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Measurement of Air Quality and Greenhouse Gases in the Atmosphere during the 2015 Pan American Games

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ABSTRACT

The measurement of air quality and greenhouse gases before and during the XVII Pan American Games is reviewed, with the objective of presenting up-to-date data and analysis on trace atmospheric gases and fine particulate matter in Toronto. The research project was completed at the Centre for Atmospheric Chemistry at York University in partnership with Environment Canada. The focus of the study is on the primary greenhouse gases; carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3), in addition to key pollutants including the nitrogen oxides (NO, NO_2 and NO_x) and fine particulate matter ($PM_{2.5}$), in the atmosphere surrounding York University's Keele Campus and at a second research site, Environment Canada's Andrew Thompson Research Laboratories in Downsview, from June 2 2015 to July 26 2015. Data was collected and analyzed on a monthly, weekly, and daily basis, to observe trends correlated to motor vehicle emissions, with consideration of seasonal and diurnal cycles as well. The effect of increased traffic during the Pan American Games was significant for all atmospheric constituents but N_2O, as seen in the weekday rush-hour data, and as confirmed by the elevated mixing ratios measured during this time. We conclude with a comparison between the two research sites, affirming that levels are generally similar yet somewhat lower at York University.

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1.0 INTRODUCTION

The 2015 Pan American Games (July 10-26) and Parapan American Games (August 7-15) saw thousands of athletes and spectators arrive in the host city of Toronto to celebrate 41 nations competing in 36 sports. The influx of visitors resulted in widely publicized anticipation of heavier than normal traffic on Ontario roads and highways. Traffic control included the temporary introduction of high occupancy lanes on many highways and roads in and around Toronto, which introduced further conjection conditions. These high traffic conditions offered a unique opportunity for a study looking at the effect of on-road traffic to regional emissions of both air quality and climate gases. The research project was completed at York University's Keele Campus, where tennis events at the Canadian Tennis Centre ran from July 10-16 and track and field events at the CIBC Pan Am/Parapan Am Athletics Stadium ran from July 21-25. A selection of air quality and greenhouse gases were studied, including ozone (O_3), the nitrogen oxides (NO, NO_2 and NO_x), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and nitrous oxide (N_2O), in addition to fine particulate matter ($PM_{2.5}$).

To obtain a complete understanding of the O_3, NO_x, $PM_{2.5}$, CH_4, CO_2, CO, and N_2O in our air, we must look at their lifetime cycles, including their sources and sinks, and everything in between, as they are transformed and transported through the atmosphere. In this paper, our primary focus is on sources of emissions, and these may be of natural origin, either biogenic or geogenic, or they may be anthropogenic, originating from human activity[1,2]. We further narrow in on emissions related to the operation of motor vehicles, and these sources include exhaust gas and to a lesser extent, fuel evaporation[3]. This release of pollutants into the atmosphere occurs through the burning of fossil fuels such as gasoline and diesel in the engines of cars and trucks and the combustion reaction is summarized below[3,4]. In this process, fuel, mostly hydrocarbons, and air, mostly oxygen and nitrogen, react under the high heat and high pressure conditions of an automobile's engine to yield volatile organic compounds (VOCs), which are unburned or partially burned hydrocarbons, along with water (H_2O) and the species of interest in this study [3,4].

$$Fuel(C_xH_y) + Air(O_2 + N_2) \rightarrow$$

$$VOCs + NO_x + PM_{2.5} + CO_2 + CO + H_2O$$

These atmospheric gases and particulate matter are directly emitted into the troposphere, which is the first layer of the Earth's atmosphere, extending from ground level to about 10-15 km above the ground[1]. For the purposes of this study, to hypothesize a possible connection to high-traffic emissions for all or certain species, and to then analyze our results, we must first present background information on the sources, the current average mixing ratios in the troposphere, and other relevant knowledge on each atmospheric species.

The concentrations of trace atmospheric gases and particulate matter are continuously changing both temporally and spatially. For current information on CH_4, CO_2, and N_2O, we refer to The Intergovernmental Panel on Climate Change (IPCC), which provides regularly updated values for greenhouse gases on a global scale[5]. The most recent publication is the Fifth Assessment Report, and in the Working Group 1: The Physical Science Basis section, it is stated that the 2011 global annual mean of CO_2 is 390 ppm, and it is 1803 ppb for CH_4, and 324 ppb for N_2O[5]. For the most up to date information on CO, as well as O_3, NO_x, and $PM_{2.5}$, we refer to The Ontario Ministry of the Environment and Climate Change, which provides current and local information, displaying pollutant mixing ratios in Toronto updated every hour[6]. The 2012 emissions estimates in Ontario, with respect to transportation, are provided here[7]. A staggering 87% of CO derives from the transportation sector, with 42% of that attributed to road vehicles[7]. The mixing ratio of CO may span anywhere from 100-1000 ppb in rural and suburban areas, and even extend into the ppm range in very polluted urban cities[1,2]. O_3 is not directly emitted from exhaust gas, instead it is formed through photochemical reactions involving VOCs and NO_x[7]. The natural amount of O_3 that should be present in the troposphere is around 10 to 15 ppb but is now closer to 30 ppb, as of 2013[9]. Looking at NO_x, for which NO_2 is the major component, 22% may be attributable to road vehicles, and 47% to other transportation[7]. The NO_x annual mean mixing ratio in 2011 ranged from about 2.5 ppb in rural Ontario to 19 ppb in a high traffic area of Toronto[8]. NO in exhaust gas enters the atmosphere and is converted to NO_2[2]. The NO_2 may then itself dissociate in the presence of sunlight to yield oxygen atoms which then react with molecular oxygen to form O_3, demonstrating the interconnectivity of these species[1]. $PM_{2.5}$ is fine particulate matter $\leq 2.5\ \mu m$ in diameter[1] and about 3% is directly from road vehicles, in addition to the 19% from other transportation[7]. The $PM_{2.5}$ annual mean in 2011 was $6.2\ \mu g/m^3$ in Toronto specifically[8]. According to more recent 2013 U.S. based estimates of greenhouse gases, 31% of CO_2 is sourced from transportation, while N_2O and CH_4 total only about 5%[10,11]. As such, we see that all species in the study may have a tie to traffic, to varying degrees, with CO acting as the primary tracer, as its leading source is the burning of fossil fuels[7]. Therefore, at the outset of the experiment, it is hypothesized that the levels of CO, CO_2, NO_x, O_3, and $PM_{2.5}$ are likely to increase due to their strong association to transportation, but it is uncertain whether there will be significant changes in CH_4 and N_2O.

Next, we must consider seasonal and diurnal variations related to the vertical stability of the atmosphere[12]. The measurements were made during the summer months of June and July, and it is necessary to take into account the progression of season, which brings about changes in meteorological conditions over the length of the study period. On a diurnal, or daily basis, day and night also bring about a change in sunli 3 ensity and temperature. In the summer and in the day-time, solar radiation warms the surface of the Earth, the air warms and rises, and we see convection currents form, effectively removing pollution from near the surface, where the measurements are made[12]. These conditions create what is known as an unstable atmosphere[12]. Conversely, in the winter and at night-time, the surface of the Earth cools and the cool air descends and stagnates under these stable atmospheric conditions, causing pollution to now accumulate at the surface[12]. These conditions initiate what is referred to as a ground level thermal inversion, with cool air below and warm air above[12]. Thermal inversions may occur higher in the atmosphere as well, forming a boundary that limits the range of pollutant dispersion[12]. Collectively then, we expect this effect to be heightened during the summer, when days are longer and temperatures are higher. Abnormally high or low temperatures may be a complicating factor, skewing the results. However, because summer generally sees less variability in temperature and sunlight intensity than the spring and autumn, it is likely the best choice for consistent day-to-day measurements over a single season. Additionally, in the summer, the difference in temperature between different days is less than the difference in temperature between day and night, and thus the diurnal effects are expected to be stronger than the seasonal variation. Therefore, the cause of any unusually large but short-lived spikes in the levels of a motor vehicle emissions-driven species may be as simple as a large truck passing by near the collection site, but if the spike is over the course of a few hours, it is likely meteorologically driven, caused by a stagnation event as described here.

The atmospheric gases in this study of particular interest are CO_2, CH_4, N_2O and O_3, as these are primary greenhouse gases (GHGs)[1]. The main component of fossil fuels is carbon, and globally, about 5 billion tonnes are release the atmosphere annually, largely as CO_2[1,9]. In the greenhouse effect, the infrared radiation emitted from the surface of the Earth is absorbed by the greenhouse gases[9]. This results in excess heat in our lower atmosphere that was originally destined to escape back out into space[9]. The consequential increase in temperature is grounds for the greenhouse effect to contribute to climate change[9]. The remaining gases in our study, namely NO_x and CO, are considered indirect greenhouse gases[1]. NO_x increases O_3 levels as briefly described above, and CO is produced by the initial oxidation of CH_4 by OH, through a series of reactions[2]. Due in part to the processes described here, it is estimated that the temperature of the Earth will rise by 3^{o}C in the next 15 years[9]. In general, climate change will manifest itself through changes in atmospheric composition and temperature, and may result in extreme weather conditions around the globe[5].

2.0 EXPERIMENTAL

In order to analyze data before and during the Pan American Games, a data collection period just shy of two months, from June 2 to July 26 2015, was selected. Local data for O_3, NO, NO_2, NO_x and $PM_{2.5}$ was acquired from the atmospheric chemistry laboratory in the Petrie Science and Engineering building on York University's Keele Campus. Data from a second neighbouring site, Environment Canada's Andrew Thompson Research Laboratories in the Downsview area, was provided for CH_4, CO, CO_2, and N_2O. To measure the mixing ratio of the trace gases, a number of instruments specific to each atmospheric species of interest were used to sample the air at the two locations and record the date/time and mixing ratio values. Data collection was a systematic and automated process, and so this section will focus heavily on the analytical methodologies of each device. Two newly installed instruments, a Picarro Cavity Ring-Down Spectroscopy Analyzer for CH_4 and CO_2 (CFADS59) and a Los Gatos Research (LGR) N_2O/CO Analyzer (#11-0014) were provided by Environment Canada to supplement the existing apparatus, including a Thermo-Electron Corporation (TECO) UV absorption photometer for O_3, a chemiluminescence spectrometer for NO_x, and a SHARP Monitor for $PM_{2.5}$. A brief overview of the working principle of each of the five instruments is presented here to describe how the mixing ratio data was internally generated by the instruments. To then analyze the data, Microsoft Excel and Igor Pro (Wavemetrics Inc.) software was used. These tools were chosen to accommodate the large quantity of raw data collected and to store, organize and manipulate the imported data sets into tables and graphs in order to extract useful information relevant to our research goals.

The Picarro G2301 (CH_4/CO_2) Analyzer and LGR N_2O/CO Analyzer both utilize a variation of cavity enhanced absorption spectroscopy (CEAS) for trace gas analysis, termed Cavity Ring-Down Spectroscopy (CRDS) and Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), respectively[13,14]. The foundatic he technique, as with other infrared (IR) absorption spectroscopy methods, lays in the fact that small gas-phase molecules, including CO, CO_2, CH_4 and N_2O, each have a characteristic absorption spectrum in the near-IR region, allowing for qualitative identification, as well as quantification by the strength of the absorption peaks[13]. To carry out the measurements, the gas-phase sample is first introduced into an optical cavity constructed from two or three mirrors[13]. A tunable diode laser beam is then directed into the cavity, radiating it with light of a single wavelength until a threshold level is reached and it is shut off[13]. The light wave is reflected by the mirrors, such that a 25 cm cavity that facilitates the creation of approximately 100,000 reflection points can result in a 20 km or longer pathlength[13]. The light intensity, as measured by a photodetector, decays or "rings down" with time due to two contributing factors; loss through the mirrors attributed to reflection of less than 100% of the light, and the absorption of light by the sample[13]. Consequently, the time required for the light intensity to exponentially decay to zero, known as the ring down time, differs whether or not the species is absorbing light at the given wavelength[13]. Therefore, the continuous stream of ambient air is fed into the instrument and the ring down times are measured at wavelengths where the gaseous species does and does not absorb, producing real-time absorption spectra and mixing ratio values simultaneously for each analyte[13]. The following formula shows how the instrument computes the absorption from the ring down times with and without the analyte, τ_0 and τ, at a specific wavelength[1]. Here, $t_r = 2L/c$ represents the time taken for one round trip between the mirrors and the L parameter is the distance between the mirrors[1].

$$A = \frac{t_r}{2}[\frac{1}{\tau} - \frac{1}{\tau_0}]$$

Then to calculate the concentration of the gas from the absorption, we simply apply the Beer-Lambert law, as reviewed below[1].

$$A = log(\frac{I_0}{I}) = \varepsilon Cl$$

Instrumentation by Thermo-Electron Corporation (TECO), now Thermo Fisher Scientific, for continuous ambient air monitoring, was used in the study for the remaining atmospheric constituents. First, the Model 49 Ozone Analyzer was used to measure ozone concentration via UV absorption photometry[15]. The ozone molecule strongly absorbs light of 254 nm and as above, the mixing ratio is determined through the use of the Beer-Lambert Law, with the knowledge that the molecular absorption coefficient for ozone at this wavelength is 308 cm^{-1} (at 0^oC and 1 atmosphere)[15]. The instrument uses a mercury lamp as its light source, given that it emits strongly at 254 nm[1]. It employs two parallel measurement cells that alternatively contain either the sample gas stream or the reference gas stream, which has been removed of all ozone[10]. For each cell, the light intensities I_o and I are detected, the concentration is calculated, and the average concentration of the two cells is provided as the final result[10]. Second, the Model 42 NO-NO_2-NO_x Analyzer was used to measure the nitrogen oxide concentrations via chemiluminescence spectroscopy[16]. In the chemical reaction between NO and O_3, electronically excited NO_2 is formed, and due to its short radiative lifetime, it is able to drop to a lower energy state and emit light, in the 590 nm to 2800 nm range, faster than it is deactivated by collision with other air molecules[1].

$$O_3 + NO \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

The chemiluminesence intensity in the reaction chamber, as monitored using a photomultiplier, and the corresponding concentration of the NO_2* product, is proportional to the concentration of the O_3 and NO reactants[1]. Therefore, the concentration of NO can be determined if an excess of O_3 is used, maintaining this reactant at a constant concentration[1]. To measure NO_2 by the same technique, it must first be transformed into NO using a heated molybdenum converter and so the instrument cycles between measuring NO (the NO mode) and the converted NO_2 (the NO_2 mode)[16]. To then determine the concentration of NO_2, the NO mode concentration is subtracted from the NO_2 mode concentration, yielding the final results for NO, NO_2, and NOx[16]. Third, for fine particulate matter, a Model 5030 SHARP (Synchronized Hybrid Ambient Real-time Particulate) Monitor was used[17]. The instrument operates using a combination of nephelometry and beta attenuation to measure the mass concentration of $PM_{2.5}$[17]. In the first step, the nephelometer measures light scattering by $PM_{2.5}$ using an 880 nm light source[17]. As before, a photomultiplier is used to detect the intensity of this scattered light and the difference in light intensity is proportional to concentration[17]. In the second step, it is β-ray attenuation that is used to measure the total mass of $PM_{2.5}$ per unit volume of air[1]. The particulate matter is deposited onto a filter and attenuates electrons from a radioactive 14C β-particle source[1]. A β-ray detector monitors the intensity of the β-rays that pass through the filter in the presence and absence of $PM_{2.5}$ and it applies the below equation, similar to the Beer-Lambert Law, to determine the mass per unit area, denoted ρX[1]. Here, X is the thickness of the $PM_{2.5}$ deposit on the filter, μ is an attenuation constant proportional to density, ρ, and together, μ/ρ is the mass absorption coefficient[1].

$$ln(\frac{I_0}{I}) = (\frac{\mu}{\rho})\rho X$$

3.0 RESULTS

Data on each atmospheric species is nted here in graphical form 5 ways. The graphs were created using high resolution minute-by-minute data, resulting in hundreds of thousands of data points collectively over the study period. The date/time and mixing ratio data is effectively continuous, with some blocks of information unavailable primarily due to instrument downtime during calibration. Further, to process the raw data and obtain meaningful results, a few random outlying points were discarded and the data sets were trimmed to align the start and end times of all of the components for purpose of comparison. As such, the data contained in all of the graphs displayed on the following pages spans from June 2 13:47 EDT (17:47 UTC and 12:47 EST) to July 26 5:26 UTC (9:26 UTC and 4:26 EST). It is important to note that in the raw data for CH_4, CO_2, CO and N_2O, dates are given in Julian Days and time is in Coordinated Universal Time (UTC) or Greenwich Mean Time (GMT). In the raw data for O_3, NO, NO_2, NO_x, and $PM_{2.5}$, time is in Eastern Standard Time (EST). For ease of analysis, we convert to Eastern Daylight Time (EDT), the current local time in Toronto, by subtracting 4 hours or adding 1 hour, respectively. The mixing ratios are reported in either parts-per-million (ppm) or parts-per-billion (ppb), with the exception of $PM_{2.5}$, which is reported in micrograms per cubic meter of air ($\mu g/m^3$). As a natural starting point, simple concentration vs. time graphs were created and these are presented in Figure 1. From these graphs, we are able to characterize monthly and weekly patterns, and most importantly, see if there is significant mixing ratio differences before and during the Pan American Games. The average mixing ratio with its standard deviation, the median, as well as the maximum and minimum mixing ratios of each atmospheric species at both locations over these two periods is displayed in Table 1. Next, to distinguish daily and hourly trends, graphs were set up to display the statistics on the data, including the mean, median, and standard deviation, when the mixing ratio data is binned by the time of day in hourly intervals, from 0:00 to 24:00. This process was completed for weekdays and for the weekend and these diurnal patterns for each species are as follows in Figure 2. Additionally, the data was binned by day of the week to produce the graphs shown in Figure 3. Finally, a series of correlation plots were created with the particular purpose of comparing and contrasting the York University and Downsview sites and these are provided in Figure 4. The mixing ratios over the course of a day, chosen to be July 10 2015, the first day of the Pan American Games, were lined up with respect to time, for the two locations. Then for each data point, the difference in mixing ratios at the two sites was calculated, as was the average difference and the standard deviation. Using this information, a plot of the difference values versus the York University mixing ratios on this day was created for each atmospheric gas, the results of which are given in Figure 5. Table 2 shows a final comparison between the average mixing ratio at York University and Downsview for every species, over the full study period.

4.0 DISCUSSION

This research project relies heavily on data analysis in order to determine if the measurements support the known links between motor vehicle emissions and the atmospheric species of interest. To identify trends in the data, thus establishing which gases are correlated to traffic emissions and to what extent, we need to dissect it on several time scales. These are, from shortest to longest, daily trends (rush hour vs. off-peak times), weekly trends (weekday vs. weekend), and monthly trends (before vs. during the Pan American Games). Before beginning the analysis, it is important to bear in mind that although our focus is on motor vehicle emissions, the mixing ratio changes we observe, even in species for which this is a significant source, may not be 100% attributable to these emissions alone. Rather, the mixing ratio changes likely are due to a combination of natural seasonal and diurnal variation, as well as variation in other natural and anthropogenic sources to some extent as well. On the other hand, it is also important to consider that the study region is an urban area; a high population city that regularly sees high traffic conditions on a daily basis and an even higher expected amount during the study period. As such, not only are the average background levels across all days and times anticipated to be higher than one would see in a remote rural area, but it is reasonable to assume the changes we observe to be significantly, albeit not completely, linked to traffic emissions, for species with strong traffic ties. This reasoning, combined with the well-known ties between these trace atmospheric constituents and motor vehicle emissions as presented in the Introduction, gives basis to the study. Lastly, a final note on the suitability of the two research sites; because York

University is a Pan American Games event venue and Downsview is a route to the venue, and because they are in Toronto, in close proximity to high traffic roads and highways where the majority of the emissions occur, they are justified as good sites for measurements conducted during the Pan American Games time frame.

First, from the simple concentration versus date/time graphs in Figure 1 that span the complete study period, we can readily discern any long-range trends over the two months, as well as zoom in on specific weeks or days. They also offer a quick look at how York University compares to Downsview for CH_4, CO_2, CO, and N_2O. Table 1 serves as an accompaniment to these graphs, summarizing the results before and during the Pan American Games. In general, the current average mixing ratio of each species was found to be on par with, or higher than, the past average mixing ratios reported in the literature, as presented in the Introduction. However, as stated, actual levels may vary widely, and we see this in our data particularly with O_3, NO_x and $PM_{2.5}$. Table 1 shows that these species fluctuated over a wide range of mixing ratios and for that reason have a large standard deviation to their averages. The mixing ratios of most species increased with time and we experienced elevated levels during the games, supporting the link to traffic emissions, as seen in Table 1. The exceptions were CO_2 and N_2O at both York University and Downsview. For N_2O, the decrease suggests that it is not as strongly associated with automobile emissions as the other atmospheric gases are, and we know this is indeed the case[1]. As predicted then, the seasonal variation likely had a greater effect in defining its pattern over the two months. The decrease in CO_2 is also very noticeable in Figure 1, where the baseline of the trace can be seen to gradually decline from around 400 ppm to around 380 ppm. However in this case, the decrease is not because CO_2 lacks a strong enough tie to transportation, but rather it may be explained by another seasonal effect. That is, we observe a decrease in mixing ratio simply because the measurements are made as the season progresses. In the northern hemisphere, in the spring and summer, the CO_2 in the atmosphere is depleted as it is used in photosynthesis by vegetation and so we observe a steady drop during these months[2]. In the fall and winter, as leaves and other greenery die, microbial decay releases CO_2 back into the atmosphere and we see the levels start to rise back up[2]. In the southern hemisphere, where they experience opposite seasons, we see this annual rise and fall at reverse times and likely to a lesser extent owing to less land mass. Next, we can also single out any individual dates, or longer lengths of time, corresponding to holidays or other special events, as these may see a increase or decrease in traffic, and thus an increase or decrease in the levels of traffic-linked species. The most notable of these is, that prior to the official start of the Pan American Games, new laws governing the HOV lanes on major Ontario highways took effect on Monday June 29 2015, requiring 3+ passengers for travel between 5:00 a.m. and 11:00 p.m. This is important to consider for our purposes, as the 400-series highways are high traffic routes in close proximity to the observation sites. The change caused major traffic congestion and we can see its effects in the data. Zooming in on the graphs in Figure 1, there was a noticeable jump in CO and CO_2, as well as CH_4 and N_2O, about a day later. Then again we saw an increase around July 3 - July 5, the first weekend after the HOV lanes were implemented, for CO, CO_2, and CH_4, but not N_2O. Spikes in mixing ratio and concentration on these two instances were also seen for NO_x, and $PM_{2.5}$, as anticipated. The temporary HOV lane laws were withdrawn on July 27, coinciding with the end of the games, at which time we would expect the levels to drop back down. If desired, we may direct our attention to the York University location in particular to analyze the data on days we expect less traffic on campus, such as on summer holidays with no work or school. The most significant instance would have been an extended summer break for undergraduates spanning from July 21 to July 25, but this coincided with the Pan American track & field events. We conclude with an instance that made the news; Environment Canada issued an air quality advisory on July 12 2015, a Sunday afternoon, for high levels of ozone at York University[18]. Looking at the concentration vs. date/time graph in Figure 1, we see that ozone shot to an all-time high of 85 ppb at 3:44-3:45 p.m. on this day, the highest it was over the entire study period.

Next, turning to Figure 2, our intent in creating these graphs was to identify hourly trends, in order to gauge the diurnal pattern of the gas, on weekdays and on the weekend. All of the individual data points are present faintly in the background, but our focus is on the set of hourly averages that together form a smooth wave, showcasing the diurnal variation of each species. From Monday to Friday, daily commuter on-peak times occur during morning and evening rush hour. Therefore, on the weekday graphs, we expect to see species that have a significant motor vehicle emissions source to peak around these times. This is the case for CO and CO_2, as well as NO_x and $PM_{2.5}$, which can be seen to peak during morning rush hour, from around 7 a.m. to around 10 a.m. Now to confirm, we direct our attention to the weekend graphs, where we anticipate these same traffic-linked species to be missing this peak. What we may see instead on these graphs is a peak at a different time, corresponding to a high traffic time on Saturdays and Sundays. It may be around noon, or the middle of the day, when most drivers are out and about, but this is entirely circumstantial, as on-peak times during the weekend may vary widely, definitely more so than on weekdays, where the routine is more dependable. In our data, we observed that the morning rush hour peak was indeed absent on the CO, CO_2, NO_x and $PM_{2.5}$ weekend graphs, and we see the daily diurnal pattern described in the Introduction instead, with the first peak occurring prior to rush hour. This tells us that on the weekend, when there is no strong and concentrated traffic source in the early morning, diurnal variation due to meteorology dominates. Next, for CH_4 and N_2O, we observe the same two peaks on both their weekday and weekend graphs; one occurring prior to the typical morning traffic peak and one near the end of the day. This finding suggests that for these species, any weak traffic induced patterns are overshadowed by the daily diurnal pattern, possibly because it is strongest in the summer and because traffic sources for CH_4 and N_2O are minor[19]. Where the diurnal meteorological pattern dominates, there is no difference between the weekday and weekend graphs for a species that has a very small traffic source. Thus, if both graphs for a species show peaks at the same time, they are more likely to be shaped by the meteorological pattern rather than the traffic pattern, and this is the case for those with a smaller motor vehicle emissions source. Taking CH_4 as an example, we see that the maximum mixing ratio occurs before sunrise, after a night of build-up, and the minimum mixing ratio occurs in the late afternoon, after a day of vertical mixing. That is, we generally see the mixing ratio spike around 6 a.m., before dipping to its lowest point later in the day, and then rising to a second peak at around midnight. This is in agreement with the findings for CH_4 in the literature, where they saw maximum mixing ratios at 6:00 local time and minimum mixing ratios at 17:00 local time[19]. Therefore, for most species, there is a competition of sorts between traffic trends and natural diurnal variation to see which one governs the graph; the traffic variable dominates only for the most strongly linked species, and diurnal variation dominates for the rest. The figures for O_3 are noticeably different than the others, with the weekday and weekend graphs peaking very strongly in the afternoon, very similarly to what we see in the literature.[20]. This is likely because during the daytime, solar radiation intensity is at its highest, and it is available to drive the photochemical production of ozone[20]. Finally, the graphs in Figure 3 summarize which days see the highest mixing ratios, which days see a greater range in mixing ratios, and whether York University or Downsview sees higher mixing ratios on a given day, and by how much. They were created as a supplement in order to view the mixing ratio data on both the weekdays and weekends at both York and Downsview on the same plot. In the O_3 Figure 3 graph, we see that the mixing ratio is highest on Sunday, and in the NO Figure 3 graph, the mixing ratio is lowest on Sunday. This weekend effect for ozone likely occurs because there is less NO emitted during the weekend and therefore less available to react with O_3 in forming NO_2.[2] For CO and CO_2, which have strong ties to motor vehicle emissions, the Downsview mixing ratio is greater than the York mixing ratio on all days, and there is no readily apparent correlation for CH_4 and N_2O, indicating weak or negligible traffic sources for these species.

Finally, we turn to the correlation plots comparing York University and Downsview in Figure 4 and Figure 5. Because the research sites are in close proximity, with only 3.4 km separating the two, we expect to see similar results for any given species. Upon plotting the mixing ratio of CH_4, CO_2, CO, or N_2O at Downsview against the mixing ratio of the same species at York University, we see that the line of best fit through the data points has a positive slope and that it roughly spans the two axes, which both encompass about the same range of values, signifying that mixing ratios at the two locations were similar on this day. Next, the difference values were calculated, equal to the Downsview mixing ratio subtracted from the York University mixing ratio at every minute of the day. On first glance, this yielded mostly positive values and the average differences were found to be 2.15 ± 23.25 ppb for CH_4, 2.46 ± 7.43 ppm for CO_2, 5.66 ± 29.26 ppb for CO, and 0.08 ± 0.47 ppb for N_2O. The positive averages for all four species mean that levels overall were higher at York, suggesting there was more traffic here on the day of July 10 2015. However, the standard deviation is large in comparison to the average, meaning that at certain times of the day, there was a large difference in mixing ratio, while at other times, this difference was much smaller. Furthermore, the range, or minimum (where Downsview > York) and maximum (where York > Downsview) were -73.5 ppb and 62.9 ppb for CH_4, -20.68 ppm and 28.2 ppm for CO_2, -133.6 ppb and 131.2 ppb for CO, and -1.02 ppb and 2.05 ppb for N_2O. In making the difference plots, when these values were graphed against the mixing ratio at York University, the best fit was again a straight line with a positive slope, demonstrating that the difference between the two locations is a function of concentration. It is important to take into consideration that this analysis was performed on July 10 2015 only, a relatively small time frame, and so the graphs in Figures 4 and 5 may not be representative of each and every other day the measurements were taken. Because the average difference on one particular day may not be characteristic of the whole two months, we turn again to Table 1, which shows that the average mixing ratio was in fact greater at Downsview than at York University for CH_4, CO_2 and CO, both before and after the Pan American Games, and also to Table 2, which shows that this is true over the entire study period as well. The difference for N_2O was likely not statistically significant, as the average mixing ratio prior to the games (330.50 ppb at York and 330.60 ppb at Downsview) differed only by about 1 ppb when compared to the average mixing ratios obtained for during the games (329.30 ppb at York and 329.52 ppb at Downsview). Comparing the two research sites also aids in determining whether there is a traffic source for each gas. A large difference in mixing ratio can be explained by the fact that the Downsview location sees more traffic, and so, those species with large difference values likely possess this traffic connection. As expected, the difference between the average mixing ratio at the two sites was largest for CO, the tracer of motor vehicle emissions, and smallest for N_2O, the species with the weakest ties to these emissions. So to summarize this York vs. Downsview comparison, the two sites see similar levels of each gas, with Downsview reporting slightly higher mixing ratios. This is likely due to the fact that Environment Canada is located next to a busy road, Dufferin St., whereas the Petrie Science and Engineering building at York University is situated near the centre of campus, making it slightly more removed from the major streets surrounding it.

5.0 CONCLUSION

In this research project, we monitored air quality and greenhouse gases, with a focus on the ozone (O_3), nitrogen oxides (NO, NO_2 and NO_x), fine particulate matter ($PM_{2.5}$), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and nitrous oxide (N_2O) in our local atmosphere, before and during the Toronto 2015 Pan American Games from July 10-26 2015. The event had a noticeable effect on traffic, with longer commute times for drivers measurably evident in our results. Upon collecting the date/time and concentration data, and compiling it into tables and graphs, the differences in the mixing ratio of atmospheric gases and particulate matter on different days and at different times led us to several conclusions. Most notably, the assessment of these trace atmospheric components on several time scales, including weekday vs. weekend and rush hour vs. off-peak times, revealed a significant correlation between motor vehicle emissions and the mixing ratios of the above species, with the exception of N_2O. This was the first time N_2O was measured at York University, and a major conclusion we can draw from our findings is that there appears to be no evidence of a motor vehicle source for N_2O. The analysis led us to ascertain that the mixing ratios of these species did in fact increase during the games, as summarized in Table 1, while N_2O conversely saw a decrease of about 1 ppb. As well, York University's Keele Campus saw increased levels in comparison to Downsview, by a small margin, particularly with CO being on average, 5 ppb higher at York, and this difference was less than 1 ppb for N_2O. Due to time constraints, the data collection period did not extend into the dates of the Parapan American Games, which took place August 7-15 2015. We would expect similar results in this case, as well as for the Rogers Cup, both of which drew large crowds to York University. Our next steps would be to look at the data collected immediately following the games, to see if the changes are reversed and whether we observe a drop back down to pre-Pan American Games levels. If we continue to actively monitor and report on the atmospheric mixing ratios of the studied gases, investigation into the long range would further strengthen the connection we suggest here to high traffic density. Further, we may incorporate measurements of sulphur dioxide (SO_2), not included in this research project, as it is also emitted from automobile engines[5]. The study was completed locally, but comparing figures on a regional scale, and even on a global scale, in collaboration with other facilities, would yield deeper insight into the larger issues at hand. Research in the natural sciences, including the chemistry of our atmosphere, is only becoming more critical as environmental issues become more prevalent and demand immediate attention. The use of fossil fuels for transportation is significant in regards to pollution, the greenhouse effect, and climate change, and the consequences only grow with each passing year. Research therefore needs to be ongoing, as we see it is no longer a concern of the future but a cause for concern in the present. Considerable changes must be implemented, including stricter laws and regulations to control and report emissions, and in regards to motor vehicles in particular, manufacturers must be made to improve the quality of fuels and to produce cleaner burning engines, to ensure the health and sustainability of the future.

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APPENDIX

Raw data and high resolution graphs are available upon request.

	O3	NO	NO2	NOx	PM2.5	CH4 (ppb)		CO2 (ppm)		CO (ppb)		N2O (ppb)	
	(ppb)	(ppb)	(ppb)	(ppb)	(µg/m3)	YORK	DOWNS VIEW	YORK	DOWNS VIEW	YORK	DOWNS VIEW	YORK	DOWNS VIEW
BEFORE													
Average	29.29	2.23	10.51	12.83	8.17	1988.27	1992.14	409.96	411.84	191.44	196.45	330.50	330.60
# of Data Points	53241	53945	53945	53945	53067	49489	44898	49490	44902	49168	44842	49168	41158
Standard Deviation	13.57	5.64	7.58	11.54	6.03	66.22	81.89	15.76	18.83	60.84	69.83	2.20	2.07
Median	30.00	1.00	8.00	9.00	6.00	1969.80	1969.50	405.85	406.63	177.90	179.90	329.79	330.01
Minimum	-1.00	0.00	0.00	1.00	0.00	1901.20	1889.90	381.28	382.25	98.80	103.60	326.95	327.68
Maximum	75.00	110.00	49.00	159.00	58.00	2740.80	2797.30	494.91	504.37	526.80	1604.60	342.73	341.13
DURING													
Average	30.73	2.91	10.50	13.47	8.36	2000.82	2005.03	402.61	403.83	192.75	198.67	329.30	329.52
# of Data Points	22983	23306	23306	23306	22939	21796	21672	21796	21681	21796	21691	21796	21648
Standard Deviation	16.91	5.58	7.62	11.61	4.22	74.61	92.31	18.65	19.53	57.43	60.17	1.16	1.27
Median	29.00	1.00	8.00	9.00	8.00	1985.70	1985.40	398.15	399.38	182.30	188.00	329.08	329.32
Minimum	-3.00	0.00	0.00	1.00	1.00	1905.20	1898.00	373.72	372.30	102.10	104.50	326.90	326.92
Maximum	85.00	93.00	55.00	117.00	28.00	2449.90	2852.90	491.78	518.75	550.00	960.70	334.22	334.14

Table 1. The average concentration, number of data points, standard deviation, median concentration, and maximum and minimum concentrations for each atmospheric gas and PM$_{2.5}$ measured at York University and Downsview before and during the Pan American Games, from June 2 2015 to July 26 2015.

Average & Standard Deviation		
	YORK	DOWNSVIEW
CH4 (ppb)	1992 ± 69	1996 ± 86
CO2 (ppm)	407 ± 17	409 ± 19
CO (ppb)	192 ± 60	197 ± 67
N2O (ppb)	330.13 ± 2.0	330.23 ± 1.9

Table 2. A comparison of the average concentration of CH$_4$, CO$_2$, CO, and N$_2$O at York University and Downsview from June 2 2015 to July 26 2015.

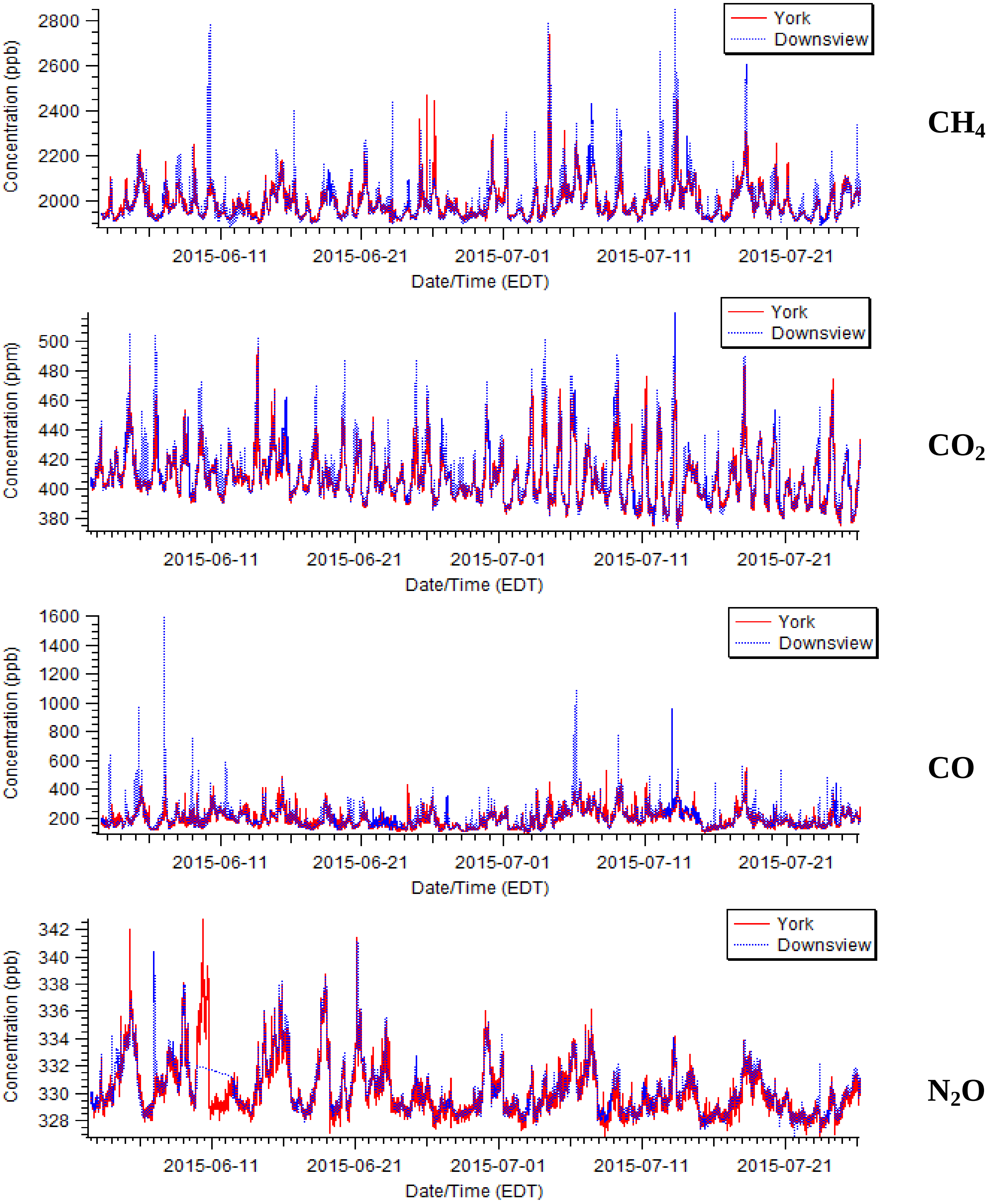


Figure 1. Concentration vs. Date/Time graphs for O_3, NO, NO_2, NO_x, and $PM_{2.5}$ at York University and for CH_4, CO_2, CO, and N_2O at both York University and Downsview, from June 2 2015 to July 26 2015.

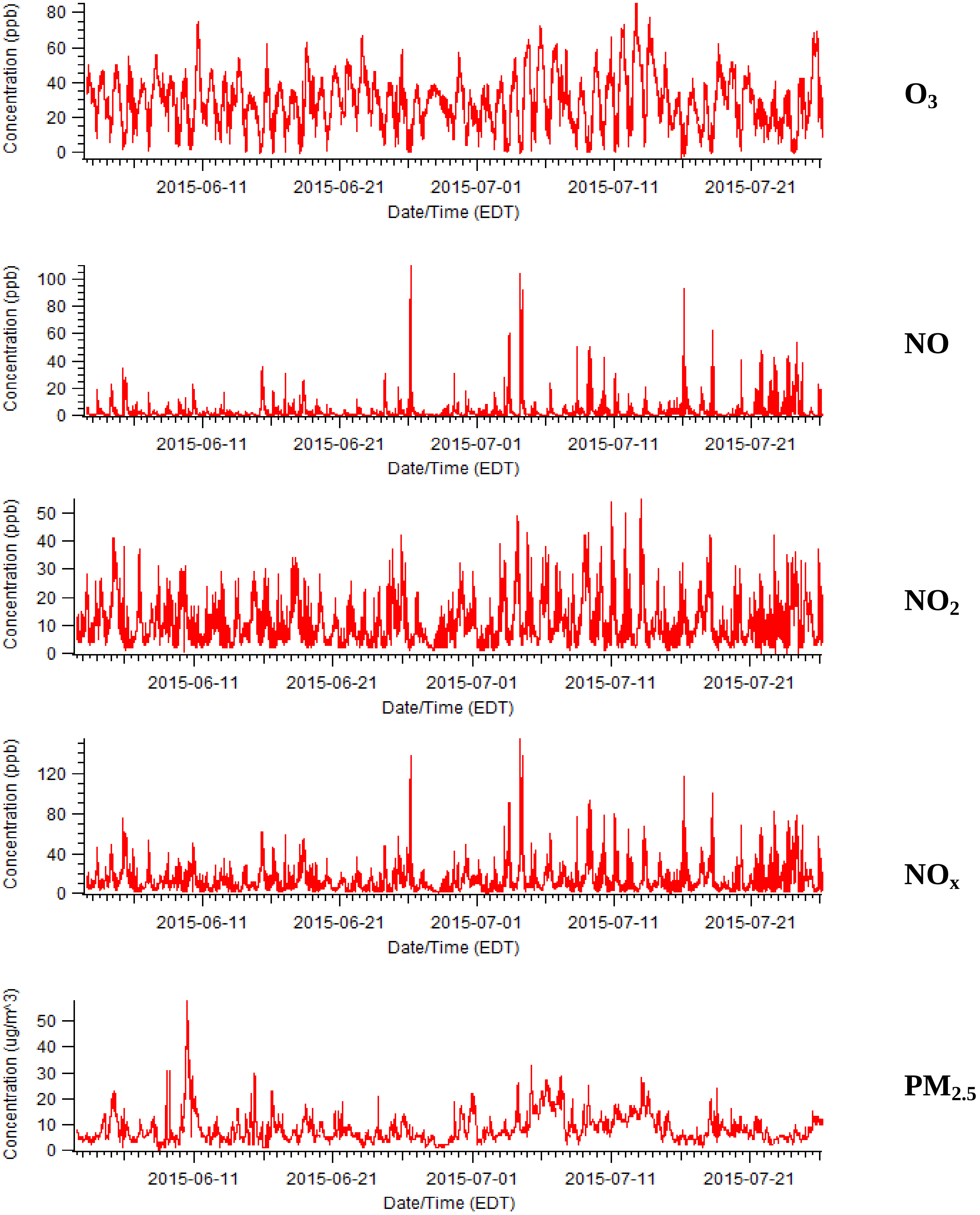


Figure 1. continued

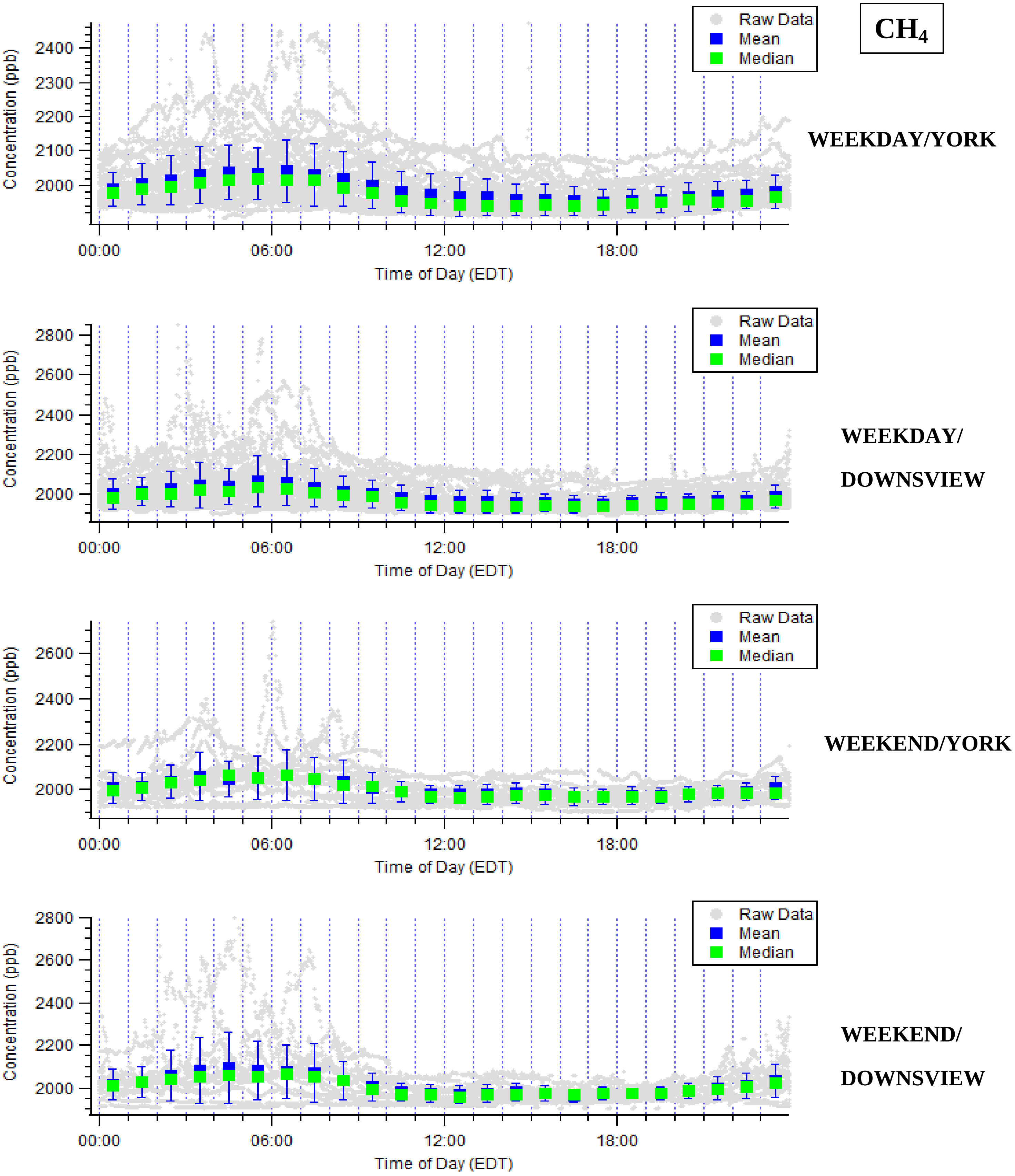
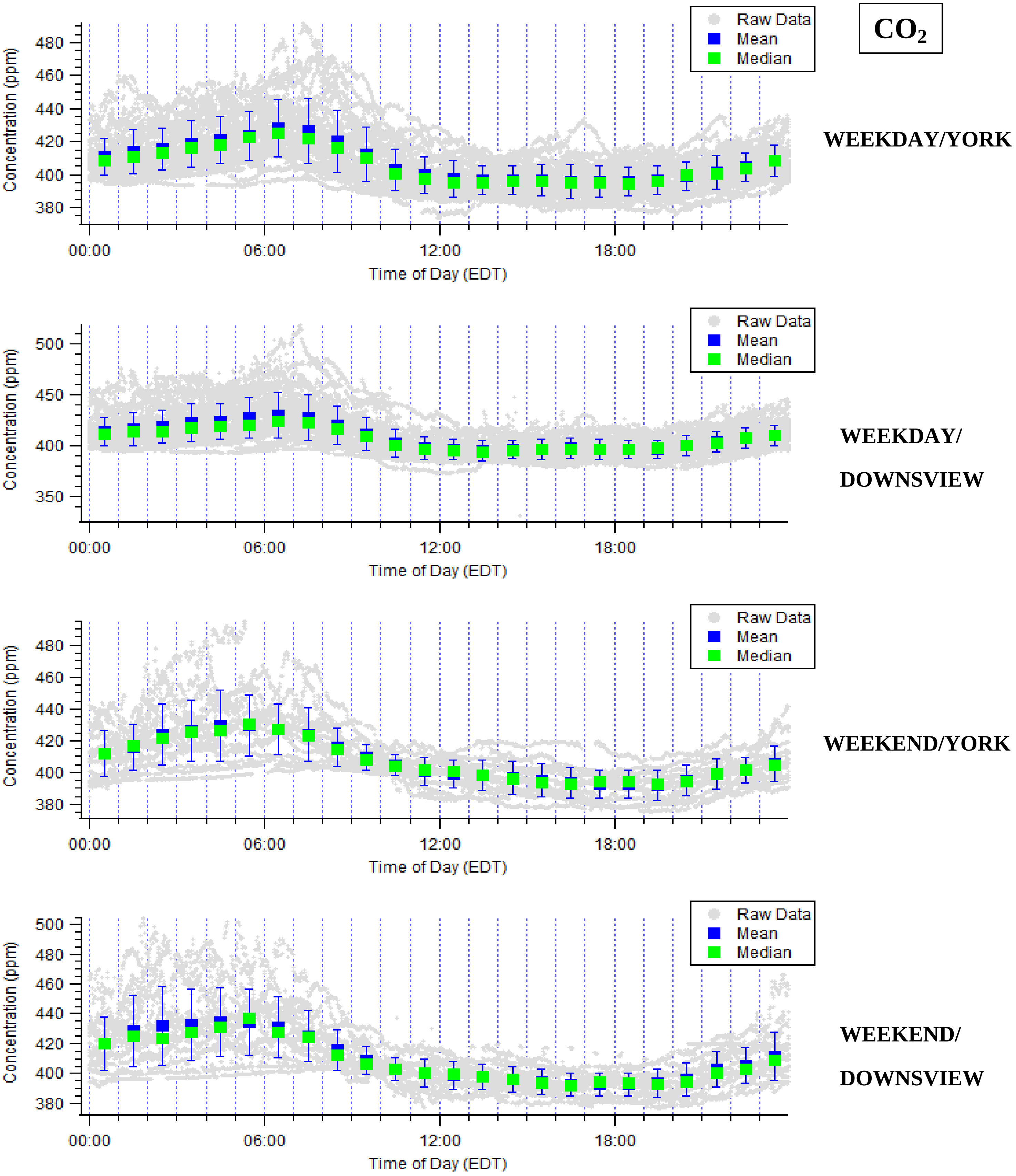


Figure 2. Weekday and weekend diurnal cycle including hourly mean and median, for O_3, NO, NO_2, NO_x, and $PM_{2.5}$ at York University and for CH_4, CO_2, CO, and N_2O at York University and Downsview, from June 2 2015 to July 26 2015.



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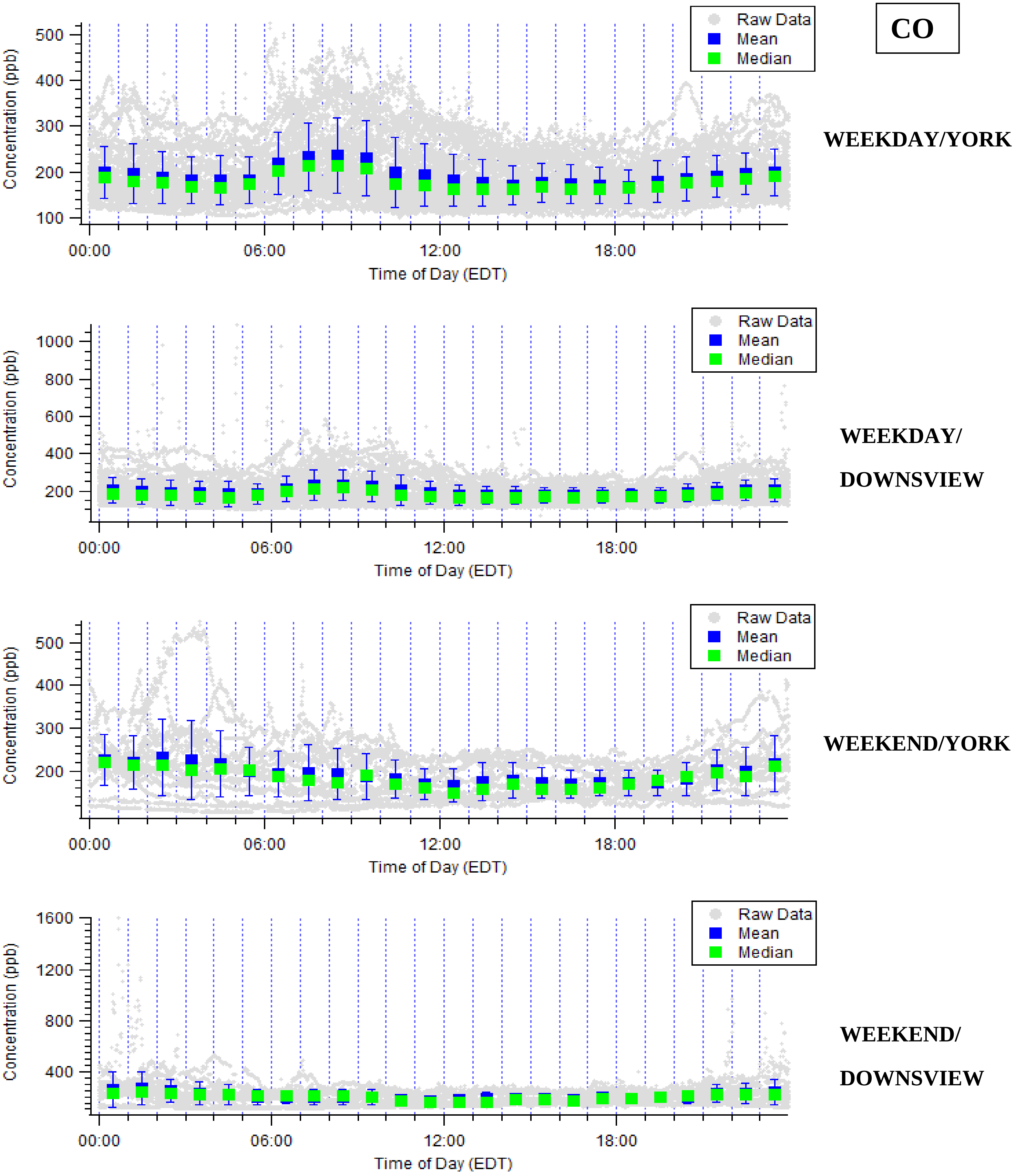

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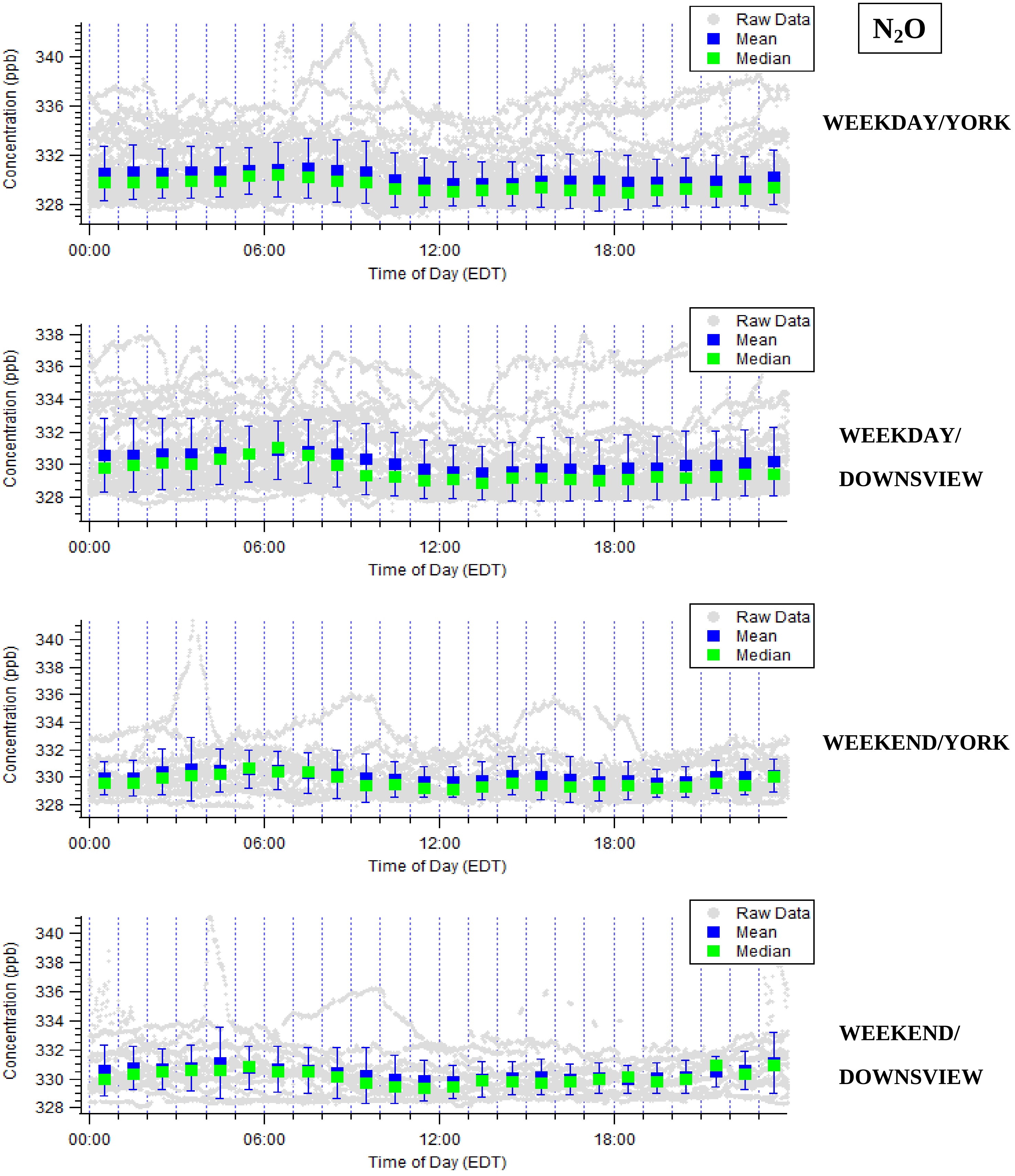
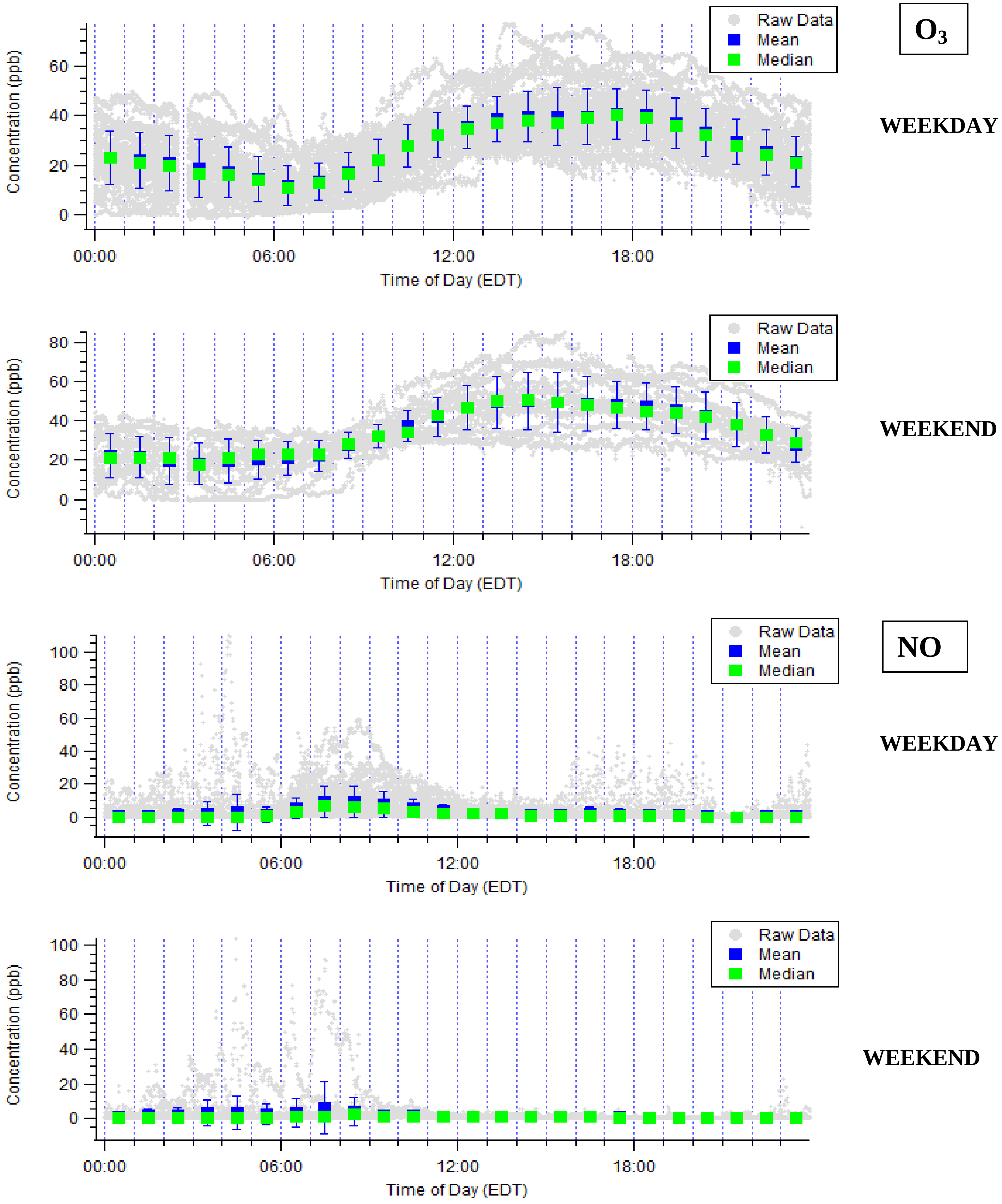


Figure 2 continued.



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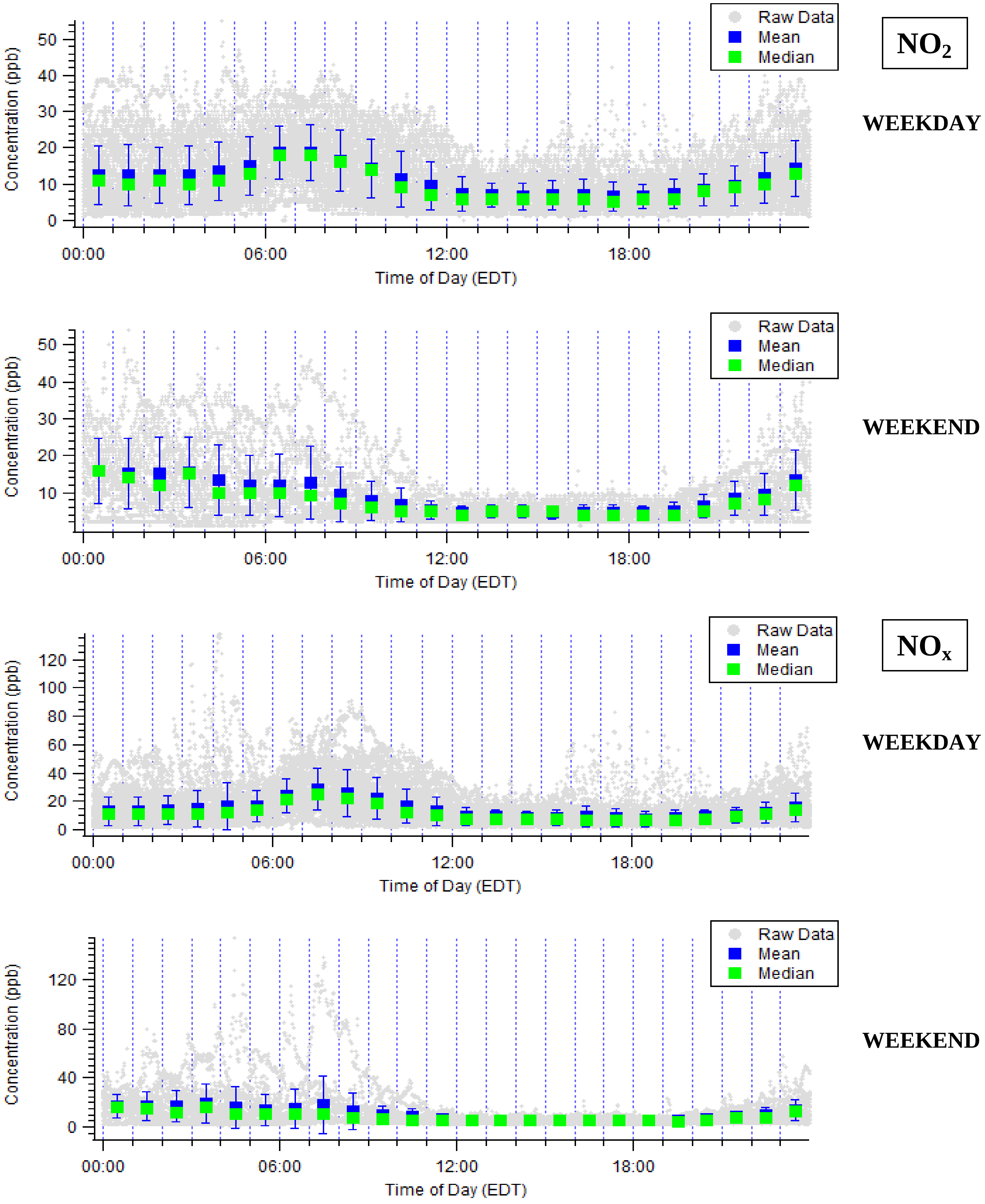

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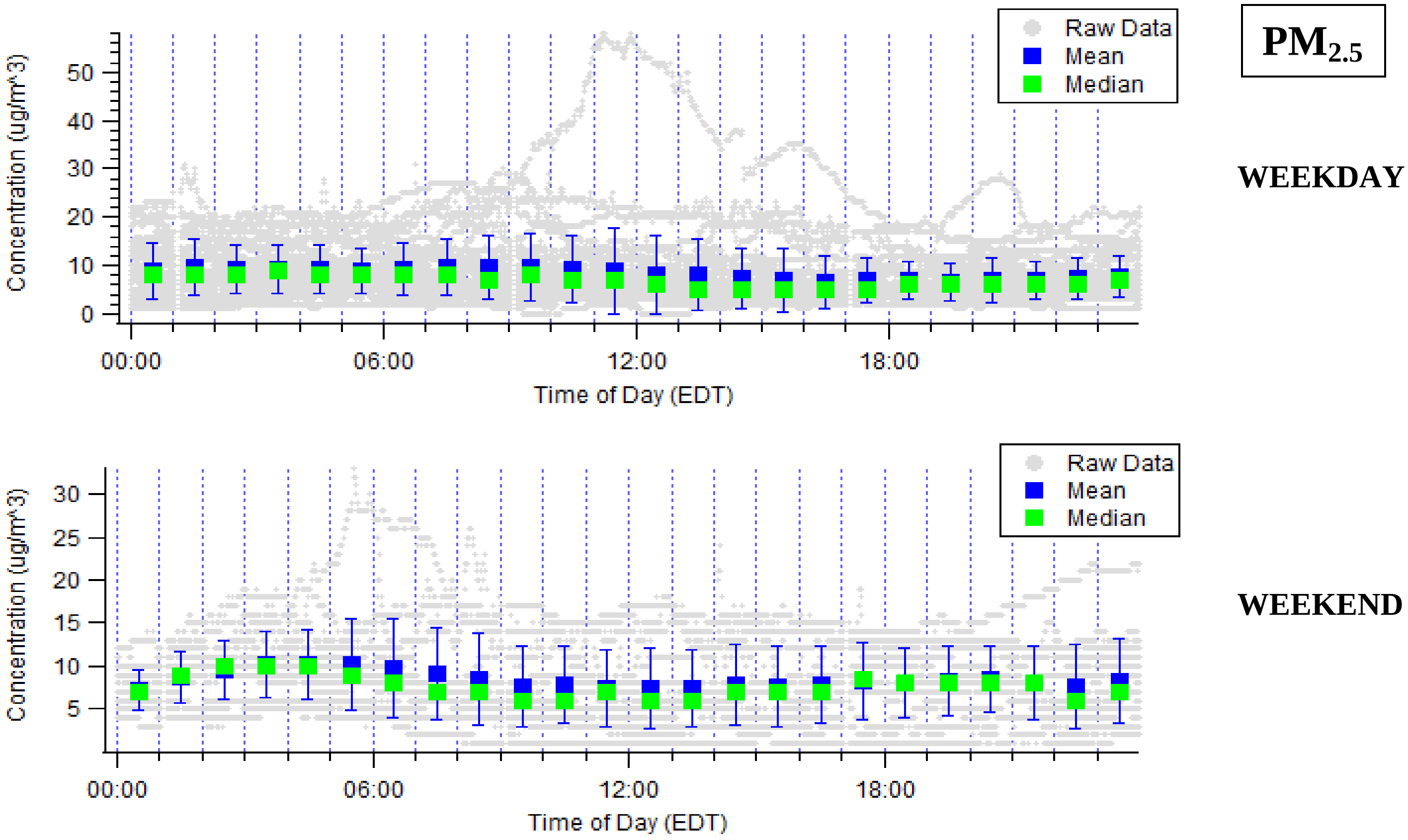

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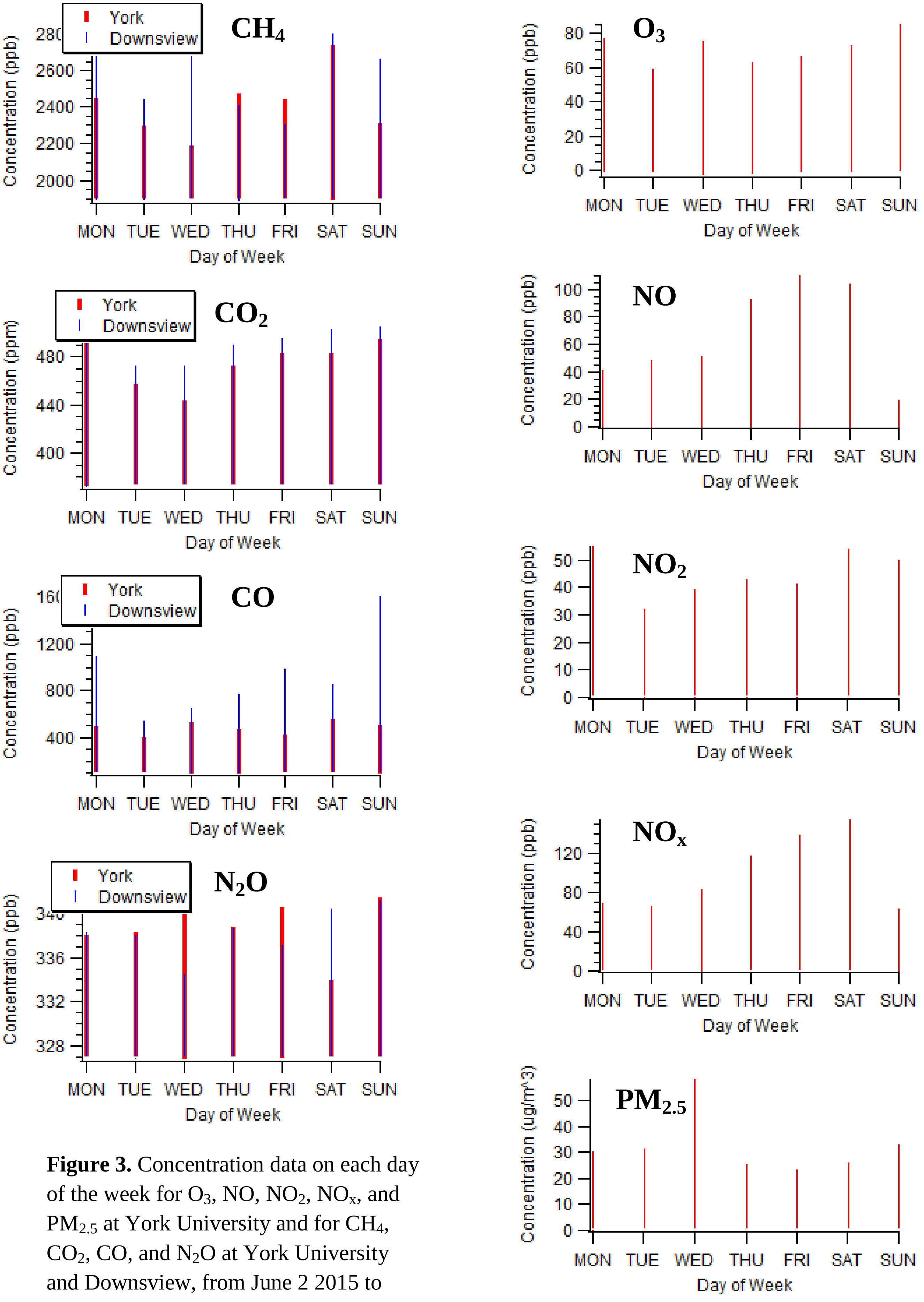

Figure 3. Concentration data on each day of the week for O_3, NO, NO_2, NO_x, and $PM_{2.5}$ at York University and for CH_4, CO_2, CO, and N_2O at York University and Downsview, from June 2 2015 to July 26 2015.

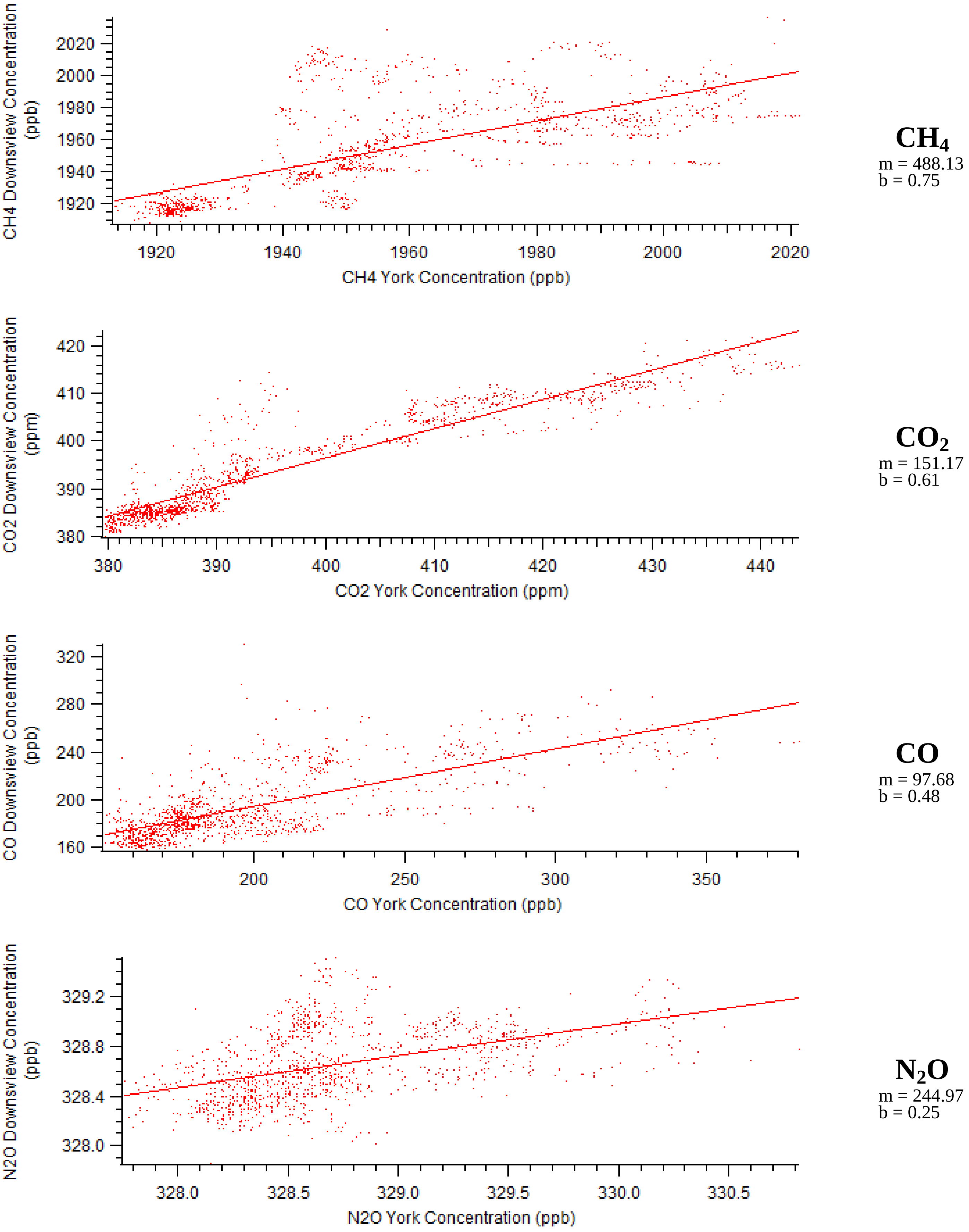

Figure 4. Correlation plots of the Downsview Concentration vs. the York Concentration for CH_4, CO_2, CO, and N_2O on July 10 2015.

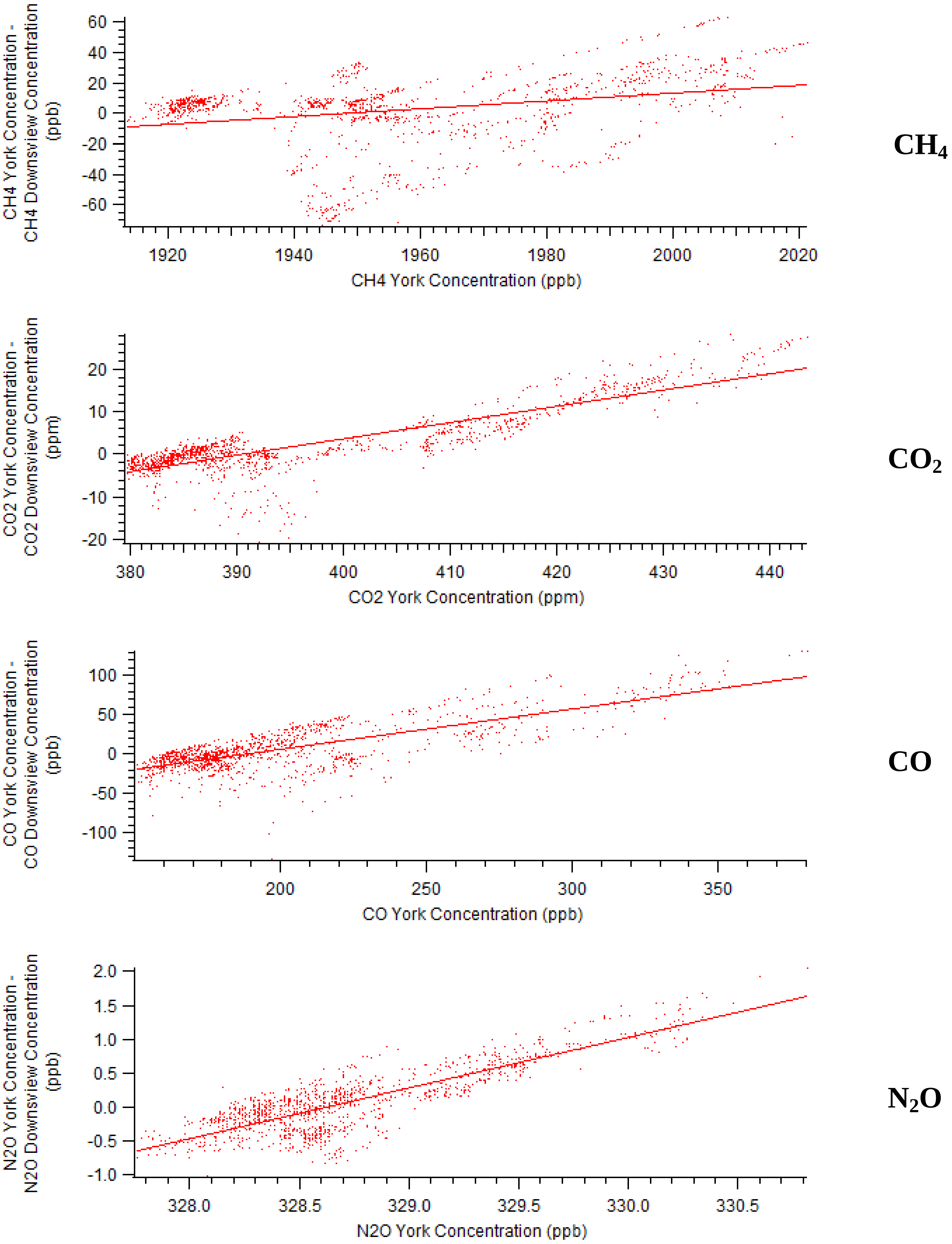

Figure 5. Difference plots of the York Concentration - the Downsview Concentration vs. Downsview Concentration for CH_4, CO_2, CO, and N_2O on July 10 2015.