AEROSOL OPTICAL THICKNESS AND TOTAL OZONE COLUMN CHARACTERIZATION USING MICROTOPS II OZONEMETER IN MANILA, PHILIPPINES

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ABSTRACT: Ground-based measurements of Total Ozone Column (TOC) and Aerosol Optical Thickness (AOT) at 1020 nm were done in Manila, Philippines (14.567° N, 120.980° E) using a MICROTOPS II ozonemeter for the period of February to April 2014 at 30-minute intervals (0900-1200H, 1300-1600H, LT).For the study period, the lowest and highest TOC (at ±1σ) were 208.30±9.30 DU and 283.40±22.07 DU that occurred last March 18 and May 17, respectively. AOT had its lowest value of 0.117±0.045 last March 12 while the maximum was 0.335±0.11 last May 2. Kruskal-Wallis H statistics, a non-parametric analogue of ANOVA, revealed that the TOC values for the observation months are significantly different from each other (p = 0.0002). The same results were also obtained for AOT (p = 0). Mann-Whitney U Test, a non-parametric analogue of t-test, showed that there was a statistically significant difference in the values of TOC and AOT between the AM and PM observations with p-values of 0.032 and 0.001, respectively.The effects of relative humidity (RH) and surface temperature (ST) on AOT and TOC were analyzed. ST and RH play important roles in modulating aerosol and ozone behavior. For the study period, ST showed a moderately negative correlation with AOT (r= -0.4206) and a moderately positive correlation with TOC (r = +0.4922). RH had a strong positive correlation with AOT (r= +0.5431) but has very weak, negative correlation with TOC (r= -0.0339) which is not significant.

KEYWORDS: Ozone, Aerosols, Aerosol Optical Thickness, Microtops II, Relative Humidity, Surface Temperature

1. INTRODUCTION

Atmospheric aerosols are particles of solid or liquid phase dispersed in the atmosphere. Aerosols are produced by a variety of natural and anthropogenic processes. They vary in size from 10^{-3} to 10^{2}μm depending upon the source and production mechanism. Aerosols play an important role in the Earth's radiation budget, air quality and environmental health. The optical properties of atmospheric aerosolsare determined by their chemical composition, concentration, size and internal structure (Prospero et al., 2002). All these characteristics vary in space and time depending on local and regional events of natural and anthropogenic nature such as biomass burning, urban and non-urban processes, volcanic eruptions and airborne soil particles. Thesemake it difficult to monitoratmospheric aerosols. Significant progress has been made to improve aerosol characterization by using in situ measurements, ground-based remote sensing, and satellite observations.

Aside from atmospheric aerosols, the ozone present in the atmosphere also plays a key role in the radiation balance of the Earth-atmosphere system. Ozone is a relatively unstable molecule made up of three atoms of oxygen. It condenses to form a liquid at -111.9° C (1 atm) and forms a solid at -192.7° C. Ozone is exceedingly rare in the atmosphere, there are ~3 moles of ozone for every 10 million air molecules(Ranjan et al., 2007). The column ozone concentration is usually measured using a Dobson or Brewer spectrophotometer. These two passive ground-based instrumentsare very expensive, heavy andhuge. Thus, there is a need for less expensive, more portable and compact instruments that can measure ozone with reasonable accuracy over different environments. In this study, a handheld MICROTOPS II ozonemeter was used to measure the diurnal variation, characteristics, and relationshipbetween the AOT at 1020 nm and TOC over Manila.

2. OBSERVATIONAL SITE, INSTRUMENTS, AND METHODOLOGY

Measurements were carried out at De La Salle University–Science and Technology Research Center, STRC (14.567° N, 120.980° E), lying in the eastern part of Manila, the capital city, and second to the largest city in the Philippines. The site is located 1.2 km away from the eastern shore of Manila bay. It is an urban area where commercial and industrial activities are predominant.

Manila features a tropical monsoon climate. Its proximity to the equator means that the temperature range is very small, rarely going below 20° C or above 38° C. Manila has a distinct dry season from late December through May, and a relatively lengthy wet season that covers the remaining period with warm temperatures. Typhoons can occur from June to September and can cause flooding in parts of the city.Due to the heavy reliance on automobiles, the city suffers from air pollution in the form of smog which affects 98% of the residents of the city and results in more than 4,000 deaths per year (National Nutrition Council, n.d.).

The MICROTOPS II (**MICRO**-processor based **T**otal **O**zone **P**ortable **S**pectrometer) is a compact, portable and handheld five-channel ozonemeter. The atmospheric total column ozone is derived from the 305-, 312-, and 320-nm channels while the 936- and 1020-nm channels are used to measure water vapor and AOT, respectively. The instrument has a full field of view (FOV) of 2.5°. A sun target and pointing assembly is laser-aligned with the optical channels. Solar Light Company (2001) provides a full description of the instrument.

In this work, AOT and TOC over the measurement site were determined using a tripod-mounted MICROTOPS II at the STRC roof deck from February to May 2014. AOT and TOC readings were obtained on all clear sky days from 0900-1200H and 1300-1600H (local time, LT) at 30-minute intervals yielding about 60 scans per day. A Davis Vantage Pro 2 automatic weather station provided simultaneous measurements of surface meteorological parameters.

3. RESULTS AND DISCUSSIONS

3.1. Temporal Variations of Total Ozone Column

Daily Variation of TOC. Total ozone column amounts were obtained for the DLSU site from February to May 2014.Figure 1A presents a box plot of the daily variation of TOC. There were only small TOC variationsfrom February to early March. TOC drastically increasedfrom late March to May wherein a maximum of 283.40 ±22.07 DU was measuredlast May 17. For the study period, the lowest TOC measurement occurred last March 18 and was about 208.30 ± 9.30 DU. These trends are similar to the results obtained by Silva & Tomaz (2011) where ozone mixing ratios are at its maximum during the relatively dry months. May is the peak month for summerin Manila. Table 1 lists the detailed summary for the lowest and highest TOC days during the study period. Equal number of observations (N = 11) were gathered for both days.

Table 1. Maximum & minimum values for TOC measurements (Manila, Feb-May 2014)

Date (mm/dd/yy)	N	Median	Min	Max	Q1	Q3	QD	Mean ± 1σ
MIN: 03/18/14	11	203.96	200.62	231.34	202.7	213.65	5.475	208.30 ± 9.30
MAX: 05/17/14	11	274.78	259.20	324.97	264.48	299.18	17.35	283.40 ± 22.07

Monthly Variation of TOC. Figure 1B shows that the TOC did not change considerably from February to Marchbut consistently increased from March to May. Medium to high levels of ozone are found during warm months with an increasing trend from March to May. This result is in agreement with Ganguly and Iyer (2005) in Rajkot, India. Valenteand Thornton (1993) stated that the primary cause of high ozonevalues for the month of May (peak of summer)can be the high solar flux acting upon a pool of accumulated NO_x and hydrocarbons built up during the past months resulting in local photochemical production. For the study period, slightly lower monthly TOC (215.66 ± 10.2 DU) was obtained for March while the highest monthly TOC (265.82 ± 17.3 DU) was found in May. Lastly, Kruskal-Wallis H statistics showed that the difference in the TOC valuesamong all the observation monthswas statistically significant, H (3, N = 251) = 19.55, p = 0.0002; with a mean rank TOC value of 168.80 for February, 114.16 for March, 127.09 for April, and 114.70 for May. Table 2 shows the numerical summary for the monthly and daytime variation for TOC.

Table 2. Summary of TOC measurements (Manila, Feb-May 2014) for different temporal scales

	N	Median	Min	Max	Q1	Q3	QD	Mean ± 1σ
Overall	251	226.15	213.18	272.27	226.63	243.24	8.185	236.1 ± 19.4
Monthly Observation								
FEB	44	216.77	200.7	245.88	209.68	222.81	6.565	217.92 ± 17.2
MAR	96	213.44	200.0	239.54	209.23	220.48	5.625	215.66 ± 10.2
APR	41	242.48	212.0	278.70	235.38	253.75	9.185	245.0 ± 33.0
MAY	70	265.21	240.0	324.97	252.23	275.90	11.835	265.82 ± 17.3
Daytime Observation								
AM (Morning)	121	235.62	203.78	324.97	219.68	272.12	26.22	242.79 ± 27.7
PM (Afternoon)	130	216.68	200.0	274.78	210.32	246.18	17.93	227.44 ± 21.5

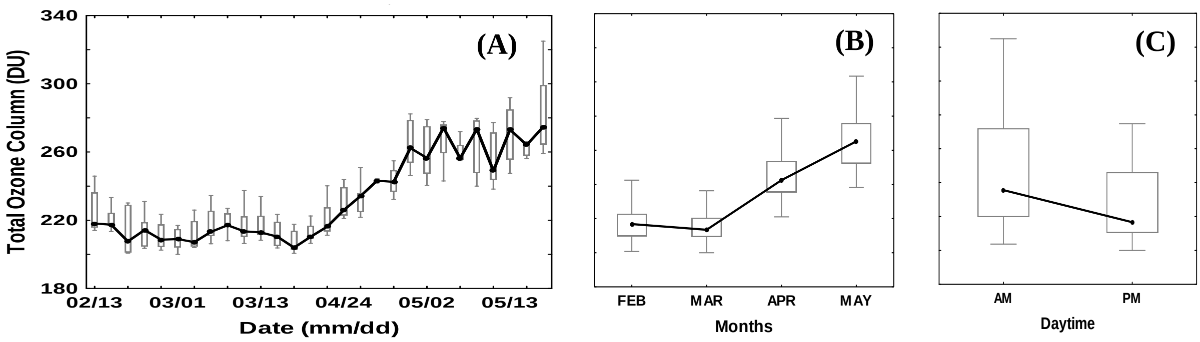

Figure 1.Temporal variation of TOC in Manila from February to May 2014. (A) daily variation;(B) monthly variation; and (C) daytime variation

Daytime Variation of TOC. Figure 1C compares the AM and PM TOC observations. For the study period, a decreasing trend was observed from AM (242.79 ± 27.7 DU) to PM (227.44 ± 21.5 DU) TOC measurements. The vertical column density of ozone is higher during the morning compared to the afternoon. For the study site, the ozone concentration is generally low at sunrise, increasing to a maximum before noon (around 10 to 11 AM) and decreasing in the afternoon. This may be due to an increase in temperature from AM to PM causing a corresponding increase in ozone by photochemical formation, as higher temperatures increase the emission rate of ozone precursors (Valente and Thornton, 1993). In the afternoon, higher surface heating causes a vertical convection and subsequent dispersion of pollutants. Mann-Whitney U Test, a non-parametric analogue of t-test, revealed that the AM TOC measurements are significantly different from the PM observations, H (1, N = 251) = 45.72, p = 0.032; with a mean rank TOC value of 158.12 for AM, and 96.11 for PM.

3.2 Temporal Variations of Aerosol Optical Thickness at 1020 nm

Daily Variation of AOT at 1020 nm. Figure 2A presents a box plot of the daily variation of AOT over the measurement site. The lowest (0.117 ± 0.045) and highest (0.335 ± 0.11) mean (at ± 1σ) AOT were obtainedlast March 12 and May 2, respectively. AOT values of 0.01 correspond to an extremely clean atmosphere with a clear sky and maximum visibility while an AOT of 0.4 indicates a very hazy condition (Brooks, 2010).Table 3 lists the detailed summary of the AOT for March 12 and May 2.

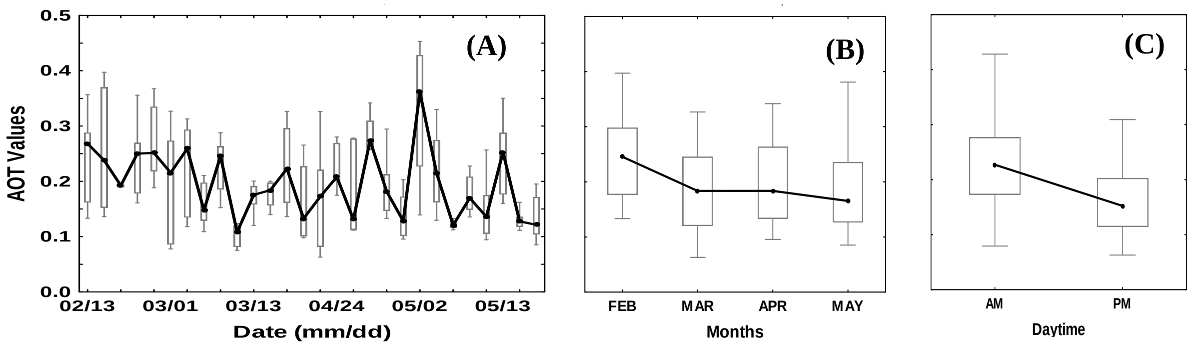

Figure 2.Temporal variation of AOT at 1020 nm in Manila from February to May 2014. (A) daily variation;(B) monthly variation; and (C) daytime variation

Table 3. Maximum & minimum values for AOT at 1020 nm measurements (Manila, Feb-May 2014)

Date (mm/dd/yy)	N	Median	Min	Max	Q1	Q3	QD	Mean ± 1σ
MIN: 03/12/14	12	0.108	0.075	0.123	0.0812	0.120	0.0194	0.117 ± 0.045
MAX: 05/02/14	12	0.227	0.139	0.453	0.227	0.428	0.1005	0.335 ± 0.11

Monthly Variation of AOT at 1020 nm. Figure 2B shows the monthly variationof AOT. For the study period, February had the highest AOT values compared with the March–May readings. The AOT only changed slightly from March to May. High AOT values may be due tohigh aerosol loading. Very busy streets along with commercial and industrial centers surround the study site. Summer vacation for most schools is from April-May. Usually, the surface temperature in February is lower compared with March–May. Kruskal-Wallis H statistics illustrates that theAOT among all the observation monthswere significantly differentfrom each other, H (3, N =

251) = 176.88, p = 0; with a mean rank AOT value of 80.83 for February, 69.76 for March, 165.59 for April, and 208.34 for May.

Daytime Variation of AOT at 1020 nm. Figure 2C indicates that AM (0.233 ± 0.15) had higher mean AOT values compared with PM (0.168 ± 0.11). AOT values areaffected bylocal events and conditions along with local weather conditions. Mann-Whitney U Test revealed that thedifference in the AM and PMAOT observations is statistically significant, H (1, N = 251) = 23.93, p = 0.001; with a mean rank AOT value of 149.29 for AM, and 104.37 for PM.Table 4 shows the summary for the monthly and daytime variation of AOT.

Table 4. Summary of AOT at 1020 nm measurements for different temporal scales(Manila, Feb-May 2014)

	N	Median	Min	Max	Q1	Q3	QD	Mean ± 1σ
Overall	251	0.195	0.094	0.363	0.139	0.271	0.0660	0.205 ± 0.11
Monthly Observation								
FEB	44	0.245	0.133	0.397	0.176	0.298	0.0610	0.247 ± 0.11
MAR	96	0.184	0.063	0.327	0.120	0.282	0.0810	0.183 ± 0.12
APR	41	0.184	0.096	0.342	0.133	0.268	0.0675	0.196 ± 0.10
MAY	70	0.165	0.0852	0.384	0.127	0.236	0.0545	0.195 ± 0.11
Daytime Observation								
AM (Morning)	121	0.227	0.0794	0.428	0.173	0.227	0.0270	0.233 ± 0.15
PM (Afternoon)	130	0.152	0.0630	0.309	0.114	0.203	0.0445	0.168 ± 0.11

3.3. Comparison of TOC and AOT at 1020 nm with Surface Meteorological Parameters

Simultaneous with the TOC and AOT measurements is the acquisition of surface meteorological parametersat the DLSU site using a Davis Vantage Pro 2 automatic weather station. Figure 3 provides the linear regression done between TOC, AOT, surface temperature (ST) and relative humidity (RH).

Figure 3A shows that the AOThas a moderately negative correlation (r = -0.4206, p = 0) with ST that is significant. This supports the results of Singh et. al. (2000) who obtained an inverse relationship between AOT and ST.On the other hand, AOT has a strong positive correlation (r = +0.5431, p = 0) with RH which is also significant (Figure 3B). This means that increasing RH results to increasing the AOT. As RH increases, there is more moisture in the air for aerosols to bind with thereby increasing the AOT.

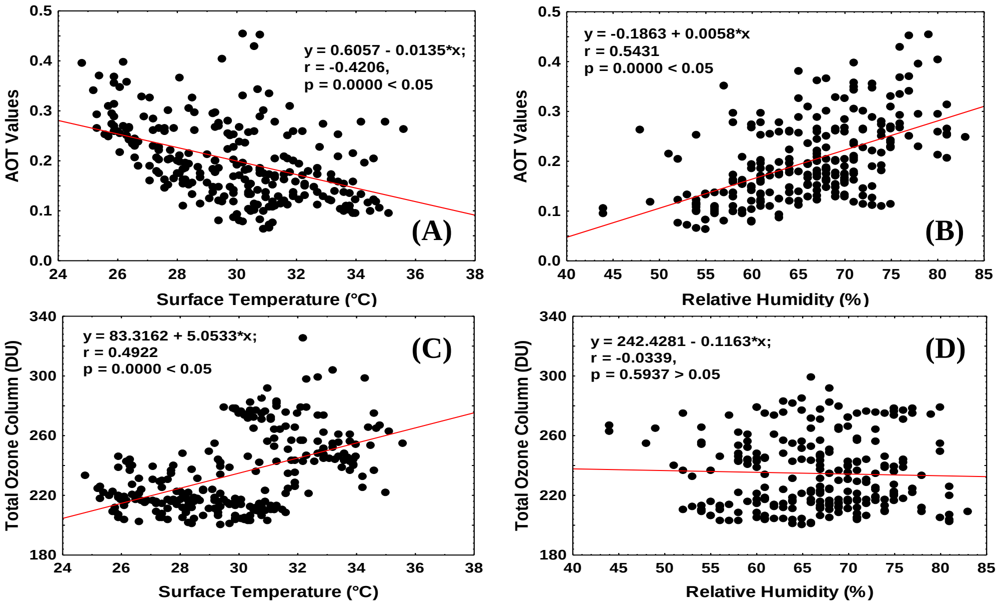

Figure 3.Correlation of TOC and AOT with surface meteorological parameters.(A) AOT vs ST; (B) AOT vs RH; (c) TOC vs ST; (d) TOC vs RH

Meanwhile, TOC has a moderately positive correlation (r = +0.4922, p = 0) with ST that is significant (Figure 3C). This supports the claim made by Ganguly and Iyer (2005) that the diurnal variation of columnar ozone is in phase with the diurnal variation in surface temperature. In addition, this is an expected result for TOC since more ozone can be produced when there is active photochemistry. Figure 3D illustrates that TOC has a weak negative correlation (r = -0.0339, p = 0.6937 > 0.05) with RH. Since p is greater than 0.05, this means that TOC and RH may not actually be correlated at all so TOC is not affected by RH.

4. CONCLUSION

The temporal variation and characteristics of TOC and AOT at 1020 nm over Manilawas studied from February to May 2014 using a MICROTOPS II ozonemeter. Further, the correlation of TOC and AOT with ST and RH was examined. The following are the summary of findings from this study:

- TOCdid not considerably vary from February to early March but drastically increased from late March to May. The TOC monthly variation during the study period was statistically significant. The higher readings obtained for AM TOC measurements was also statistically different fromthe PM TOC values.

- For the study period, AOT readings were highest in February and decreased up to May. The characteristics of the study site, local events and local weather conditions affect the AOT. Statistical analyses showed that the differences in the monthly and daytime (AM & PM) observations were statistically significant.

- ST had a moderate positive and negative correlation with TOC and AOT, respectively.RH had a strong positive correlation with AOT, but a weak negative correlation with TOC which is not significant so it can be interpreted that RH does not affect TOC.

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