# Diurnal variations of air pollution over metropolitan Manila

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#### RESUMEN

Se estudia la variación diurna de la concentración de contaminantes atmosféricos en el área metropolitana de Manila. Los contaminantes que se incluyen en el estudio son SO<sub>2</sub>, CO, NO<sub>2</sub>, NO, HC, Ox y partículas suspendidas. Los datos consisten de observaciones horarias provenientes de cinco (5) estaciones monitoras seleccionadas, localizadas en centros urbanos y para el periodo que comprende 1975-1978.

Los resultados muestran dos tipos de variaciones en las concentraciones exhibidas por los contaminantes y dependiendo de que éstos sean reactivos fotoquímicamente  $(NO_x, SO_2, HC y Ox)$  o no (CO y partículas). La variación que corresponde a los contaminantes no reactivos fotoquímicamente muestra dos máximos, uno en la mañana a las 8:00 am y otro secundario en la noche a las 8:00-9:00 pm. Sin embargo los contaminantes fotoquímicamente activos exhiben un solo máximo a mediodía o temprano en la tarde.

También se ha estudiado la dependencia de la variación diurna con respecto a la estación; en general la tendencia de las variaciones de todos los contaminantes es similar, pero la concentración de éstos es menor durante la estación del monzón del suroeste.

#### ABSTRACT

The diurnal variations of the concentrations of atmospheric pollutants in the Metropolitan Manila area is studied. The pollutants included in the study are SO<sub>2</sub>, CO, NO<sub>2</sub>, NO, HC, Ox and particulate matter. The data consist of hourly observations from five (5) monitoring stations at selected urban centers for the period covering 1975-1978.

The results show two types of concentration variations exhibited by the pollutants depending upon whether they are photochemically reactive (NO<sub>x</sub>, SO<sub>2</sub>, HC and Ox) or non-photochemically reactive (CO and particulate matter). The variation corresponding to non-photochemically reactive pollutants show two maxima, one in the morning at 8:00 am and a secondary in the evening from 8:00-9:00 pm. However, the photochemically reactive pollutants exhibit only a single maximum at about noontime or early afternoon.

The dependence of the diurnal variation with respect to the season has also been studied. In general, the trend of the variations for all pollutants are similar but the concentration of the pollutants is lower during the southwest monsoon season.

#### 1. Introduction

Air pollution is a common problem in densely populated cities, like Manila. In order to develop an air pollution control program for these areas, it is imperative to have a thorough knowledge of the space and time variations of the concentrations of the pollutants. Previous studies over some cities indicate large diurnal variations in the pollutants' concentrations. Diurnal variations of the concentration of pollutants are presumably due to the variations in the different factors directly affecting the complex processes which determine the concentration of atmospheric pollutants. Some of these factors are:

- 1. Space-time variations of pollutant sources.
- 2. Diffusion (horizontal and vertical) by small-scale turbulence.
- 3. Transport by the large-scale (mesoscale) flow.
- 4. Photochemical reactions.
- 5. Wash-out, rain-out, deposition, sedimentation and other similar processes.

The relative importance of each of these processes depends on the existing meteorological conditions, and the pattern of human as well as industrial activities which prevail in a particular location. In general, the effects of the above-mentioned factors are greatest during the daytime.

The diurnal variations of pollutants have been studied previously by many investigators. For example, Bizjak et al. (1988) found that the  $SO_2$  concentration in Ljubljana, Yugoslavia shows two maxima over a 24-hour period. One maximum occurs at 9 am while the other occurs at about 9 pm. Similar variations with the two maxima have been found by Stevens (1987) in the Greater Johannesburg region for non-methane hydrocarbons and oxides of nitrogen  $(NO_x)$ . In the case of  $NO_x$ , the morning maximum is greater than the afternoon maximum. García (1988) also found two maxima for the concentration of suspended particulates over Oviedo, Spain. The first maximum occurs at about 9 am while the second occurs at about 6 pm.

Diurnal variations with two maxima (semi-diurnal or 12-hr periodicity) appear to be characteristic of certain types of pollutants. Other pollutants exhibit different modes of diurnal variation. For example, in the case of ozone, Stevens (1987) found only one maximum during a 24-hour period, which occurs in the afternoon.

The studies cited above have been done over inland areas located far from shorelines. In coastal areas, the occurrence of diurnal wind variations associated with local circulations, e.g. land and sea breezes, tend to accentuate the diurnal variation of air pollutants. The effects of land and sea breezes on air pollution have been studied by Lyons and Cole (1976), Shair et al. (1982) and Kitada et al. (1986). In general, these studies indicate the importance of local circulation in transporting pollutants back and forth across the shoreline —seaward in the early morning hours and landward during the daytime. Similar diurnal effects are observed in areas affected by mountain and valley breezes (e.g. México City).

All of the observational studies mentioned in the preceding paragraphs have been done in areas at temperate latitudes. A similar study in a tropical region like the Metropolitan Manila area was desired and ventured on. This paper presents the results of the endeavor. The diurnal variations of CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, HC, Ox and particulate matter were studied. In Section 3, the diurnal variations averaged annualy are presented, and the seasonally averaged diurnal variations are discussed.

# 2. Observational data and method of analysis

The area of study is shown in Figure 1. The area is generally flat from the coast towards the foothills of the Sierra Madre Mountains, about 20 km to the east of the Manila Bay shoreline. In the southeast sector lies another body of water, the Laguna de Bay. The large-scale prevailing flow is monsoonal –southwest monsoon (rainy season) during the period June to September, and northeast monsoon (dry season) from December to March (Francisco et al., 1984). Thus, the

prevailing flow is towards land during the southwest monsoon, and towards Manila Bay during the northeast monsoon season. There are two transition periods (October-November and April-May) between the monsoons, which are generally characterized by relatively weak prevailing flow. During these periods, land and sea breezes are well-developed, most especially in April and May.

The concentration of pollutants were measured by the NPCC (National Pollution Control Commission) at five monitoring stations (Fig. 1): Cubao, Bicutan, Quiapo, Herran and Pasay.

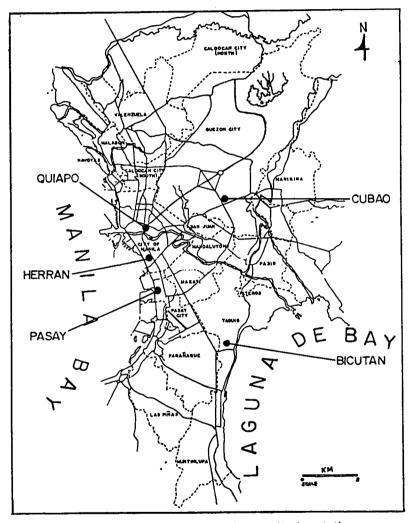


Fig. 1. Map showing the location of the five monitoring stations.

Note that the last three are only within about 3 km from Manila Bay, while Herran is practically at the shoreline. Bicutan is only about 1 km from Laguna de Bay. The farthest inland station is Cubao, which is about 10 km from Manila Bay. There is heavy vehicular traffic during the day from 6 am to 7 pm in the vicinity of four of the stations, except at Bicutan. Motor vehicles, both diesel and gasoline-powered, account for about 70% of the total air pollution, while the remainder comes from industrial sources. The diesel-powered vehicles emit exhaust gases containing hydrocarbons, organic acids, aldehydes, sulfur oxides, and nitrogen oxides. On of the other hand, gasoline powered vehicles emit carbon monoxide, hydrocarbons, nitrogen oxides,

and lead compounds. Most of the industrial sources of pollution such CO, SO<sub>2</sub> and Ox are located in the areas to the southeast, which are about 10 km northwest in Cubao. An oil-fired power plant is located near the Herran station.

The pollutants which have been observed are particulate matter (dust), CO,  $NO_x$ ,  $SO_2$ , HC and Ox. Hourly sampling and analyses of concentrations were made by means of automated techniques. A short summary of the various analytical principles and methods used in the analyses are described in the succeeding paragraphs.

## Sampling

Routine sampling is done on an hourly interval. Ambient air is sucked into the system by a built-in pump of the analyzer. It is purified by the first filter and brought to the electronic cooling dehumidifier, then coursed to the dryer. The sample is brought to the second filter, and finally into the analyzer unit chamber. The excess air sample is discharged and discarded through a by-pass tube.

#### Carbon Monoxide

The Type APMA-10 (AM) Hitachi Horiba Air Pollution Monitoring CO Analyzing System is a combination of a Non-Dispersing, Infrared Ray Analyzing System (NDIRS) used for microanalysis of carbon monoxide. This works on the principle that molecules consisting of different atoms absorb infra-red (IR) radiation in different wavelength regions. In a gaseous sample under constant pressure, the energy of the IR rays absorbed corresponds to the concentration of the molecules. Based on this principle, the IR analyzer determines the concentration of carbon monoxide in the sample by measuring the quantity of IR rays absorbed by the carbon monoxide molecules.

## Oxides of nitrogen

The use of the Salzmann colorimeter (Horiba Type APNA-1S Nitrogen Oxides Analyzer) automatically measures trace quantity of nitrogen oxides in the air. The Salzmann reagent develops a distinct red color (550 m $\mu$ ) upon absorbing nitrogen dioxide gas in the sample. The color intensity of the liquid reagent is proportional to the concentration of NO<sub>2</sub>. After this, the remaining nitric oxide in the air sample is oxidized to nitrogen dioxide [NO  $\Rightarrow$  NO<sub>2</sub>] by passing it through a sulfuric acid solution of potassium permanganate (KMnO<sub>4</sub>). The procedure with Salzmann reagent is repeated and the color intensity difference represents the concentration of nitric oxide in the sample.

### Oxidants

Iodine coulometry using the Horiba Type APOA-1A Oxidant analyzer based on Coulomb's Law is utilized in this analysis. Neutral buffered potassium iodine solution (KI) is the reagent used for the purpose, whereby the oxidants of the sample air frees the iodine of the reagent when passed through it. The electro-chemical coulometry of the free iodine produced by the oxidation of KI measures the amount of oxidants in the sample. The reaction showing the free iodine in the oxidation process is given by:

$$0_3 + 2KI + H_2O --- I_2 + 2KOH + 0_2$$

Free iodine is electro-chemically reduced by an electrolytic voltage of 0.23 v as shown by the equation:

$$I_2 + 2e^-$$
 ---  $2I^-$ (cathode) and

$$2I^{-}$$
 ---  $I_2 + 2e^{-}$  (anode)

The reduction current of this iodine is amplified to indicate and record the concentration of the oxidants which is proportional to the electric current produced, and is equivalent to the free iodine too.

In the case of the oxidant analyzer based on iodine freeing method,  $NO_2$  and  $SO_2$  are the most serious interferents. A chromic anhydride ( $CrO_3$ ) scrubber is equipped in the sampling line of the analyzer to eliminate  $SO_2$  interference from the system.

## Hydrocarbon

This is determined by the use of a Hydrogen Flame Ionization Detection System (FID) using type APHA-10 Hydrocarbon Analyzer which provides a continuous measurement of the total concentration of hydrocarbon in the air. HC is introduced into the hydrogen flame of the analyzer. The hydrocarbon is decomposed by the high temperature energy flame which produces ions proportional to the total carbon content of the hydrocarbons in the sample. The hydrocarbon detectors provide stable output with high sensitivity, provided the hydrogen flame is maintained at a constant rate.

### Sulfur dioxide

The sulfur dioxide content of the air is measured by electro-conductometric method. When air is introduced into hydrogen peroxide solution acidified with sulfuric acid, the  $SO_2$  in the sample is perfectly absorbed by the solution and forms  $H_2SO_4$  by the following reaction:

$$S0_2 + H_20_2 --- H_2S0_4$$

The change in electric conductivity caused by the formation of sulfuric acid is detected by the measuring electrode in the impinger. The electric conductivity of the original reagent solution is measured by the reference electrode immersed in the reagent contained in the jacket surrounding the impinger.

As the temperature of the measuring reagent solution (into which the air sample is introduced) and the temperature of the original reagent solution is equalized by the heat exchanged through the thin glass wall, the ratio of the change in the electric conductivity of the original becomes free of temperature effect since the change in electric conductivity due to temperature change is cancelled. Taking the ratio of the electric conductivities obtained gives the concentration of SO<sub>2</sub> in air, which corresponds linearly to the numerical value of the ratio.

Interference from CO<sub>2</sub> concentration existing in urban air is prevented by adjustment of the absorbing reagent to ph 4.5, at which level equilibrium is attained with the normal concentration of CO<sub>2</sub> in air. Interference from ammonium can be assessed by separate determination of the ammonia present in the solution.

Total suspended particulates (dust)

There are two ways by which the total suspended particulates are determined: by the light scattering method which is used in hourly sampling, and by the use of the high volume sampler for 24-hour sampling. The latter is particularly used to determine other particulate matter concentrations which are not within the measuring range of the dust analyzer.

When the air stream is exposed to a light beam, the light is scattered by the dust particles in the air sample, and the dust concentration is obtained by measuring the scattered light intensity, by a highly sensitive photo-multiplier tube [Dust Analyzer Model D-3(S)]. The amount of scattered light intensity is converted into pulse signals, such that one count of pulse per hour corresponds to 0.001  $\mu$ g/m<sup>3</sup> of the hourly average particulate matter concentration. The pulse signal, is converted into analogue signal by the D/A converter, and transmitted to the recorder.

#### 3. Results and discussion

### A. Annually-averaged diurnal variations

The results of the present study generally confirm the existence of the two types of variations namely, diurnal periodicity and semidiurnal periodicity which have been reported by previous investigators. In the case of the Metropolitan Manila, diurnal variations with two maxima tend to occur in the concentrations of particulate matter, SO<sub>2</sub>, NO, CO and hydrocarbons. In contrast, a single maximum usually occurs for NO<sub>2</sub> and oxidants. These results indicate that the diurnal variations with double maxima are associated mainly with primary pollutants or direct emissions, while the secondary pollutants (products of photochemical reactions) tend to have only one maximum during a 24-hour period.

The best example of the diurnal variation with two peaks is the concentration variation of particulate matter as shown in Figure 2. Note that there is a remarkable similarity among the curves for all five stations. The principal maximum concentration occurs in the morning between 7 and 8 am while the secondary maximum occurs about 12 hours later at night. These maxima are separated by two minima which occur at about 2 pm and 2 am. The concentration of particles at the time of the secondary maximum is about 50% to 60% of the primary maximum. The secondary maximum is well-defined at three stations namely, Cubao, Quiapo and Herran. Among the five stations, Cubao has the greatest primary maximum with a value of about 170  $\mu$ g/m<sup>3</sup> particulate matter. On the other hand, Bicutan is the least dusty with a primary maximum of only 63  $\mu$ g/m<sup>3</sup>.

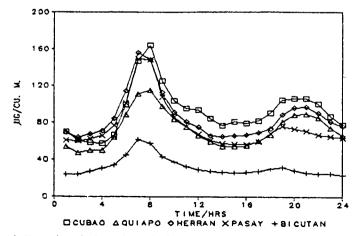


Fig. 2a. Average annual diurnal variation of particulate matter concentrations for Manila.

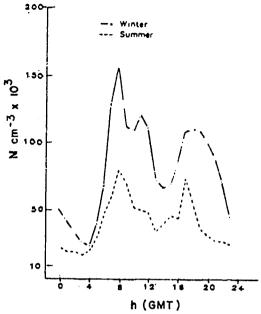


Fig. 2b. Average daily variation of concentration of particles for winter and summer (working days) for Oviedo, Spain. (After García et al., 1988).

The variation of particulate matter concentration over Manila as shown in Figure 2a is very similar to that found over Oviedo by García et al. (1988) in Figure 2b, except for the earlier occurrence of the secondary maximum at 6 pm over Oviedo. This similarity in the trend of particulate matter concentration may be indicative of the similarity in the physical processes which produce the variations. In particular, the sharp increase in particle concentration from the early morning minimum to the 8 am maximum is due to two factors: (1) the rapid increase in particulate matter sources due to the increased vehicular activity during the morning rush hours and (2) the concomittant existence of a shallow surface temperature inversion which confines the particles within the inversion. The rapid decrease in concentration following the morning maximum is due mainly to the strong upward flux of particles by turbulent motions, which occurs as soon as the inversion is destroyed by solar heating after sunrise. The decrease of particles due to turbulent flux is reinforced by the advection of less dusty air by the sea breeze later in the day; thus, a minimum in particulate matter concentration is produced at about 3 pm. The subsequent increase from this minimum to the secondary maximum at 8 pm may be due to two factors: increased vehicular traffic (more particulate matter sources) during the afternoon rush hours and the return of stable thermal stratification (less turbulent flux upward) after sundown. The diurnal cycle is completed by a decrease from this secondary maximum to the early morning minimum. This decrease may be due to two processes: (1) sedimentation or settling of the particulate matter to the ground, and (2) transport of less dusty air by downslope motions (katabatic flow) from the less polluted hills east of the city in the early morning.

The variations in the other primary pollutants (SO<sub>2</sub>, NO, CO, HC) are shown in Figures 3 to 6. As expected, all of these tend to have two maxima during a 24-hour period, with some exceptions. For example, the late evening maximum is generally weak or absent for the two stations – Pasay and Bicutan. These stations also appear to be the least polluted. In contrast, the evening maximum is very strong in Cubao (NO, CO), equalling or exceeding the usual primary morning maximum. To a certain extent, this same behavior is seen in Quiapo for CO and HC.

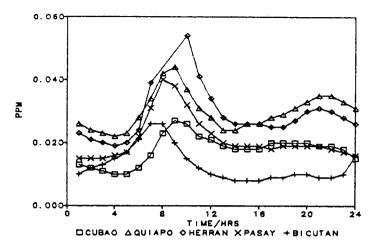


Fig. 3. Average annual diurnal variation of SO<sub>2</sub> concentrations.

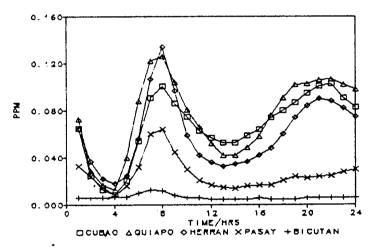


Fig. 4. Average annual diurnal variation of NO concentrations.

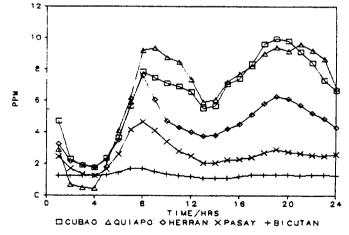


Fig. 5. Average annual diurnal variation of CO concentrations.

It may be noted that among the five stations, Bicutan has the smallest concentration of all the pollutants, presumably due to the fact that the monitoring station is located about 30 meters atop a building in contrast with other four stations which are located 3 meters above the ground. In the case of SO<sub>2</sub>, Herran has the highest concentration. This is a result of the existence of an oil-fired power plant in the vicinity.

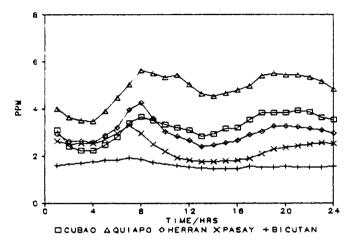


Fig. 6. Average annual diurnal variation of HC concentrations.

Obviously, the common features of the diurnal variations of the primary pollutants consist of a maximum which occurs at about 8 am, a minimum at about 4 am and another minimum at about 2 pm. A less common variation is a tendency to exhibit another maximum at about 8 pm. In some stations, this maximum is ill-defined or practically absent. However, in other stations, this maximum in the concentration of the primary pollutants is very strong and is at times even greater than the morning maximum. The difference in the behavior of the evening maximum is difficult to explain. It has been expected that these differences would not exist because similar physical processes are simultaneously affecting the concentration of these pollutants. The similarity is not exactly perfect though, because the particulate matter and NO concentrations are affected by sedimentation and photochemical reaction respectively; while the other pollutants are not. However, these are presumably minor processes.

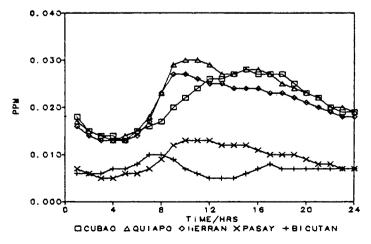


Fig. 7. Average annual diurnal variation of NO2 concentrations.

We now turn our attention to the secondary pollutants (NO<sub>2</sub>, and Ox) which are produced by photochemical processes. The diurnal variations for these pollutants are shown in Figures 7 and 8. In general, these figures show a large variety of shapes. Looking at Figure 7, it can be noted that there are three types of variations for NO<sub>2</sub>. One type has a single maximum during a 24-hour period, as shown by the diurnal variations at Quiapo, Herran, and Pasay. At these stations, the maximum occurs between 9 and 10 am after a sharp rise from an early morning minimum. The second type, which is observed at the Cubao station, also shows one maximum during a 24-hour period. However, the maximum occurs much later in the afternoon at about 3 pm. Sharply in contrast with the first and second types, the third type (see Bicutan) shows two concentration maxima – a primary morning maximum at 8 am and a secondary maximum at 5 pm.

Figure 8 shows the diurnal variations for oxidants at the five stations. Gauging from the characteristic of the Ox concentration curves, the diurnal variations exhibit a large variety of shapes. The variations for Bicutan and Pasay show the expected single afternoon maximum similar to that which has been observed previously by Stevens (1987). Note that the peak in Ox concentration is reached before midday. This may be attributed to the fumigation of the trapped oxidants at higher levels which are brought down due to the destruction of the inversion layer after sunrise. On the other hand, both Herran and Quiapo show the two-maxima variation which is generally associated with particulate matter and other primary pollutants. Finally, Cubao shows a curve which is slightly different from the diurnal variation of these pollutants in Quiapo. This curve is characterized by plateau with more or less constant pollutant concentrations from 8 am up to 12 pm. The occurrence of this plateau casts a suspicion about the accuracy of the concentration measurements at the Cubao station.

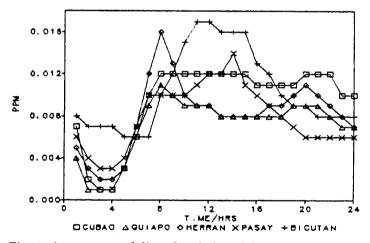


Fig. 8. Average annual diurnal variation of Ox concentrations.

In retrospect, the observed diurnal variations of pollutants over metropolitan Manila do not completely agree with the observations of other researchers which show that primary pollutants have a semi-diurnal periodicity (two maxima), while secondary pollutants have a diurnal periodicity (one maximum). For example, we found that the diurnal curve for some primary pollutants have only one maximum at some stations over metropolitan Manila. Moreover, there are some stations where the curves for secondary pollutants have two maxima. This study found no clear evidence of the effect of the sea breeze in transporting less polluted air from the sea.

# B. Monsoonally-averaged diurnal variations

As mentioned in Section 2, the Metropolitan Manila Area is affected by the southwest monsoon in summer and the northeast monsoon during winter. The southwest monsoon season is characterized by rainy weather and onshore flow. In contrast, generally dry conditions and offshore flow prevail during the northeast monsoon season. These two contrasting conditions would have opposite effects on the concentrations of the pollutants through the processes of transport and rain scavenging. During the southwest monsoon season, the onshore prevailing flow would tend to transport unpolluted air into Metropolitan Manila; furthermore, the frequent rains will result in the scavenging of pollutants. Thus, these two processes would tend to decrease the concentration of pollutants. However, these two processes would be practically absent during the northeast monsoon season. Therefore, it is expected that the air would be more polluted during the northeast monsoon season. In order to confirm this expectation, the average diurnal variations were computed separately for each of the two seasons: southwest monsoon (July to August) and northeast monsoon season (December to January).

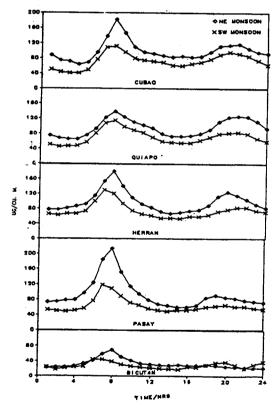


Fig. 9. Average diurnal variation of dust concentrations during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

The monsoonally-averaged diurnal variations are shown in Figures 9 to 15. The variations in the particulate matter concentration are presented in Figure 9. It indicates that the southwest monsoon curves are parallel to those of the northeast monsoon, except for a small segment during the night at Bicutan. Note that the southwest monsoon concentrations are lower than the corresponding northeast monsoon concentrations, except for the above-mentioned segment. Moreover, the largest differences between the pollutant concentrations generally occur during the time of maxima in the morning and at night. In the case of the Pasay station, the maximum

concentration in the morning during the northeast monsoon is approximately twice that of the southwest monsoon concentration. However, in the case of Quiapo, the corresponding differences are surprisingly much smaller. The trend of the diurnal variation of the particulate matter concentration appear to confirm our expectations that the southwest monsoon air over Metropolitan Manila would be less polluted due to the effects of transport and rain scavenging. But it is not determined by looking at Figure 9 as to which one of the two effects is more dominant.

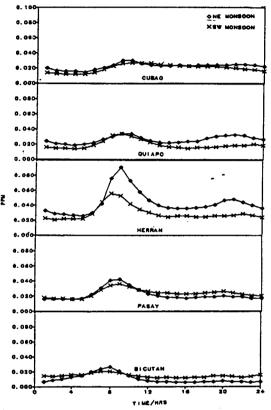


Fig. 10. Average diurnal variation of SO<sub>2</sub> concentrations during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

The characteristics of the diurnal variations of the other primary pollutants (SO<sub>2</sub>, NO, CO and HC) in Figures 10 to 13 are, by and large, similar to the dust variations. However, there are some interesting deviations. For example, note that in the case of SO<sub>2</sub> at Pasay and Bicutan, the concentrations from 10 am to 6 am of the following day are actually greater during the southwest monsoon than during the northeast monsoon season. To a certain degree, this behavior is also observed for NO at Pasay. Note also that the two curves for CO (Quiapo) are almost coincident, indicating that there is practically no monsoonal effect on the diurnal variation.

This may be explained by the over-crowded condition in Quiapo, being the center of commercial activities in downtown Manila. The building structures are constructed literally wall-to-wall with very narrow streets separating one block from the other. Even the vehicular traffic is at most times bumper-to-bumper, and sometimes at a standstill everytime it rains. Hence, the increased amount of exhaust gases in the air negates the effect of the monsoon rains.

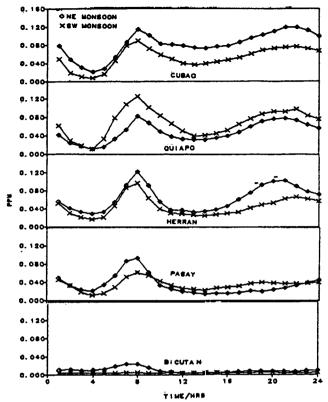


Fig. 11. Average diurnal variation of NO concentration during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

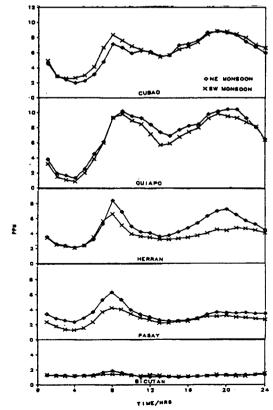


Fig. 12. Average diurnal variation of CO concentration during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

Next, we look at the monsoonally-averaged diurnal variations for the two secondary pollutants (NO<sub>2</sub> and Ox) shown in Figures 14 and 15. Again, as in the case of the primary pollutants in the preceeding figures, the two monsoon curves are more or less parallel to one another. Moreover as expected, the southwest monsoon concentrations are generally less than the corresponding

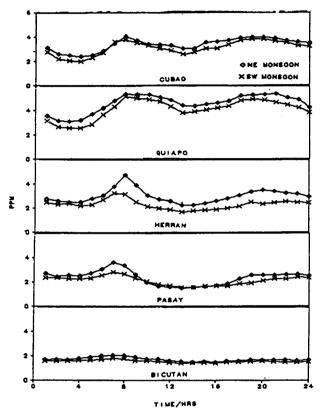


Fig. 13. Average diurnal variation of HC concentration during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

northeast monsoon concentrations. The largest differences in concentration between the two monsoon are found in the afternoon at Cubao station, while at the Pasay station, large differences occur during the earlier time of the day. In contrast to these large differences in concentrations, the monsoonal effects are small over Quiapo and Herran and also over Bicutan for Ox. Lastly, one may note the anomalous behavior of the NO<sub>2</sub> concentrations over Bicutan, where the southwest monsoon concentrations are higher than those during the northeast monsoon season. Another anomalous behavior is the occurrence of two maxima instead of one maximum in the diurnal variations of both NO<sub>2</sub> and Ox over Herran.

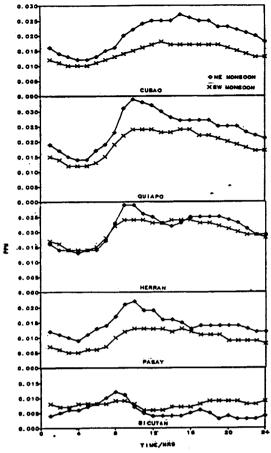


Fig. 14. Average diurnal variation of NO<sub>2</sub> concentration during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

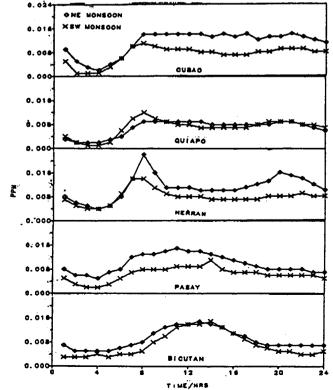


Fig. 15. Average diurnal variation of Ox concentration during the NE monsoon (diamond) and the SW monsoon (cross) seasons.

## 4. Concluding comments

The study indicates that the primary pollutants show a typical diurnal variation which is characterized by two maxima and two minima during a 24-hour period. The maxima occur in the morning and at night, while the minima occur in the early morning and in the mid-afternoon. In contrast, the secondary pollutants tend to show a single maximum during a 24-hour period. In general the maximum occurs before noon, while the minimum occurs in the early morning at about the same time as that of the primary pollutants. The process which decreases the concentrations from their night time values to this minimum is not entirely understood.

In summary, the analysis of the diurnal variations of the concentrations indicate the following general characteristics:

- a. Semi-diurnal periodicity for primary pollutants and diurnal periodicity for secondary pollutants.
  - b. Minimum concentration for both primary and secondary pollutants at about 4 am.
- c. Maximum concentration at about 8 am for the primary pollutants and few hours later for secondary pollutants.
- d. Minimum concentrations again at about 2 pm for the primary pollutants followed by a relative maximum at about 8 pm.

As mentioned previously in this section, there are some exceptions to these general characteristics. It may be noted that, if one compares the diurnal variations over different stations for one particular pollutant (e.g. Ox), there are differences among the variations which have no obvious explanation based on transport, scavenging, or other processes. Moreover, the comparison of the diurnal variations of all primary pollutants at one particular station (e.g. Cubao), indicated differences which cannot be readily explained.

The dependence of the diurnal variations on the various large-scale conditions associated with the southwest (rainy and onshore flow) monsoon and the northeast (dry and offshore flow) monsoon have been studied. This was done by determining the average diurnal variations separately for each of the two monsoons. It was observed that the diurnal variations for the two monsoons have similar trends. However, the concentrations during the southwest monsoon are generally lower than the corresponding concentrations during the northeast monsoon season. This is presumably due to the transport of less polluted air from the sea into the area and to the scavenging by rain during the southwest monsoon.

It is recognized that there are many unusual deviations from the typical diurnal variations in the concentration of the primary and the secondary pollutants; yet the reason for the occurrence of such deviations are not defined. It is suggested that future investigations, observational as well as theoretical, be conducted to study the nature of these deviations.

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