ and NO_x concentrations in 2009. From the average plot, January recorded the highest in O₃ concentration (23 ppb) followed by February (16.2 ppb). However, the highest average concentrations for NO and NO₂ were recorded on July and October with 17.4 ppb and 15.22 ppb, respectively. Results also exhibits that, the lowest monthly average concentration recorded on November for O₃ (11.8 ppb) and on December for both NO (5.42 ppb) and NO₂ (7.6 ppb) concentration. Meanwhile, based on Fig. 4(b) the highest maximum concentrations of O₃, NO₂ and NO is all recorded on May with 91 ppb, 63 ppb and 169 ppb, respectively. It is also observed, lower maximum concentration of all pollutants during December and January which most probably induced by monsoonal effect. According to Toh [11], there are two major monsoonal period occurs in Malaysia which are North East Monsoon (November to March) and South west Monsoon (June to September) accompanied by two inter-monsoon periods. Heavy rainfall, which always associated with North East Monsoon, may contribute to the reductions of the O₃ and NO_x concentrations in the atmosphere. Increasing in intensity of the rainfall will be promoting wet deposition of air pollution molecule in ambient air, thus reducing the pollution concentration [3, 11]. All pollutant especially ozone shall have scouring effect due to rainfall and PM₁₀ will be effected by wet deposition. Scavenging of air pollutants in ambient air also can be triggered by chemical reactions such as NO titration as well as dispersion and transport of the pollutants by winds [2, 3, 4, 11].

Conclusion

The result demonstrated that NO is more prominent air pollutant in Pasir Gudang compared to O₃ and NO₂. However, since O₃ formation was controlled by NO_x concentration, O₃ can also plays significant role towards air pollution status in Pasir Gudang. This study proved that, annual

variations in O₃ concentration is negatively correlated with annual NO₂ and NO. Even though, there are several spikes were observed on the pollution annual time series plots, there are zero exceedences of the guidelines limit were recorded. The maximum monthly O₃ concentration with 91 ppb is observed on May 2009, while the monthly maximum of NO and NO₂ concentrations are 169 ppb and 63 ppb, respectively. Heavy rainfall that is associated with North East Monsoon during November to March every year promoting pollutants scouring effect, hence O₃ and NO_x concentrations during the periods is significantly lower than the rest of the year.

Acknowledgement

The authors acknowledge the Department of Environmental, Malaysia for proving the air pollutions monitoring records. This study was funded by Universiti Sains Malaysia under grant 1001\PAWAM\811206. Thanks to Ministry of Higher Education Malaysia for providing financial support under MyBrain Program to carry out this study.

References

- [1] Ghazali, N.A., N.A. Ramli, A.S. Yahaya, N.F.F.M.D. Yusof, N. Sansuddin, and W.A. Al Madhoun. "Transformation of Nitrogen Dioxide into Ozone and Prediction of Ozone Concentrations Using Multiple Linear Regression Techniques." *Environmental Monitoring and Assessment* 165, no. 1 (2010): 475-89.
- [2] Seinfeld, John H, and Spyros N Pandis. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons, 2006.
- [3] Han, Suqin, Hai Bian, Yinchang Feng, Aixia Liu, Xiangjin Li, Fang Zeng, and Xiaoling Zhang. "Analysis of the Relationship between O₃, NO and NO₂ in Tianjin, China." *Aerosol Air Quality Research* 11 (2011): 128-39.
- [4] Clapp, Lynette J, and Michael E Jenkin. "Analysis of the Relationship between Ambient Levels of O₃, NO₂ and NO as a Function of NO_x in the UK." *Atmospheric Environment* 35, no. 36 (2001): 6391-405.
- [5] Ahamad, Fatimah, Mohd Talib Latif, Rosy Tang, Liew Juneng, Doreena Dominick, and Hafizan Juahir. "Variation of Surface Ozone Exceedance around Klang Valley, Malaysia." *Atmospheric Research* 139 (2014): 116-27.
- [6] Malaysia, Ministry of Transport. "Transport Statistics 2012." Putrajaya, Malaysia, 2012.
- [7] MMD, Malaysia Meteorological Department. "General Climate of Malaysia." Ministry of Science, Technology and Innovation, http://www.met.gov.my/index.php?option=com_content&task=view&id=75&Itemid=1089
- [8] Mohammed, Nurul Izma, Nor Azam Ramli, and Ahmad Shukri Yahya. "Ozone Phytotoxicity Evaluation and Prediction of Crops Production in Tropical Regions." *Atmospheric Environment* 68 (2012): 243-49.
- [9] Teledyne. "Model 200a Nitrogen Analyzer." San Diego, California: Teledyne Instruments, 2005.
- [10] Teledyne. "Model 400a Ozone Analyzer." San Diego, California: Teledyne Instruments, 1999.
- [11] Toh, Ying Ying, Sze Fook Lim, and Roland von Glasow. "The Influence of Meteorological Factors and Biomass Burning on Surface Ozone Concentrations at Tanah Rata, Malaysia." *Atmospheric Environment* 70 (2013): 435-46.