EVALUATION OF NO_2 IN AMBIENT AIR IN INDUSTRIAL AREA OF SUNGAI BULOH BY USING PASSIVE SAMPLING METHOD

[1]THARANIYA S NAIR SUTHESAN, [2]SHAMSUL IZHAR, [3]CHIKAYOSHI YAMADA

[1,2]Chemical & Environmental Engineering Department Universiti Putra Malaysia, [3]Shicoson DobukuKeikaku Co. Ltd
E-mail: [1]thara.2993@gmail.com, [2]shamizhar@upm.edu.my, [3]chika@shichoson.co.jp

Abstract - Air pollution has been a concern to mankind since peak of Industrial Revolution. Over the years, the increasing concern of air pollution has led to establishment of ambient air quality standards. One of the six major pollutants listed in most ambient air quality standards is nitrogen dioxide (NO_2). NO_2 is typically emitted due to incomplete combustion of diesel, from vehicles and high thermal unit operations like cement-kilns and power plants. Measurement of pollutants, such as NO_2 in ambient air can be conducted in two ways; active sampling or passive sampling. Conventionally, active sampling is used to measure the presence of nitrogen oxide in ambient air. However, in recent years, there have been various developments in passive sampling methods. Passive sampling does not require power source for operation whereby the air pollutants are trapped onto sorbent material by diffusion mechanism. This project was carried out to evaluate NO_2 concentration by using passive samplers in industrial area in Sungai Buloh. The measurement of NO_2 from passive sampling is then compared with the data of NO_2 concentration from nearest Continuous Air Quality Monitoring Station (CAQMS) in Petaling Jaya to measure accuracy of the passive sampler. Average concentration of NO_2 measured by using passive samplers in Sungai Buloh was 0.034 ppm, while CAQMS Petaling Jaya which uses active sampling showed an average NO2 concentration of 0.042 ppm. The data collected using passive samplers in Sungai Buloh is lower by 19% compared to data at CAQMS Petaling Jaya. This is due to distance of approximately 10.5 kilometers between the two points. In Sungai Buloh, major sources of NO_2 pollution is due to transportation and manufacturing activities. From this project, it can be concludedthat passive sampling can be considered as a alternative to measure NO_2 in ambient air which can be implemented in monitoring stations in Malaysia.

Keywords - Air Pollution, Nitrogen Dioxide, Passive Sampling, Air Monitoring

I. INTRODUCTION

With the backdrop of rapid development, air pollution remains a constant threat to mankind and environment since the early days of industrial revolution. Despite the advancement in air pollution control technologies, the deteriorating quality of ambient air has been a lingering problem. According to Katsouyanni (2003), air pollutants consist of mostly gaseous pollutants which contribute significantly towards the change of compositions of ambient air. Nitrogen dioxide (NO_2) is one of the six major pollutants listed by the Environmental Protection Agency (EPA) under its Clean Air Act. Main sources of NO_2 in ambient air are due to both mobile and stationary combustion. Nitrogen oxides are emitted to air as nitrogen monoxide (NO), which reacts with ozone and radicals to form nitrogen dioxide (NO_2) (Kampa&Castanas, 2008). In 2016, EPA published Integrated Science Assessment (ISA) for Nitrogen Dioxide. The purpose of the ISA was to evaluate the relationship between NOx pollution with health and ecological effects as reference point to establish ambient air quality standards. Based on the publication, it was reported that short-term exposure to NO_2 can lead to respiratory health problems, namely asthma. Besides that, ecological effects due to NO_2 are also evident. Oxides of nitrogen react with water, oxygen and chemicals in the atmosphere to form acid rain. Acid rain is known to be harmful to the environment. Due to the known adverse effects of nitrogen oxides in the atmosphere, various nations have established ambient air standards to control the emission of NO_2 in ambient air. In the USA, for example, the National Ambient Air Quality Standards (NAAQS) was implemented. Similarly, countries like Australia, India and Malaysia have also set up standards in their respective countries. Adherence to the standards requires monitoring and measurement of NO_2 present in ambient air.Measurement of pollutants in ambient air can be conducted in two ways; active sampling or passive sampling. Conventionally, active sampling is used to measure the presence of nitrogen oxide in ambient air. Active sampling involves use of a pump to draw in air to the device. However, in recent years, there have been various developments in passive sampling methods. Passive sampling employs the mechanism of molecular diffusion of NO_2 onto the adsorbent of the sampling device. This method is less energy intensive, which makes it more environment friendly air sampling device. According to a publication by Department of Environment (DOE) Malaysia, main sources of nitrogen dioxide emission in Malaysia are transportation, manufacturing activities and power generation plants. The sampling location chosen for this project is industrial area in Sungai Buloh. This location has two out of three mainsources, which are transportation and manufacturing activities. This research aimed to measure the NO_2 concentration in industrial area of Sungai Buloh by using passive sampling method. It is hoped that this research can further improve the passive air sampling data

collection and promote passive air sampling method in Malaysia.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

2.1.1 Materials

All chemicals were used as purchased from respective suppliers without a further purification step. Deionised water was used for dilution and washing during the preparation of air samplers.The details of chemicals used for this research work are, sodium hydroxide (NaOH), sodium iodide (NaI), methanol, sulfanilic acid, sodium nitrite ($NaNO_2$), phosphoric acid (85%), N-1-napthylethylenediamine-2-hydrochloride.

2.1.2 Passive Sampler

The passive sampler that is used for this research was developed by Dr M. Harper from Australia (Ong et al., 2016). This passive sampler is assembled in three layers, as illustrated in Figure 1. The first layer consists of polyethylene cap, stainless steel mesh and a Teflon filter. This layer functions as a filter to minimize inflow of dust particles into the sampler. Second layer of the passive sampler is made up of polypropylene ring which acts as a support structure. The third layer of consists of a filter paper and polyethylene cap. Filter paper in the third layer is the main component of the passive sampler, as it serves as a medium of NO_2 absorption from the ambient air.

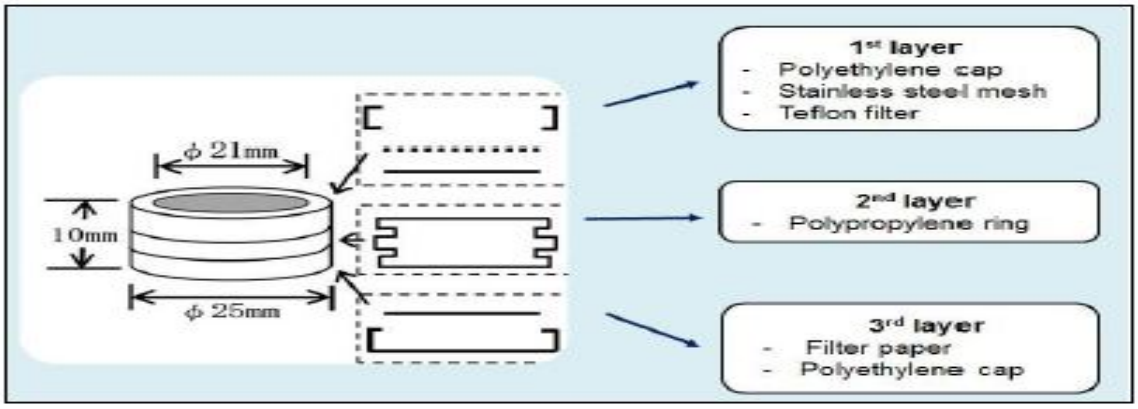


Fig. 1 Three Layers of Passive Samplers

2.1.3 Preparation of NO_2 Absorbing Layer

The key function of the passive sampler is its ability to absorb NO_2 from atmosphere. NO_2 absorbing liquid was prepared by dissolving 0.44 g of sodium hydroxide into 1 mL of distilled water. The solution was stirred, and 3.69 g of sodium iodide was further added into the mixture. The mixture is transferred t0 50 mL volumetric flask. Methanol was added until volume of mixture reached 50 mL mark. Mixture is shacked to ensure complete mixing. The solution produced is NO_2 absorbing liquid.Prior to being placed in the field, the filter paper from the third layer was dipped onto 50 µL of NO_2 absorbing liquid that was prepared previously.

2.1.4 On-Site NO_2 Sampling

The performance of the passive air sampler was evaluated in the industrial area of Sungai Buloh, which is in the state of Selangor, Malaysia. Figure 2 shows the sampling locations on a bird-eye map view, scale 1



Fig. 2. Locations for Passive Samplers in Sungai BulohMap Scale (1cm: 200 m)

Four passive samplers (Sample 1 – Sample 4) were placed along 1.9 kilometers of JalanKusta in the industrial area of Sungai Buloh. Samplers were located at approximately 500 meters of distance between one another. Along the road of JalanKusta, there are many factories and warehouses. This is one of the main reasons for high traffic in the area, which is the major source of air pollutants in the area. Besides that, there is also a concrete processing factory located near Sample 1. There is high potential that the elevated temperature concrete kiln process emits pollutants into air, which contains NO_2.Another additional sample (Sample 5) was placed at Bukit Rahman Putra Golf Club, which is a recreational golf park situated 4.1 kilometers away from the industrial area. Due to less traffic in this area, one sample was placed in in this location as a measure of comparison between the measurements of NO_2 in ambient air in 2 different areas. All samplers were placed at 1.5 m height above ground at their respective sampling locations. This is to reduce the load of dust particles to interfere the absorption of NO_2. High loading of particulate at the first layer of the sampler would cause reduction in absorption efficiency, which will result in underestimation of NO_2 concentration. Other considerations for the placement of the passive sampler include shade from rain and potential disturbance by passers-by or animals.All five samplers were set stationary on-site for a week to absorb NO_2 from the air. After 1 week of on-site sampling, the filter paper is removed from the passive sampler, and soaked in distilled water overnight. The solution is added with Saltzman reagent, and analyzed using UV-Vis Spectrometer for measurement of NO_2.

2.1.5Preparation of Saltzman Reagent

Saltzman reagent is the coloring solution which is responsible to determine the absorption values of the NO_2 containing solution. First, Saltzman reagent is prepared by the mixing of 0.8 g of sulfanilic acid, 0.02 g of N-1-napthylethylenediamine-2-hydrochloride, 0.8 mL of phosphoric acid and 100 mL of distilled water. The solution will turn to red color once it is shacked for few minutes. Saltzman reagent is produced.

2.1.6Determination of NO_2 Value

The passive air sampler is placed at the designated location for one week. The sampler is then collected, and analysis is done at the laboratory. The filter paper of the 3rd layer of passive air sampler is removed from the sampler and placed in a plastic bag containing 5 mL of distilled water. The sampler is kept overnight with room temperature to ensure the NO_2 absorbed in filter paper and diffuse out to the distilled water. The following day, 1 mL of the solution in the plastic bag is placed in test tube and mixed with 2 mL of distilled water to produce a total of 3 mL of NO_2 containing solution. 1 mL of Saltzman reagent is then added to the 3 mL solution to yield 4 mL of solution. The prepared solution is shacked for even mixing. Next, its absorption values are determined using UV-spectrometer operate with the wavelength of 540 nm. The concentration of the solution with absorbed atmospheric NO_2 can be determined from the standard curve calibration which was prepared with different NO_2 concentrations.

III. RESULTS AND DISCUSSION

3.1. NO_2 Standard Calibration Curve

When Saltzman reagent is added to solution with different concentration of NO_2, the solution will turn into light purple color. The color of the solution is darker with the increasing amount of NO_2^- ions. Increasing number of NO_2^- ions intensifies the color of solution because there are more NO_2^- ions that can be reacted with Saltzman reagent to produce the purplish color.Graph of absorption values against NO_2 concentration was plotted as shown in Figure 3. The concentration of NO_2 used to plot the standard curve range between 0 µM to 100 µM. Using the equation obtained from the standard curve, the concentration of NO_2 can be calculated for absorption values.The standard curve with different NO_2 concentrations is used as reference in the determination of the amount of NO_2 in the air relative to the concentration of ions contained in the filter paper after on-site air sampling. The higher the number of ions present in the solution, the higher absorption value. From Figure 3, the relationship between NO_2 concentration and absorption value is linearly proportional. The equation obtained in Figure 3, $y = 0.0242x + 0.0797$ is used in further analysis. Based on the absorption values obtained from the passive air samplers, NO_2 ions concentration is calculated using the equation from the standard curve in Figure 3.

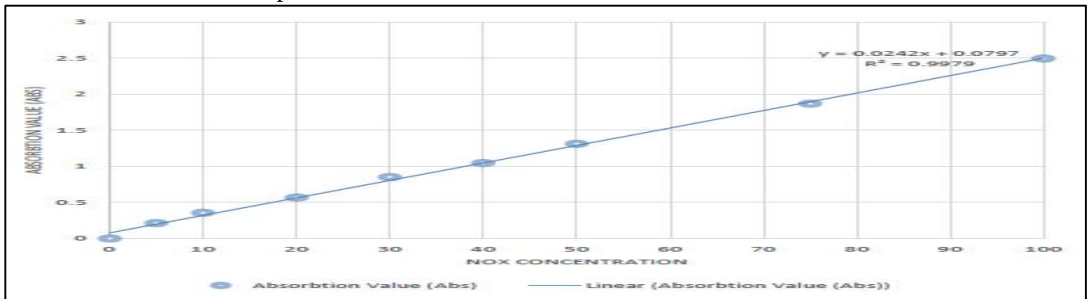


Fig. 3 Absorption Values versus NO_2 Concentration

3.2 Meteorological Data

3.2.1 Ambient Temperature

Since the measurement of air quality is conducted in outdoors, there have been skeptical notions that the performance of passive sampler is affected by various meteorological factors such as wind speed, ambient temperature, wind direction and relative humidity. However, the most important criteria are ambient temperature at the site of air sampling. For calculation to convert NO_2^- ions into concentration of NO_2, Fick's Law is applied. Molecular diffusivity of NO_2 into the passive sampler is dependent on the surrounding temperature (McLagan et al., 2017).In this experiment, temperature of Sungai Buloh over 3 months of sampling period is obtained from the daily update on the website of Weather Underground. the highest temperature recorded was 29□C, whereas the lowest recorded temperature was 26□C. For the calculation, average temperature of 28□C is used in derived equation. There is no major fluctuation in ambient temperature as weather in Malaysia is hot and humid throughout the year.According to Šerevičienė and Paliulis (2012), temperature below 35□C has insignificant effect on the accuracy of passive samplers. This shows that the recorded ambient temperature has negligible effect on accuracy of the passive sampler. Other researchers who have conducted similar studies on the relationship between ambient temperature and performance of passive samplers concluded that despite the correlation in the diffusivity of NO_2 into the passive sampler, there is insignificant evidence to show a significant effect of temperature.

3.2.2Wind Speed and Wind Direction

Wind speed recorded during the 3 months of sampling period is between 4 km/h to 7 km/h, which is considered as light air with reference to Beufort scale. The wind speed is relatively low, hence potential for debris and dust to block the mesh of passive samplers is low. This shows that throughout the sampling period, diffusion of NO_2 into the passive is not interfered by particulate matters, compared to a location with higher wind speed.Wind direction is also a key factor in passive air sampling. For this project, the data of NO_2 concentration in Sungai Buloh is compared to data from nearest Continuous Air Quality Monitoring Station (CAQMS) which isinPetaling Jaya. Hence, the wind direction is a crucial input for data analysis.Data for wind direction is extracted from Weather Underground website. Figure 4 shows the wind direction at sampling locations and CAQMS of Department of Environment. For the three months of sampling period, the wind direction did not vary significantly. On average, movement of wind has been between 180□ to 270□ in West direction.



Fig .4 Wind Directions at Sampling Location and CAQMS Map Scale (1cm: 20 km)

3.2.3 Traffic Data at Sampling Location

Number and types of vehicles that passed by sampling location in industrial area of Sungai Buloh is estimated from the report published in 2016 by Ministry of Transport, Malaysia. All sampling location are located along JalanKusta, which is categorized as 'Jalan Perindustrian', or Industrial Road. Average daily traffic is taken for Jalan Kuala Selangor, which is a nearby location to industrial area of Sungai Buloh. From the data from Ministry of Transport, the average hourly traffic is calculated.

The summarized data of traffic is as tabulated in Table 1.Table 1 shows that number of vehicles passing by the sampling location is high, especially with heavy vehicles.

Table 1. Number of Vehicles according to Types at Sampling Location

Average Hourly Traffic (Units/Hour)				
Cars	Trucks	Lorries	Busses	Motorcycles
532	65	283	12	210

Total traffic hourly in sampling location is estimated to be 1102 vehicles per hour. A similar study was conducted by Ong et al (2016), which showed higher traffic in the PLUS Highway nearby Serdang. The relationship between the number of vehicles and the concentration of NO_2 in air is further discussed inSection 3.2.6.

3.2.4Passive Air Sampling Data

On-site passive air sampling was carried out at 5 locations at the industrial area of Sungai Buloh. The samplers were taken back to laboratory for further analysis. The filter paper with absorbed NO_2^- ions are soaked in deionized water overnight. Saltzman reagent is added to the deionized water and its absorption value is determined by using UV-Vis spectrometer. 3 readings were taken for each sample to ensure accuracy of data obtained.To calculate the NO_2^- ion concentration from the absorption value, equation from standard curve in Section 3.1, y = 0.0242x + 0.0797 is used. The conversion of from concentration of NO_2^- ions to concentration of NO_2 in atmosphere in parts per millions is as shown below in Equation 1.

$$Concentration\ of\ NO_2\ in\ atmosphere\ (ppm) = \frac{c_{No2}-VLRT}{PDt}\ x\ 10^6\ x\ 2.5$$

(Equation 1)

- Device constant value, L is 41.2 m^{-1}
- Volume occupied by NO_2 absorbed on the filter paper, V is 0.002 L.
- Average sampling temperature, T= 301.15 K
- Pressure, P 101325 Pa or 101325 N/m2
- Diffusion coefficient, D is 1.54 x 10-5 m2/s,
- Gas constant is 8.314 J/mol.K or N.m/mol.K
- Sampling time, t is 1 week or 604800 s

This concentration factor of 2.5 is included in calculation due the dilution of the solution with distilled water. All these values are to be substituted into Equation 1 for the calculation of the concentration of NO_2 present in the air. The final data obtained from the passive air sampling at 5 locations is as tabulated below in Table 2 below:

Table 2. Passive Air Sampling Data in 5 Locations in Sungai Buloh

Sampling Site	ABS Value	μM (NO_2)	ppm (NO_2)
Location 1	10.56	455.07	0.025
Location 2	7.35	314.15	0.017
Location 3	6.38	271.82	0.015
Location 4	32.86	1433.27	0.079
Location 5	2.57	104.81	0.006

Location 1 – Location 4 is located at industrial area in Sungai Buloh, whereas Location 5 is a recreational infrastructure with restricted access. From the results obtained, it can be seen that NO_2 concentration is significantly less at Location 5. This is due to reduced number of vehicles in the area. Highest concentration of NO_2 recorded by passive sampler is 0.079 ppm

3.2.5 Comparison of Data with Continuous Air Quality Monitoring Station

Through the Public Private Partnership initiative, DOE has appointed PakarScieno TW SdnBhd under Environmental Quality Monitoring Program which was established by the government of Malaysia. There are 52 air quality monitoring stations located nationwide. Air quality data collected from the monitoring stations are coordinated by the Environmental Data Center (EMC) which serves to manage, process and disseminate environmental data online to relevant government bodies. Air monitoring at CAQMS are carried out using active sampling method. The equipment used in CAQMS is Thermo Scientific Analyzer. This sampling device employs chemiluminescence technology to measure the amount of nitrogen oxides in the air from sub-ppb levels up to 100ppm. On average, the analyzer draws in 0.6 L/min of air and consumes 300 W power.

Based on the data obtained and presented in Table 2, comparison of passive samplers' data is done with the data collected from the nearest Continuous Air Quality Monitoring Station (CAQMS) in Petaling Jaya, Selangor.Distance between sampling site and CAQMS Petaling Jaya is approximately 10.5 kilometers. As discussed in Section 3.3.2, the wind direction is towards 270□ to West. Due to distance between these locations and presence of wind, the data of NO_2 may not be 100% accurate. However, this approach of comparison is similar to real situations whereby the air pollution index (API) is obtained based on nearby monitoring stations.

At passive sampling site in Sungai Buloh, air sampling was carried out using passive samplers, whereas the data from CAQMS is obtained using active sampling method. Figure 5 shows the summarized data for the two sampling points in a graphical representation. The average concentration of NO_2 at the passive sampling site in Sungai Buloh is 19% lower than the concentration measured at CAQMS in Petaling Jaya.

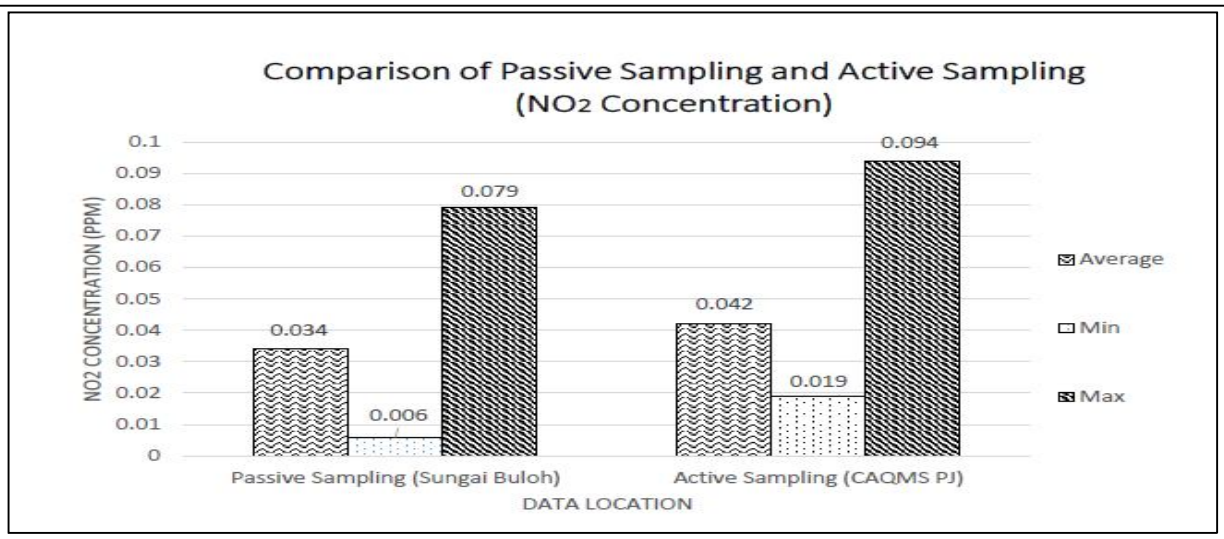


Fig .5 Wind Directions at Sampling Location and CAQMS

From Figure 5 above, it can be deduced that there is variance between data from all two locations. This is due to distance between the locations. Other than that, there is potential that wind speed, wind direction and rain precipitation that affects the concentration of NO_2 in air. The maximum concentration recorded in this project is still below the limits of Malaysian Ambient Air Quality which is 0.16 ppm. The concentration of NO_2 in the atmosphere may also be varies from one city to another depend on the air pollution level in that area. For example, in Japan, many studies had been done as early as in 2004 to study the concentration of NO_2 in the air. Yoshi et al. reported that the average concentration of NO_2 within the area of Tokyo, Japan throughout the year of 2004 was around 0.025 ppm with the minimum concentration of 0.005 ppm and maximum concentration of 0.035 ppm. A more recent study conducted along the PLUS Highway nearby Serdang by Ong et al. (2016) showed average NO_2 concentration of 0.037 ppm. This shows that passive samplers provide consistent reading.

3.2.6 Evaluation of NO_2 Emission in Sungai Buloh

Based on a publication by Department of Environment (DOE), three main sources of NO_2 emission are power generation plant, transportation and manufacturing, as shown in Figure 6. However, in the location of this research, there is no power generation plant within the vicinity. Hence, the source of emission in the location of passive sampling are transportation and manufacturing activities. By obtaining the ratio of the sources in Figure 4.8, excluding the power generation, rough estimation of percentage of NO_2 source can be deduced. 79% of NO_2 is from transportation activities, whereas 21% is from manufacturing activities. This can be said true for the location of passive sampling in Sungai Buloh as there is only one cement processing plant in the industrial area. Other manufacturing activities do not emit high concentration of NO_2. Hence, in Sungai Buloh major source for NO_2 pollution is transportation. As discussed in Section 3.2.3, the number of heavy vehicles is high in industrial area of Sungai Buloh. Heavy vehicles are powered by diesel engines which emits high concentration of NO_2 due to incomplete combustion.

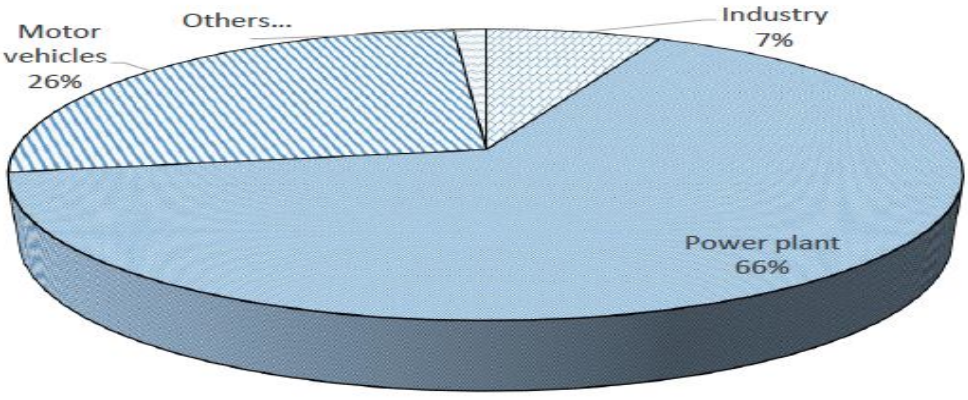


Fig .6 NO_2 Emission Sources in Malaysia

CONCLUSIONS

In conclusion, the results of the passive air sampler were quite comparable to the data of throughout the sampling period although with only minor fluctuation due distance between the passive sampling points and Continuous Air Quality Monitoring Station. During the sampling period, ambient temperature was 28□C and wind speed of between 4 km/h to 7 km/h, which is considered as light air with reference to Beufort scale. This meteorological data has insignificant effect on the performance of passive sampler due to constant hot and humid weather of Malaysia. Average NO_2 concentration from passive air sampling method was recorded at 0.034 ppm which is below the limits of Ambient Air Quality Guideline of 0.16 ppm. The passive sampler is also able to show reading of maximum 0.079 ppm and minimum of 0.006 ppm of NO_2 concentration in air. This proves the performance of passive sampler in ambient air monitoring.

Based on this research work, there are some additional improvements that can be considered to further increase the validity of the results obtained. Therefore, some of the recommendations is stated here to help the other researchers to perform better in their next researches which related to this field. The recommendations given are as follow:

- To measure and record real-time metrological data such as temperature, wind speed and precipitation is better representing the data with sampling period
- The data of the number of vehicles pass by both the highways per hour should be taken for the exact location for more accurate data.
- To conduct passive air sampling at the location of Continuous Air Quality Monitoring station, for better estimation on the variance of data.

ACKNOWLEDGMENTS

I would like to thank officers from Department of Environment (DOE) Putrajaya, Malaysia who have been very helpful in providing data from the Continuous Air Quality Monitoring Stations and valuable additional information for this project.

REFERENCES

[1] Marć, M., Zabiegała, B., &Namieśnik, J. (2014). Application of passive sampling technique in monitoring research on quality of atmospheric air in the area ofTczew, Poland. International Journal of Environmental Analytical Chemistry, 94(2), 151-167.

[2] McLagan, D. S., Mitchell, C. P. J., Huang, H., Abdul Hussain, B., Duan Lei, Y., &Wania, F. (2017). The effects of meteorological parameters and diffusive barrier reuse on the sampling rate of a passive air sampler for gaseous mercury. Atmospheric Measurement Techniques 10(10),3651–3660, https://doi.org/10.5194/amt-10-3651-201

[3] Ševičienė, V., &Paliulis, D. (2012). Influence of Temperature and Relative Humidity on the Performance of Nitrogen Dioxide Diffusive Sampler. Research Journal of Chemical Sciences, 2(5), 89–92.

[4] Chong, O. B. (2017). Passive Air Sampling of Nitrogen Dioxide Within Serdang Area. Journal of Built Environment, Technology and Engineering, 2, 191–197

★★★