HAMPTON UNIVERSITY EASTERN SEABOARD INTERMODAL TRANSPORTATION APPLICATIONS CENTER

INVESTIGATION OF FINE PARTICULATE MATTER, NO_x and TROPOSPHERIC OZONE TRANSPORT AROUND A MAJOR ROADWAY

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ABSTRACT

In the Eastern Seaboard Intermodal Transportation Applications Center at Hampton University, we started an investigation of the air pollutants around heavily-travelled roadways, shipping channels, airports, and railroads with the purpose of obtaining real time measurements of pollutant concentrations and relating them to real-time weather and traffic information. In the first two cycles of our research program, we built a mobile unit containing a NO_x and an ozone analyzer, and a weather station to provide simultaneous measurements of wind speed, wind direction, temperature, and solar intensity with the concentration measurements. The measured NO_2 concentrations were compared to the predictions of CALINE4. Considering the effects of $PM_{2.5}$ on public health and the 2008 US Census Bureau report, which showed that around 16% of American households live within 100 m of a highway having four or more lanes, an instrument for the measurements of PM_{10} and $PM_{2.5}$ were added to our measurement capabilities for the current research cycle.

The first mobile unit contained the NO_x, ozone, weather monitoring units and a pyranometer for measuring solar intensity. These equipment are Thermo Fisher Scientific Inc. (Franklin, MA) Model 42i chemiluminescence NO-NO_2-NO_x analyzer; Thermo Fisher Scientific Inc. (Franklin, MA) Model 49i ozone analyzer utilizing UV Photometric technology; Climatronics Corp. (Bohemia, NY) AIO compact weather station with capabilities to measure temperature, relative humidity, wind speed, wind direction, and barometric pressure; and LI-COR Inc. (Lincoln, Nebraska) pyranometer (LI 200SA) with a light meter (LI 250A). The NO_x and ozone sampling tube inlets were located 2.9 m above the ground. The second mobile unit had the particulate monitoring system in an outdoor temperature-controlled shelter. This equipment is the TEOM 1405-DF dichotomous ambient particulate monitor with a filter dynamics measurement system (FDMS) (Thermo Scientific, Franklin, MA). It is designed to provide long and short term PM concentration measurements for both non-volatile and volatile PM10, PM2.5, and PM-coarse (particles between 2.5-10 µg/m3) components. It is housed in an outdoor shelter designed to house the TEOM 1405-CF and keeps it at the desired temperature. The air sample inlet for the PM measurements is located about 3.5 m above the ground. These units are powered by the 7.5-kW Generac GP7500E generator. Due to the weight and size of the equipment we needed four students to move all the equipment to the measurement locations. The installed equipment was too high to fit through doors and inside the elevator. Since we could not find an outdoor place to store the equipment, it had to be dismantled and reassembled again every time it was taken outside. In addition, when moving, the carts shook excessively. This, combined with the frequent disassembly and reassembly, resulted in excessive wear and tear on the equipment. To reduce the effect of shaking during transportation a location closer to the

Engineering Building was chosen for the measurements. To allow for at least one hour of sampling time it was decided to have only three measurements per day, which required a minimum of 6 hours considering the start up times of the instruments.

Only a small number of measurements could be made in this funding period because there were several requirements that limited the days on which the measurements could be taken, namely, the proper functioning of the equipment especially the generator; presence of at least three students; and no rain. As the result of these constraints there are only three sets of measurements, on dates 4/5, 4/13 and 4/27, that are at downwind locations. The other three data sets are for upwind conditions. Since we lacked the ability to take simultaneous measurements on both sides of the road, the upwind measurements provided information about the background concentrations.

Some of the upwind PM measurements had to be discarded due to instrument malfunction. From the limited data available it was difficult to get a good estimate of the PM background concentrations.

Downwind measurements of PM_{10} and $PM_{2.5}$ on 4/5, 4/13, and 4/27 showed significant decreases in PM concentrations between receptors 1 and 2 mainly due to plume dilution. The increases in the PM_{10} and $PM_{2.5}$ concentrations at receptor 3 were tentatively attributed to the effect of the traffic on the Emancipation Drive and Marshall Avenue (receptor three was located at the corner of intersection of these two streets). The majority of the measured PM was in the $PM_{2.5}$ range. There was a concern about the measurements showing PM_{10} less than $PM_{2.5}$. This was attributed to positive reference concentrations measured by the FDMS unit. We found some examples of such readings in the literature, but their cause was not identified.

I. INTRODUCTION

I. i. Background

In the Eastern Seaboard Intermodal Transportation Applications Center at Hampton University, we started an investigation of the air pollutants around heavily-travelled roadways, shipping channels, airports, and railroads with the purpose of obtaining real time measurements of pollutant concentrations and relating them to real-time weather and traffic information. In the first two cycles of our research program, we built a mobile unit containing a NO_x and an ozone analyzer, and a weather station to provide simultaneous measurements of wind speed, wind direction, temperature, and solar intensity with the concentration measurements. The measured NO_2 concentrations were compared to the predictions of CALINE4. Considering the effects of $PM_{2.5}$ on public health and the 2008 US Census Bureau report, which showed that

around 16% of American households live within 100 m of a highway having four or more lanes, for the last research cycle of ESITAC funding, we proposed to include an instrument for the measurement of $PM_{2.5}$. These measurements were expected to provide $PM_{2.5}$ data near roadways, shipping channels, airports, and railroads and would make it easier to predict the impact of these sources on the air quality in the surrounding areas, thus aid the planning of the placement of buildings that will house sensitive populations such as hospitals, day care centers, retirement and assisted living centers**.** Due to the role of nitrogen oxides in the generation of secondary aerosols that contribute to the atmospheric PM, it would be meaningful to measure the particulate matter concentrations simultaneously with NO_x and ozone. But unfortunately, in the third research cycle, due to budget constraints, the equipment for PM measurements could not all be purchased and PM measurements could not be done. Instead, a more in depth analysis of the previously obtained NO_x and ozone data was undertaken.

The results of that analysis showed that in most cases, the measured NO_X concentration decreased rapidly with the distance from the roadway, and then remained fairly constant for distances greater than about 100 m from the I-64 median. The reason for this decrease is the atmospheric dispersion and conversion of NO_X to other nitrogen-containing compounds. Close to the roadway, the majority of NO_X was NO, which converted to NO_2 and other nitrogen compounds within 100 m from the median. The decrease in nitrogen dioxide concentration was significantly less. This indicated the combined effects of plume dilution and atmospheric photochemical reactions. When the wind directions were such that the receptors were upwind of the roadway, the ozone concentrations were relatively higher and the changes in nitrogen oxide concentrations were lower compared to the other cases. This was due to the dominance of convective transport, which prevented the transport of traffic-generated nitrogen oxides to the receptors and the measured values were indicative of the background concentrations.

Comparison of nitrogen dioxide measurements with CALINE4 results indicated that for most cases with receptors in upwind positions relative to the roadway, CALINE4 produced concentrations close to the measured ones. When the wind was close to parallel to the roadway, receptor positions shifted frequently between upwind and downwind, thus, simulations produced results that were not very representative of the measurements. At some sampling points located downwind of the roadway, predicted values were significantly larger than the measured values. This may be due to the presence of a wire fence between receptor positions 1 and 2 with some hedge growth and single line of trees along it that might have disrupted the plume extending from the roadway and enhanced the mixing of the plume contents with the ambient air reducing the measured concentrations[1]. The only way to reduce the effects of the fence and trees will be to obtain measurements at more suitable locations. This will only be possible if all the instruments were installed in a van and can be taken out of the Hampton University campus to more convenient locations. There are some limitations in using CALINE4 for the prediction of NO_2 concentrations. CALINE4 gives NO_2 results in increments of 10 ppb and only a few of the measured concentrations were at or above this

value. Secondly, the location permitted measurements only up to about 100 meters from the road and for some cases, this was not sufficient to obtain accurate background values and therefore, extrapolated values were used in the models. The best way to establish background concentrations will be to take measurements on both upwind and downwind locations under the same conditions. This would also be made possible by the availability of the van. Additionally, for NO_2 predictions, CALINE4 uses a very simple kinetic model involving only three reactions (ozone formation, NO oxidation, and NO_2 photodissociation). Therefore, in comparing the measured concentrations with those predicted by CALINE4, these limitations needed to be considered.

To test the importance of the other factors, namely, the road height, photodissociation constant, deposition velocity, emission factor (estimated using MOVES), mixing zone width, mixing height, altitude, a sensitivity analysis was done using CALINE4. To obtain the effect of averaging period used during measurements, a series of new, longer measurements were made. From those results, it was seen that the only variable that could produce predictions close to measured concentrations at downwind receptor locations was the wind direction, but a systematic error that would have caused this could not be identified. Therefore, the only plausible explanations were the effect of vegetation between the roadway and the receptors and the limitation of the CALINE4 reaction scheme[1].

I. ii. Literature review

I. ii. A. Particulate Matter

Particulate matter is a complex mixture of organic and inorganic matter that is present in atmosphere as liquid droplets and solid particles. Two PM sizes are regulated by U.S. National Ambient Air Quality Standards (NAAQS): Fine particles are those with nominal aerodynamic diameters less than 2.5 µm ($PM_{2.5}$) and contain secondary aerosols, combustion particles, and condensed organic and metallic vapors. The particles with nominal aerodynamic diameters less than 10 µm are PM_{10}; therefore $PM_{2.5}$ is a subset of PM_{10}. Acid component of particulates (like nitric and sulfuric) is mostly contained in fine particulates. About 35% of particulate matter is produced by transportation activity and about 24 % of the total PM_{10} emitted by all sources in US is $PM_{2.5}$. Seventy two per cent of the transportation-related $PM_{2.5}$ emissions are due to diesel vehicles. Ten per cent of the nonroad emissions are due to marine mobile sources and 7% is attributed to each of railroads and aircraft[2].

Atmospheric particulate matter is formed through various mechanisms: Fuel evaporation and pyrolysis; processes involving elemental carbon such as nucleation, aggregation and agglomeration, deposition and reentrainment; atmospheric processes including coagulation, adsorption/desorption, surface reaction, and dispersion. Particulate matter in vehicle exhaust is diluted significantly in a few seconds after it leaves the vehicle. An estimated dilution of 100:1 after 0.4 seconds and 1000:1 after 1 second was reported. Another study showed a reduction of 90 % in total particle number in a few minutes and 100 – 1000 meters.

Recent research[3] conducted in freeway sides indicated high PM concentrations due to motor vehicles. It was observed that PM concentration depended on the distance from the freeway, with a large spike next to the roadway, which decayed to background levels within 100-150 m. Magliano and Najita[4] observed that the high concentration of O_3 and $PM_{2.5}$ occur together in some locations in summer; and the correlations were stronger at urban sites than at rural sites. Oanh, et al.[5] measured $PM_{2.5}$, SO_2, NO_2, and BTEX both using static monitoring on both sides of roadways and on-route measurements using equipment placed on various vehicles. Van Poppel, et al.[6], investigated the influence of roadway height on the pollutant concentrations around the roadway. The measurements were taken at two locations on one side of each roadway. The impact of the road traffic to the pollutant concentrations appeared to be higher at ground level compared to that at the elevated road section. Concentration gradients of ultra-fine particles, black carbon, CO_2, NO, and NO_2 were measured at distances up to 850 m on both sides of a major highway by Gordon, et al.[7] Their measurements were compared to the estimates obtained from a physically-based dispersion model, which did not take into account evaporation, chemical reactions, or deposition and reported good agreement with the measurements. Kim, et al.[8] modeled the fate of reactive pollutants using CFD simulations with a full reaction chemistry. They found that the concentrations of the secondary oxidation products such as NO_2 and O_3 vary differently from the concentrations of primary pollutants indicating the importance of using a full photochemical reactions model in their simulations. Padro-Martinez, et al.[9] reported the results of an extensive mobile monitoring of particle number concentration, particle size distribution, $PM_{2.5}$ mass, particle-bound polycyclic hydrocarbons, black carbon, carbon monoxide and nitrogen oxides using instruments placed in a van, which was driven at slow speed in a 2.3-km^2 area near an eight-lane highway. Highest concentrations of pollutants were measured within 0-50 m of the highway. All pollutant concentrations except that of $PM_{2.5}$ decayed with distance from the highway. $PM_{2.5}$ gradients were relatively flat, which was attributed to the $PM_{2.5}$ coming from regional sources.

Vehicular and industrial emissions additionally contribute heavily to air pollution by reacting in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog. Oxides of nitrogen react with oxygen in the air to form a complex mixture of pollutants that includes ozone, PANs, and other organic compounds. Photochemical smog often has a similar appearance and similar effects to those of industrial smog. Indeed, in most cities, the two forms of smog occur in combination with each other. Secondary PM sources directly emit air contaminants into the atmosphere that form or help form PM. Hence, these pollutants are considered precursors to PM formation (Figure 1). These secondary pollutants include SO_x, NO_x, VOCs, and ammonia. Control measures that reduce PM precursor emissions tend to have a beneficial impact on ambient PM levels.

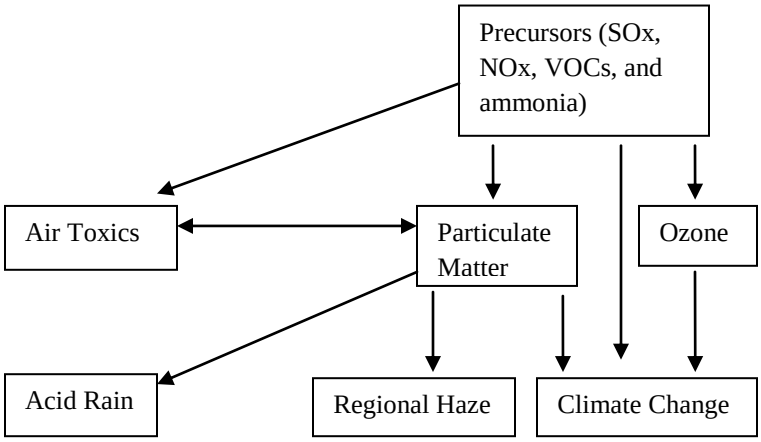

Figure 1. Relationships between PM from mobile source and its precursors[2,10].

I. ii. B Health and Environmental Problems Due to PM

Particulates less than 10 µm diameter can penetrate into the lung while coarser particles are filtered out in the upper respiratory system. Inhalation of fine particulates affect the lower respiratory system, damage the lung tissue, worsen respiratory diseases such as emphysema and bronchitis, aggravate existing heart conditions and as a result cause significant number of premature deaths especially among sensitive populations like children and elderly. Relationship between lung cancer and fine particulate matter associated with diesel exhaust was also suggested and this led to the listing of these particulates as a mobile source air toxic by EPA. Diesel exhaust PM contains polycyclic aromatic hydrocarbons that are known to be mutagens and carcinogens. Smith, et al.[11] analyzed the impact of road traffic on human health based on the emissions data obtained in UK between 1995 and 2005. They found that although there was a decrease of about 25% in the number of car-related deaths due to more stringent emission regulations, the number was still twice as many as those due to car accidents. Their morbidity results based on hospital admissions were not as clear. Caiazzo, et al.[12] applied a multiscale air quality model to assess the health effects of emissions from various sectors. They found that out of the 200,000 combustion-produced $PM_{2.5}$ related deaths in the U.S., 53,000 could be attributed to road transportation. Those numbers for ozone-related deaths were 10,000 and 2,000, respectively. Studies indicate that $PM_{2.5}$ rather than PM_{10} (inhalable coarse particles) is linked more closely to health effects. Naval traffic also results in appreciable NO_x and PM emissions; Corbett et al.[13] reported that by 2012, approximately 64,000 premature deaths will be attributable to ships' emissions of particles with especially the coastal areas being affected. The other pollutants we are investigating, namely, tropospheric ozone (O_3) and NO_2 can also

trigger chronic respiratory and cardiopulmonary ailments[14,15]. Children were found to be more susceptible to pollutant exposures that lead to asthma. Positive associations between O_3 and NO_2 levels and human mortality were reported[16,17]. In addition to these health effects, air pollutants may also have psychological effects such as annoyance or minor disorders, which are important for human well-being[18]. In this work our focus was on $PM_{2.5}$; other issues such as the health effects of ultrafine particles ($PM_{0.1}$) and the source and chemical composition of particles have also gained attention recently[19].

PM also contributes to global climate change and acid rain. $PM_{2.5}$ causes reduced visibility (haze). Black carbon, which is a constituent of PM absorbs radiated energy in the atmosphere, and when deposited on ice and snow. While black carbon on ice and snow reduce their reflectance and can contribute to global warming, reflective particles in atmosphere may help reduce the amount of radiation absorbed by earth[20].

I. ii. C. <u>EPA Regulations on PM</u>

The National Ambient Air Quality Standards for $PM_{2.5}$ are set at 15.0 $\mu g/m^3$ as the annual standard and 35 $\mu g/m^3$ as the 24-hour standard; and for PM_{10}, 150 $\mu g/m^3$ as 24-hour standard. In January 2009, EPA has proposed to make some changes to these standards[21]. EPA finalized guidance on PM hotspot modeling on December 20, 2010, and initiated a two-year grace period before these new requirements become mandatory. According to World Health Organization (WHO), adverse health effects were associated with $PM_{2.5}$ for background concentrations ranging from 3 and 5 $\mu g/m^3$. Therefore, WHO finds the present standards too low, and suggests a target ceiling value of 10 $\mu g/m^3$ for yearly averages[22].

The U. S. heavy duty truck PM emission standards were lowered significantly during 1990's and underwent an order of magnitude reduction in 2007 from 0.13 g/kW.h to 0.013 g/kW.h. In March 2008, EPA finalized a program to reduce emissions from diesel locomotives of all types: This will reduce PM emissions by as much as 90% and NO_x emissions by 80% when fully implemented[21].

Therefore, U. S. transportation planning agencies, state departments of transportation, and metropolitan planning organizations have a vested interest in understanding PM problems and the factors contributing to their effective control.

II. WORK DONE

In the previous research cycle a TEOM 1405-DF dichotomous ambient particulate monitor with a filter dynamics measurement system (FDMS) (Thermo Scientific, Franklin, MA) was purchased. This equipment is designed to provide long and short term PM concentration measurements for both non-volatile and volatile PM_{10}, $PM_{2.5}$, and PM-coarse (particles

between 2.5-10 μm) components. TEOM 1405-DF needs to be operated within a specified temperature interval (46 to 77°F). For this purpose, the manufacturer offers a custom-made outside shelter with an air conditioning and heating unit. Also, to be taken to the measurement locations, this enclosure needed to be installed inside a suitable vehicle. Since the financial support for the vehicle did not materialize, we had to install the PM equipment on a hand cart to make it mobile. This method had three disadvantages. First, due to its weight and size, it required four students to move all the equipment to the measurement locations. Secondly the installed equipment was too high to fit through doors and inside the elevator. Since we could not find an outdoor place to store the equipment, it had to be dismantled and reassembled every time it was taken outside. Lastly, when moving, the cart shook excessively. This, combined with the frequent disassembly and reassembly, resulted in excessive wear and tear on the equipment. To reduce the effect of shaking during transportation a location closer to the Engineering Building was chosen for the measurements (Figure 1). To allow for at least one hour of sampling time, it was decided to have only three measurements per day, which required a minimum of 6 hours considering the start up times of the instruments.

II. i. Equipment

The first mobile unit contained the NO_x, ozone, weather monitoring units and a pyranometer for measuring solar intensity. These equipment are Thermo Fisher Scientific Inc. (Franklin, MA) Model 42i chemiluminescence NO-NO_2-NO_x analyzer; Thermo Fisher Scientific Inc. (Franklin, MA) Model 49i ozone analyzer utilizing UV Photometric technology; Climatronics Corp. (Bohemia, NY) AIO compact weather station with capabilities to measure temperature, relative humidity, wind speed, wind direction, and barometric pressure; and LI-COR Inc. (Lincoln, Nebraska) pyranometer (LI 200SA) with a light meter (LI 250A). These units are powered by the 7.5-kW Generac GP7500E generator. The NO_x and ozone sampling tube inlets were located 2.9 m above the ground.

Figure 2. Measurement Locations

The second mobile unit had the particulate monitoring system in an outdoor temperature controlled shelter. This equipment is the TEOM 1405-DF dichotomous ambient particulate monitor with a filter dynamics measurement system (FDMS) (Thermo Scientific, Franklin, MA). It is designed to provide long and short term PM concentration measurements for both non-volatile and volatile PM10, PM2.5, and PM-coarse (particles between 2.5-10 µg/m3) components. It is housed in an outdoor shelter designed to house the TEOM 1405-CF and keeps it at the desired temperature. It is also powered by the Generac GP7500E generator. The air sample inlet for the PM measurements is located about 3.5 m above the ground.

III. RESULTS

Several mishaps had to be overcome to take meaningful data: the proper functioning of the equipment especially the generator; presence of at least three students; and no rain. Initially there was a significant delay in getting the 7.5-kW generator. Finding four research students and processing the contracts took about six weeks. A significant number of days were lost to rain or potential rain. After about three days of successful operation, the generator started having start-up problems. The engine did not have an automatic choke and therefore, it took some time starting. As a result and due to the fact that the fuel was gravity-fed, the engine frequently flooded. It was decided to change the spark plug and waited several days for the delivery of the special spark plug. When this did not solve the problem, rather than delaying the measurements longer by servicing the generator, the principal researcher bought a generator paying from his pocket, to be able to obtain some data before the student contracts expired. After a few successful measurements, due to the wear and tear on the PM equipment as explained above it started malfunctioning. A leak test was performed and a large leak inside the equipment was found. The PM equipment was opened up and the leak was repaired, but unfortunately the last days of student contract were lost to rain limiting the number of measurements, which gave dependable data.

These measurement conditions are shown in Table 1 and the main results are given in Table 2.

Table 1. 2013 pollution measurement conditions.

Date	Dist. From Ramp, m	Temp. ºC	P atm	Rel. Hum. %	Wind sp.	wind dir.	wind sd	solar int.	Traffic EB veh/h	Traffic WB veh/h	Traffic,tot veh/h	EB-ONR veh/h,est
4/3/2013	37.8	10	1.01	33	2.93	99.8	6.2	668				
4/5/2013	37.8	14.5	0.999	42.4	2.24	173.2	12.3	510				
	84.3	15.2	0.983	43.3	3.02	105.5	8.57	412				
4/13/2013	37.8	13.6	1.003	60.3	2.43	45.4	7.9	195	2464	3737	6201	372
	84.3	14.5	1.002	56.2	3.42	84.4	12.2	789	3176	2799	5975	359
	129.8	14.3	1.002	57.6	4.32	87.5	15.4	764	3524	2981	6505	390
4/27/2013	37.8	16.7	1.018	45.4	2.43	117.6	6.91	722	2449	4067	6516	391
	84.3	17.6	1.017	36.1	2.11	75.8	13.5	869	3024	3813	6837	410
	129.8	17.7	1.016	42.7	2.78	84	13.6	651	2975	3899	6875	413
5/9/2013	37.8	17.3	1.005	79.2	1.79	185	14.2	818				
	84.3	21.8	1.004	63.7	1.05	238	33.8	921				
	129.8	24	1.004	49.5	1.1	186	34.6	749				
5/21/2013	37.8	22.4	1.005	84.5	1.29	204	22.5	382	2309	2462	4771	286
	84.3	26	1.005	69.6	1.71	233	23	598	2857	2355	5212	313
	129.8	26.5	1.004	67.5	1.66	246	22.9	425	3855	3660	7516	451
5/22/2013	37.8	23	1.015	75.4	2.18	222.9	18.6	531	2640	2902	5542	333
	84.3	25.9	1.015	67.2	1.95	236	26.3	598	2406	2731	5137	308
	129.8	28.2	1.014	59.4	2.29	228.9	23.5	846	3148	2170	5318	319

The wind directions on 4/3, 4/5, 4/13, and 4/27 indicate that for those measurements the receptors were at downwind positions, while on 5/09, 5/21/ and 5/22 they were at upwind positions.

Table 2. 2013 Measurement Results

Date	Dist. From Ramp, m	NO ppb	NOx ppb	NO2 ppb	Pred. NO_2 ppb	O3 ppb	PM-2.5 mg/m^3	PM-10 mg/m^3	PM10 pred.
4/3/2013	37.8	10.8	19.8	9		20.25	3.89	5.69	
4/5/2013	*37.8*	*28.9*	*33.6*	*4.7*	*0*	*30.63*	*4.83*	*5.73*	*1*
	84.3	5	12.1	7.1	0	40.38	2.09	2.70	3.2
4/13/2013	37.8	4.58	10.5	5.92	10	27.28	15.38	17.30	5.3
	84.3	2	5.65	3.65	10	35.42	9.34	9.43	4.5
	129.8	11.38	19.52	8.14	10	36.92	10.25	10.61	5.8
4/27/2013	37.8	3.3	12.56	9.26	0	40.83	17.87	21.76	1
	84.3	5.63	11.21	5.58	20	50.04	12.25	8.82	6
	129.8	2.8	6.83	4.03	30	62.9	12.50	11.37	7.5
5/9/2013	37.8	8.91	12.84	3.93	0	31.05	11.09	12.52	1

	84.3	9.84	14.06	4.22	0	29.09	14.66	13.59	1
	129.8	19.11	21.99	2.88	0	31.43	13.91	13.04	1
5/21/2013	37.8	4.86	8.57	3.71	0	22.84	26.26	26.17	1
	84.3	3.52	5.58	2.06	0	26.38	35.80	25.30	1
	129.8	2.55	4.72	2.17	0	30.44			1
5/22/2013	37.8	1.005	2.039	1.034	0	26.01			1
	84.3	3.47	5.57	2.1	0	26.3			1
	129.8	2.51	4.16	1.65	0	30.38			1

IV. DISCUSSION

In table 2, there are three sets of measurements, on dates 4/5, 4/13 and 4/27, that are at downwind locations. The rest of the data are all for upwind conditions. Since we lacked the ability to take simultaneous measurements on both sides of the road, the upwind measurements provided information about the background concentrations. Table 2 shows that the background NO_2 concentrations ranged between 1 ppb and 7 ppb. The main factors that are expected to influence the background NO_2 values are the emissions due to local sources and from traffic on the side streets, and the background ozone concentration, relative humidity, solar intensity, and the temperature that may affect the formation of secondary pollutants in the atmosphere. The local emissions are expected not to change much between the measurements. The indicated background ozone concentrations are between 22 and 33 ppb and are mainly around 30 ppb. Among the other factors, the only consistent relationship is between the temperature and background NO_2 concentration, which shows that the background NO_2 concentration decreases with an increase in temperature.

The upwind measurements of PM on 5/22 and the measurement at the 3rd receptor on 5/21 were excluded from Table 2 because of negative values that indicated a leak in the FDMS module. The integrity of the measurements at receptors 1 and 2 on 5/21, which showed significantly higher PM concentration are also in question. They may be affected by the onset of a leak inside the instrument. There was a significant amount of pollen in the atmosphere at the time of measurements. The presence of pollen could have been a factor in the PM amounts obtained in the earlier measurements. Pollen sizes cover a range between 6 µm and 100 µm[25]. Therefore, most pollen will be outside the PM_{10} range and its direct effect on the measured PM_{10} and $PM_{2.5}$ concentrations is expected to be small. From the limited data available, it was difficult to get a good estimate of the PM background concentrations.

Downwind measurements of PM_{10} and $PM_{2.5}$ on 4/5, 4/13, and 4/27 show significant decreases in PM concentrations between receptors 1 and 2 mainly due to plume dilution. The increase in the PM_{10} and $PM_{2.5}$ concentrations at receptor 3 can be tentatively attributed to the effect of

the traffic on the Emancipation Drive and Marshall Avenue (receptor three was located at the corner of intersection of these two streets). Table 2 also shows that majority of the measured PM was in the $PM_{2.5}$ range. There was a concern about the measurements showing PM_{10} less than $PM_{2.5}$. This observation is discussed in the next paragraph.

To understand the observation mentioned above, we need to understand how the particulate concentrations are determined by the TEOM 1405-CF. The instrument first separates the PM_{10} fraction into $PM_{2.5}$ and PM coarse streams, which are then sent to separate mass transducers to obtain the base mass concentrations. In order to account for the volatile portion of the particulates, the PM_{10} and $PM_{2.5}$ streams are sent through a chilled filter to create a particulate-free reference stream every 6 minutes by a switching valve before they are sent to the mass transducers. When the flow is switched to the reference stream after measuring the base concentrations, the volatile matter on the mass transducer filters evaporate, giving negative results. When the reference concentration is subtracted from the base concentration, the volatile particulates are added to the nonvolatile particulates giving the PM concentrations as they exist in the ambient air. If the measured reference concentration is positive, the final mass concentration will be less than the base concentration. During the operation of FDMS, the reference mass concentration is generally negative, but positive values are occasionally encounterd[26, 27]. Jessica Sheldon[26] reports incidences of positive reference mass readings when the existing FDMS 8500 unit being used, was replaced by a new one. They could not find a problem with the instrument, which passed all the tests including the leak test. Cleaning of the unit did not stop the positive reference mass measurements. Reinstalling the old unit was reported to again result in negative reference mass measurements. Since the PM_{10} values are obtained by adding the measured $PM_{2.5}$ and PM coarse readings, a negative PM coarse value will produce a condition where PM_{10} is less than $PM_{2.5}$. This is what we suspect in some of our data, which show PM_{10} less than $PM_{2.5}$. Due to the very limited data, this issue remains unresolved.

Discussion of the downwind results is complicated. Although each data set is obtained on a single day, there may be significant variations in the temperature, relative humidity, wind direction, wind direction standard deviation, wind speed, and the traffic volume when the data was taken at different receptor locations. The effect of the traffic volume is through the increased emissions, increased mixing due to mechanical turbulence, and increased vertical thermal dispersion at high vehicle volumes. The last two effects tend to decrease the effect of increased emission. The effect of wind direction is very significant. When the measurement locations (receptors) are located downwind, the wind creates a plume toward the receptors and carries the emitted and formed species to the receptors. Also, for downwind measurements wind direction can change between almost parallel from the north to almost parallel from the south. The northerly and north easterly wind concentrations may be affected

from the traffic at the I-64 interchange 267 and the local traffic on the Settler's Landing Road, and the concentrations in the southerly and southeasterly winds may be influenced by the marine traffic over the Hampton Roads Bridge Tunnel. Higher wind speeds create longer and slender plumes, and thus, determine how fast the plume is diluted with the surrounding air. Standard deviation of the wind direction and the atmospheric stability class are also factors determining the dispersion rate. In addition, the nitrogen dioxide concentrations at the receptor locations were observed to be strongly affected by the ambient ozone concentrations[1]. Ozone plays a primary role in the generation of NO_2 from NO. It is also significant in the formation of secondary nitrogen-containing species, thus depleting NO_2 and increasing the PM content. Therefore, in order to have a better analysis of the measured ozone and nitrogen oxides concentrations, a large number of data sets are needed to compare the results under similar conditions.

The NO_2 and PM_{10} concentrations predicted at the three receptor locations using the model CALINE4 are also shown in Table 2. Since there was no reliable estimate for the background concentrations of O_3, NO, NO_2, and PM_{10}; they were roughly based on the lowest values observed under upwind conditions as 30 ppb, 1 ppb, 1ppb, and 1 $\mu g/m^3$, respectively. Therefore, the predicted values given in the table should be considered to be only relative values. Consequently these estimates cannot be used to judge the accuracy of CALINE4 predictions. In addition, the predictions do not consider the effect of the low level vegetation and trees that exist between the roadway and the first receptor. A study on the effects of the vegetation barrier[28] reports that the vegetation barrier affects the turbulent mixing and dry deposition rates of atmospheric constituents. It was found that an increase in leaf area density reduces particle concentration and wind speed increase increases particle impaction, but reduce particle diffusion, which result in reduction in the concentration of particles greater than 50 nm. The study by Terzaghi, et al.[29], on the effect of vegetation on the particle deposition reports PM_{10} deposition velocities between 0.02 and 0.04 cm/s which are significantly higher than the settling velocities obtained by using the equation suggested by CALINE4. For more discussion on CALINE4 predictions of NO_2 concentrations, please refer to the 2012 report submitted to ESITAC and our 2012 presentation at the 2nd International Conference on Environmental Pollution and Remediation[1].

V. CONCLUSIONS

Although due to various constraints, the amount of data obtained was not adequate for a conclusive analysis. The work described in this report laid the groundwork for a comprehensive study of the transportation-related pollution and its temporal and special variations. We have realized that it is not possible to extend the work anymore using the equipment loaded on hand carts. Therefore, our recommendations for further study in this area are as follows:

- Install all equipment in a suitable van.
- Select locations around the roadway being investigated that will allow for measurements on both sides of the roadway up at least 500 m from the roadway. Alternating measurements should be taken on each side of the roadway at each receptor location so that the conditions for the measurements are similar.
- Each measurement should be at least 1 hour long.
- Installing a recording camera on the van to record the traffic will provide information on traffic flow and vehicle type at the measurement location.
- The measurement capabilities may be extended to include CO_2 concentration, ultrafine particle count, and particle analysis.

VI. STUDENTS

In this research cycle the following students were employed: Darrion Crenshaw (Electrical Engineering), Courtney Dansby (Chemical Engineering), James Reed (Chemical Engineering), Travian Sampson (Chemical Engineering), Ervin Woodfork (Chemical Engineering), and Courtney Watts (Chemical Engineering). They assisted in the assembly of the instruments on hand carts, moving the carts to measurement locations, disassembly and reassembly of the PM instruments during transportation, and obtaining the traffic data from the traffic camera at interchange 267 on I-64.

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