

**EFFECT OF OZONE AND DISTANCE FROM A MAJOR ROADWAY ON NITROGEN  
OXIDES CONCENTRATIONS**

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**FINAL REPORT**

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## ABSTRACT

### I. Significance of NO<sub>x</sub> and Ozone Emissions

Despite recent advances in the automobile industry in reducing emissions from individual vehicles, air pollution in localities, where there are regional increases in the traffic volumes, still persist at problematic levels. Vehicular emissions are the major contributors to atmospheric NO<sub>x</sub> constituting about half of all anthropogenic emissions. Most of NO<sub>2</sub> and all other nitrogen species are formed in air as a result of the chemical reactions of NO with other pollutants. Therefore, nitrogen oxides play a major role in the atmospheric photochemistry, controlling ozone formation and generation of the hydroxyl (OH) and other reactive radicals. These reactions produce a complex mixture of chemicals, which can further transform into secondary aerosols that increase the particulate matter (PM) content of the ambient air.

### II. Health and Environmental Effects of NO<sub>x</sub> Emissions

The secondary species formed in the atmosphere are known to cause a wide variety of health and environmental problems. Tropospheric ozone, NO<sub>2</sub>, nitrate particles, and acid aerosols can trigger chronic respiratory and cardiopulmonary ailments. Children were found to be more susceptible to NO<sub>x</sub> exposures that lead to asthma; and positive associations between O<sub>3</sub> and NO<sub>2</sub> levels and human mortality were reported. Environmental effects of NO<sub>x</sub> include the formation of acid rain that can lead to nutrient overload and deterioration of water quality and aquatic life. They are also greenhouse gases and contribute to global warming. Ozone and NO<sub>2</sub> are potent oxidizers and cause oxidative stress on biological organisms. High levels of NO<sub>2</sub> harm vegetation by disturbing the nitrogen balance, and ozone is known to have phytotoxic effects. EPA is proposing a new 1-hour standard at a level between 80 and 100 ppb while retaining the current average NO<sub>2</sub> standard of 53 ppb. This EPA proposal increases the importance of measuring the peak concentrations over shorter time periods especially near major roads in urban areas. EPA also proposes to change the standard for ground level ozone to no more than 0.06 to 0.07 ppm from the current value of 0.075 ppm. Since ground level ozone is formed by the reaction of nitrogen oxides, this change emphasizes the importance of the investigation of nitrogen oxide concentrations around major roadways.

### III. Motivation for Work

Measurements done at the air pollution monitoring stations provide regional data with some temporal resolution. Air pollutant concentrations can be significantly higher close to major roadways. This makes the local pollutant concentration measurements and ***finding ways to predict concentrations with a much higher spatial resolution essential in making decisions about locating buildings that will house sensitive populations.***

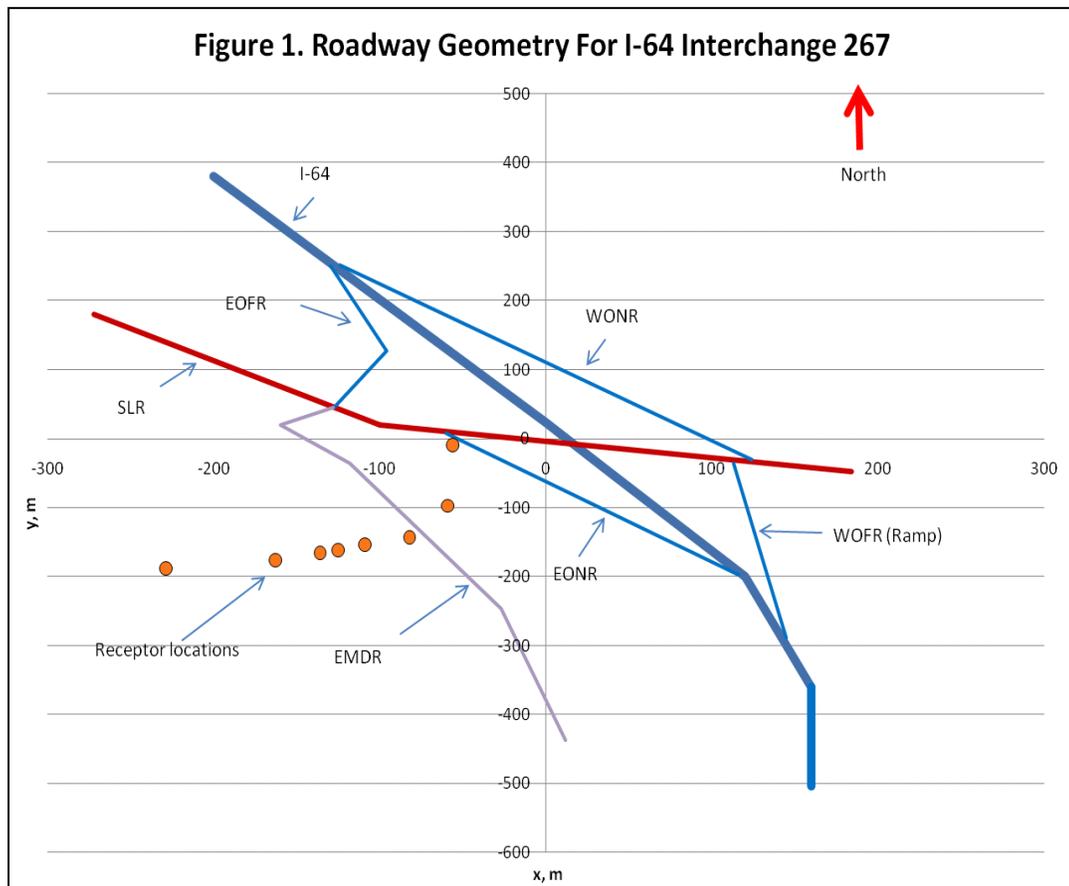
### IV. Work Done

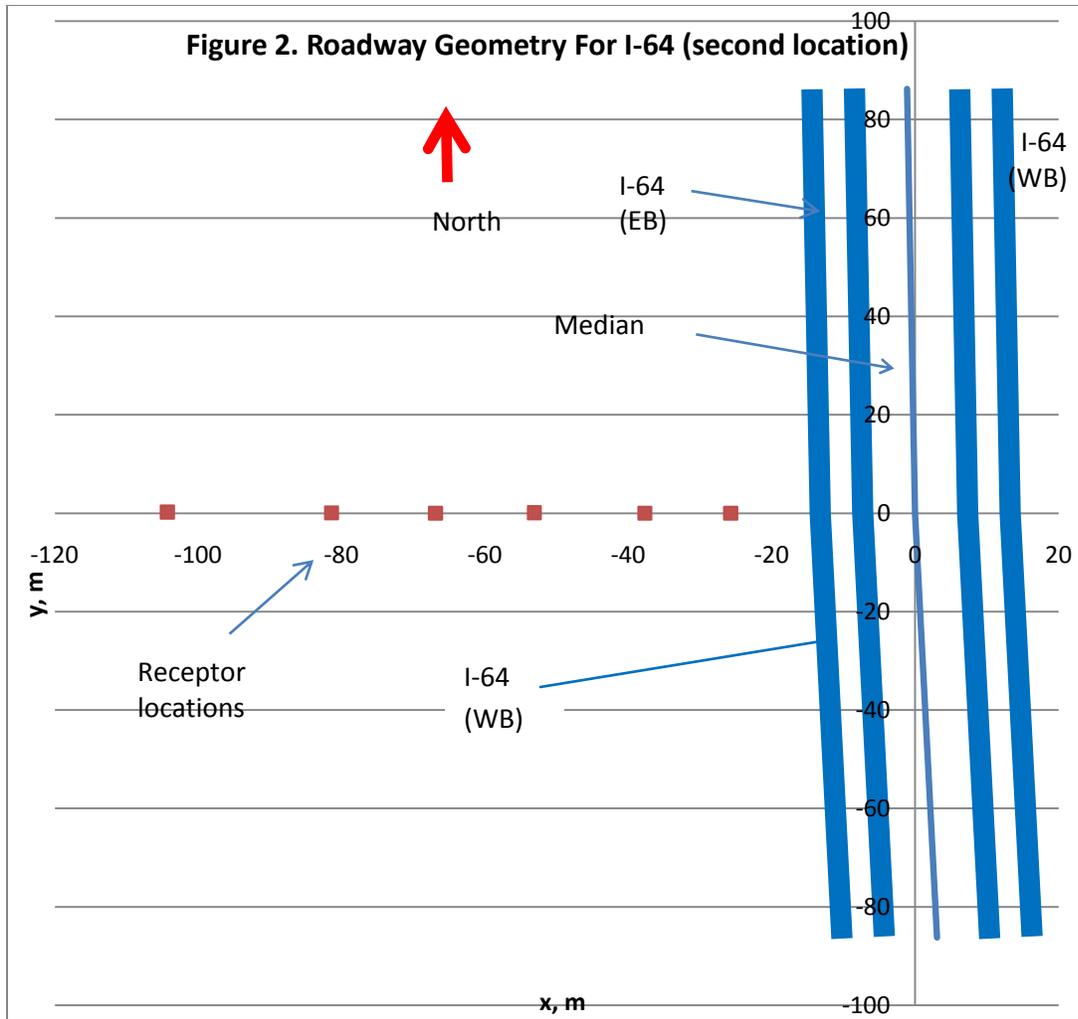
A mobile NO, NO<sub>2</sub> and O<sub>3</sub> measurement unit with the associated weather monitoring instrumentation was built. Coordinated measurements of NO, NO<sub>2</sub> and ozone concentrations and

meteorological conditions at varying distances from the roadway, together with the traffic volume data were obtained. CALINE4 was used to estimate the NO<sub>2</sub> concentrations at receptors located at the measurement points. Since the concentrations measured at the original location of the receptors were not high enough for the validation of CALINE4 results, a new set of measurements were taken at a new location closer to the roadway.

#### IV. i. Site Selection

The first site selected for the proposed monitoring and modeling work was a section of I-64 containing the Hampton University interchange (interchange 267). The reasons for this selection were the proximity to Hampton University and the existence of a traffic camera at the Hampton University I-64 interchange 267, so that real time traffic data could be obtained for the road section of interest. The sampling locations were not close enough to the roadway to provide concentrations high enough to be used for the validation of CALINE4 results. Therefore, a new site was selected that provided higher concentrations (Figures 1 and 2).





## VI. Equipment Used

For **NO<sub>x</sub> measurements** a Thermo Fisher Scientific Inc. (Franklin, MA) 42i chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer was mounted on a 3-shelf cart so that the analyzer intake was at a level about 1.0m above the ground. **Ozone measurements** were done using a Thermo Fisher Scientific Inc. (Franklin, MA) Model 49i utilizing UV Photometric technology. A Climatronics Corp. (Bohemia, NY) AIO compact weather station with capabilities to measure temperature, relative humidity, wind speed, wind direction, and barometric pressure was used for **weather measurements**. LI-COR Inc. (Lincoln, Nebraska) pyranometer (LI 200SA) with a light meter (LI 250A) was used to measure **sunlight intensity** (cloud cover). **Data** was acquired and analyzed using a Dell Inspiron 8100 laptop computer. The mobile monitoring system was powered by a 2-kW Honda generator EU2000i connected to the cart by a 50-ft extension cord. **Traffic Volume** was measured using the traffic camera on Interchange 267 and by direct count.

## VII. Prediction of NO<sub>2</sub> Concentrations

CALINE4 is a line source Gaussian plume dispersion model that was mainly developed by the California Department of Transportation-University of California at Davis Air Quality Project to predict carbon monoxide, particulate matter, and nitrogen dioxide concentrations near roadways. As inputs, the model requires source strength, meteorology and site geometry and can predict pollutant concentrations within 500 meters of the roadway. The measured temperatures, cloud cover, wind speed, wind direction, standard deviation of wind direction were used. Data were acquired for 15 minutes at each receptor location and the model input values were taken as the average values during the data acquisition period.

The NO<sub>x</sub> composite emission factor was computed using MOVES for the City of Hampton and for the months of June and July of 2010. Only running exhaust and crankcase running exhaust emissions from gasoline and diesel vehicles on a restricted urban roadway were considered. A sample MOVES output is shown in Figure 3.

**Figure 3.** MOVES output file

```
Run:  Header Item      Header Item Value
0   Report Description  Summary Report
0   Report Date/Time    2011-2-25 17:43:44
0   MOVES Output Database national_june_july.basic2
0   Emission Process    All
1   Run Date/Time       2011-01-28 15:35:32.0
1   Run Specification    MOVES2010aExample JuneJulyInput
1   Run Spec File Date/Time 2011-01-28 15:35:20.0
1   Run Spec Description  Example Run Specification for MOVES2010a. NO, NO2, N2O,
NOx All vehicles, restricted urban road. Gasoline and diesel fuel transit busses.
Run at preaggregated national level. Time fully preaggregated.
1   Mass Units          kg
1   Energy Units        J
1   Distance Units      mi
1   Time Units          hour

Year  Month  County  NO2    NO     N2O    NOx    Distance
2010  6       51650  49641  427994  1514   477635  332429312
2010  7       51650  49035  420680  1533   469915  336478720

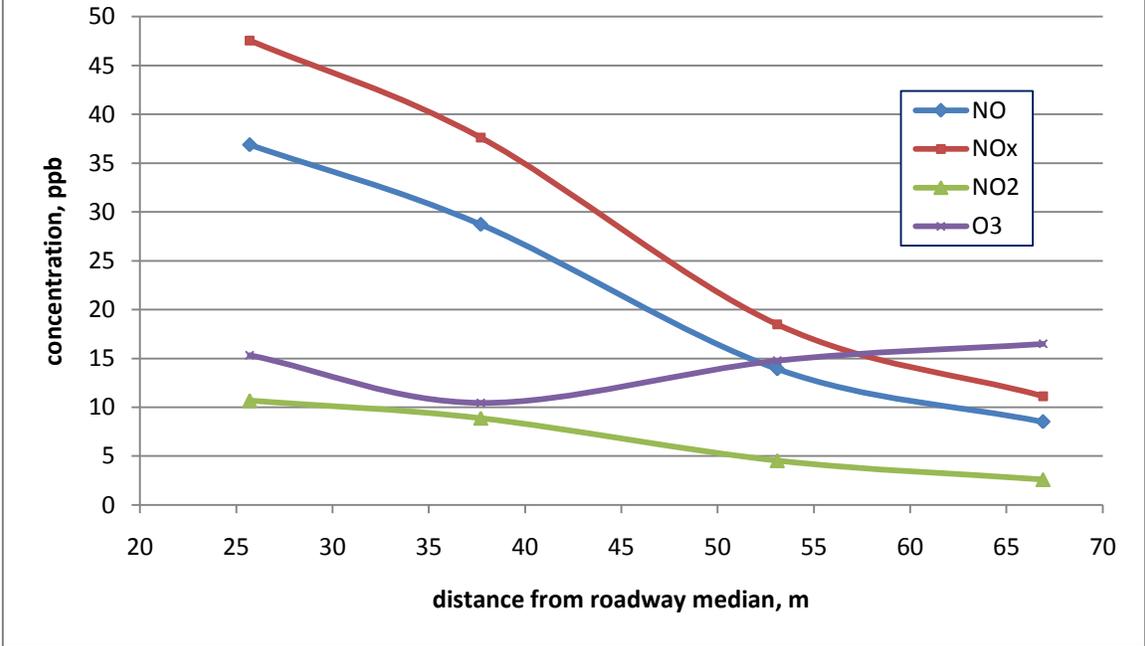
Category Field  Value  Description
countyID       51650  Hampton city
```

## VIII. Results

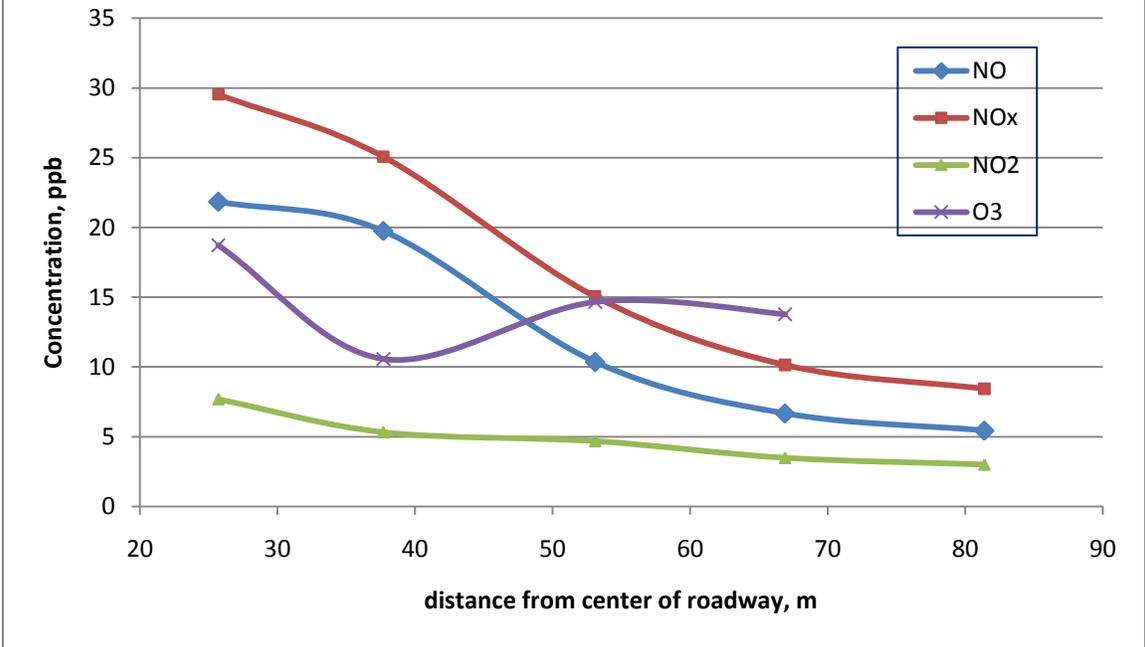
### **NO<sub>x</sub> Concentrations**

The results of NO<sub>x</sub> and ozone measurements were given in Figures 4 - 18.

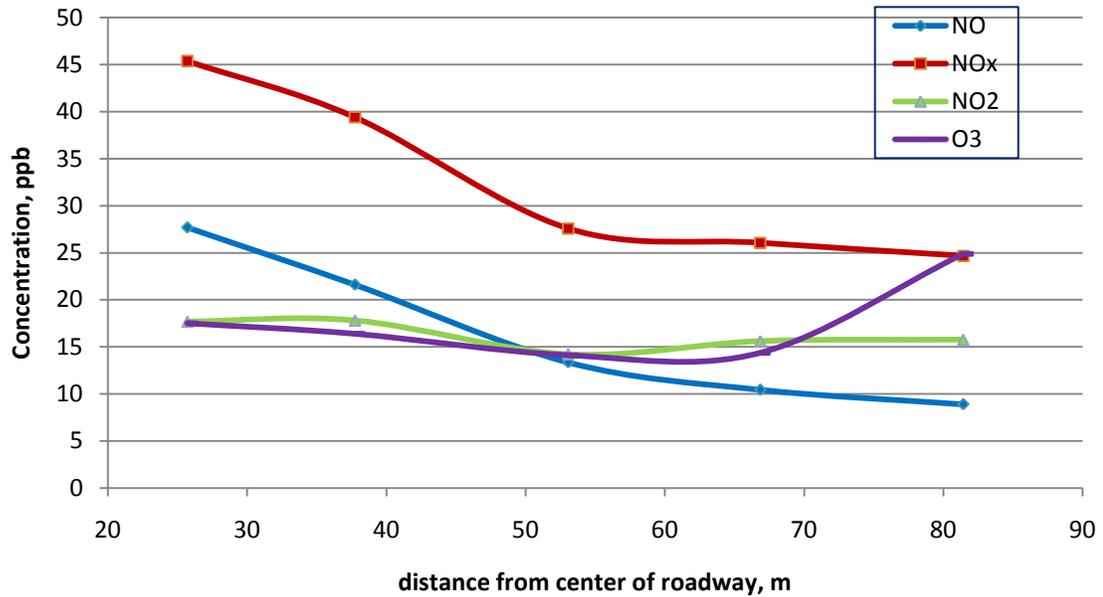
**Figure 4.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=0.7 m/s, wind direction= 76°, stability class=C



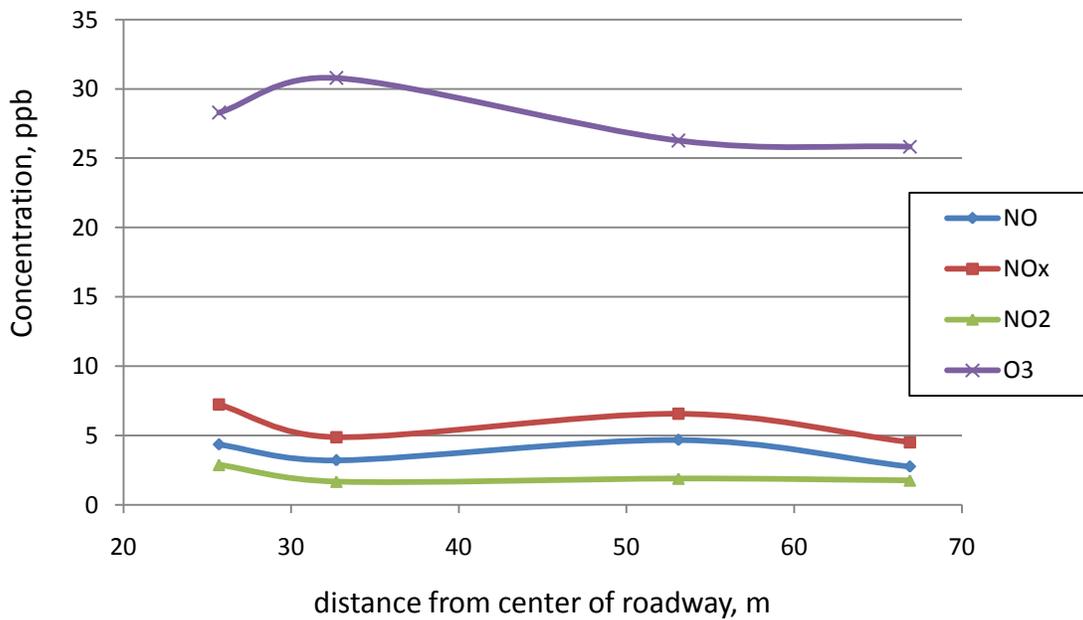
**Figure 5.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=0.8 m/s, wind direction= 83°, stability class=A



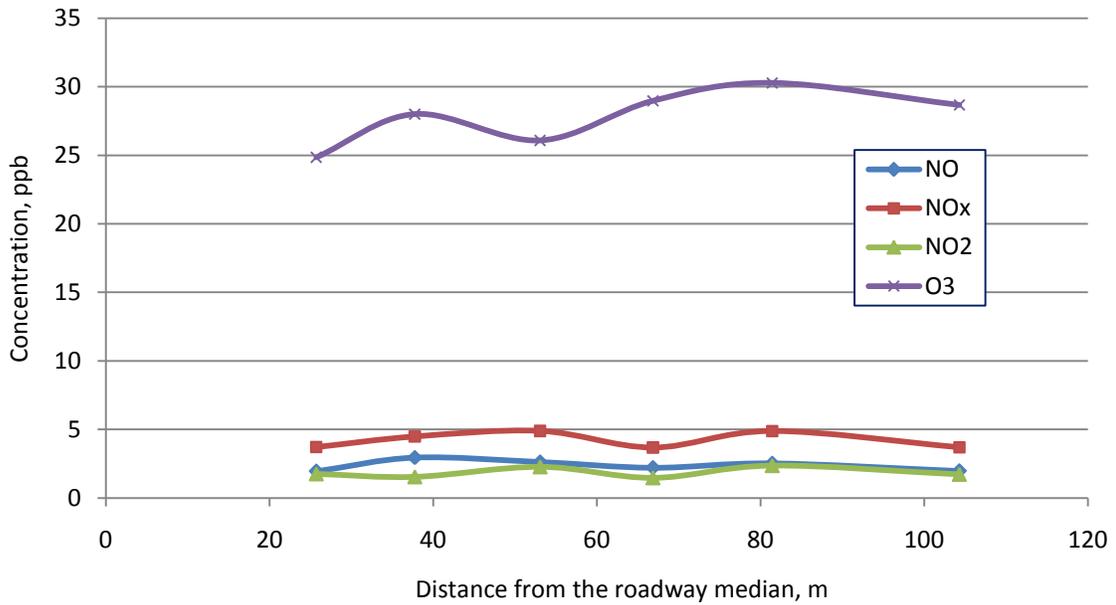
**Figure 6.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=2.0 m/s, Wind direction= 319°, stability class=B



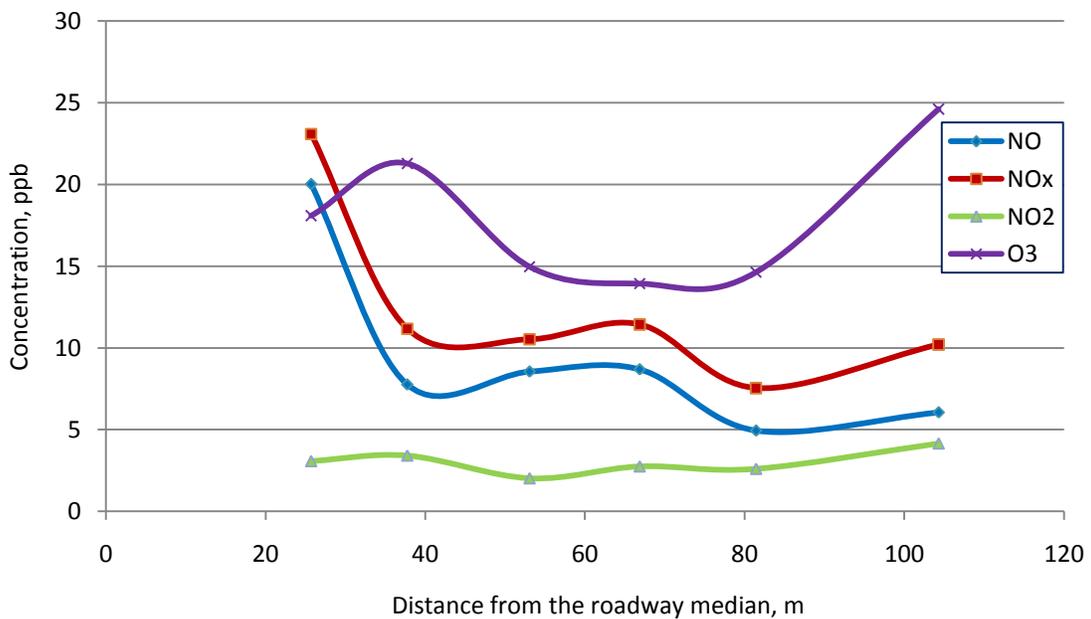
**Figure 7.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.65 m/s, Wind direction= 312°, stability class=A



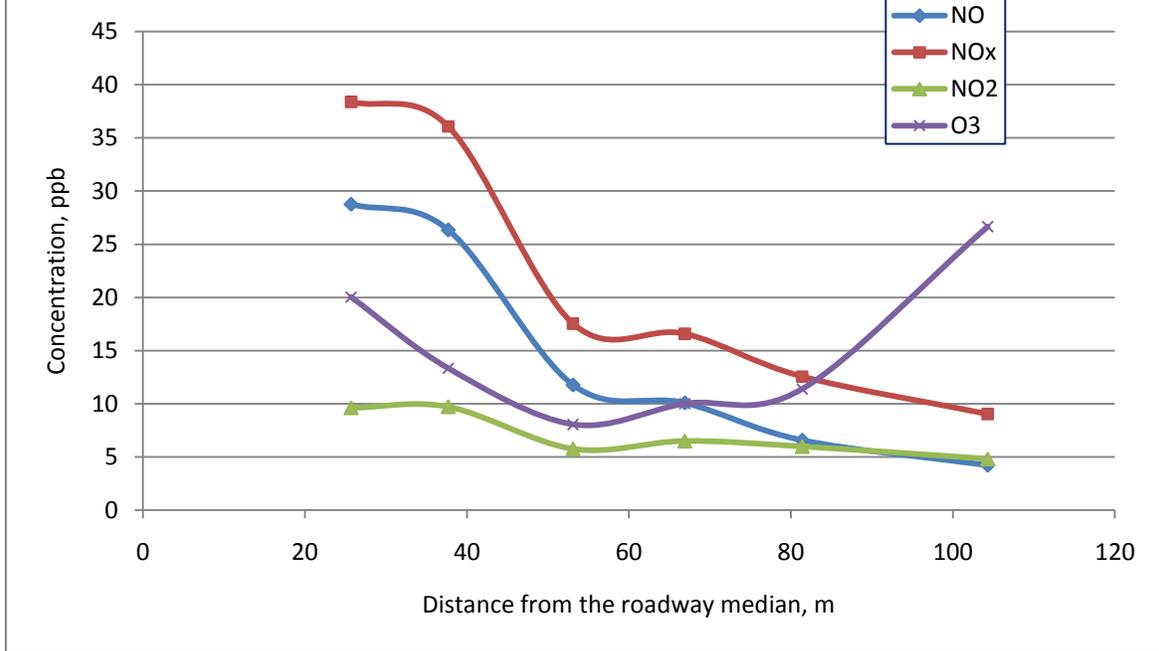
**Figure 8.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=2.07 m/s, Wind direction= 303°, stability class=C



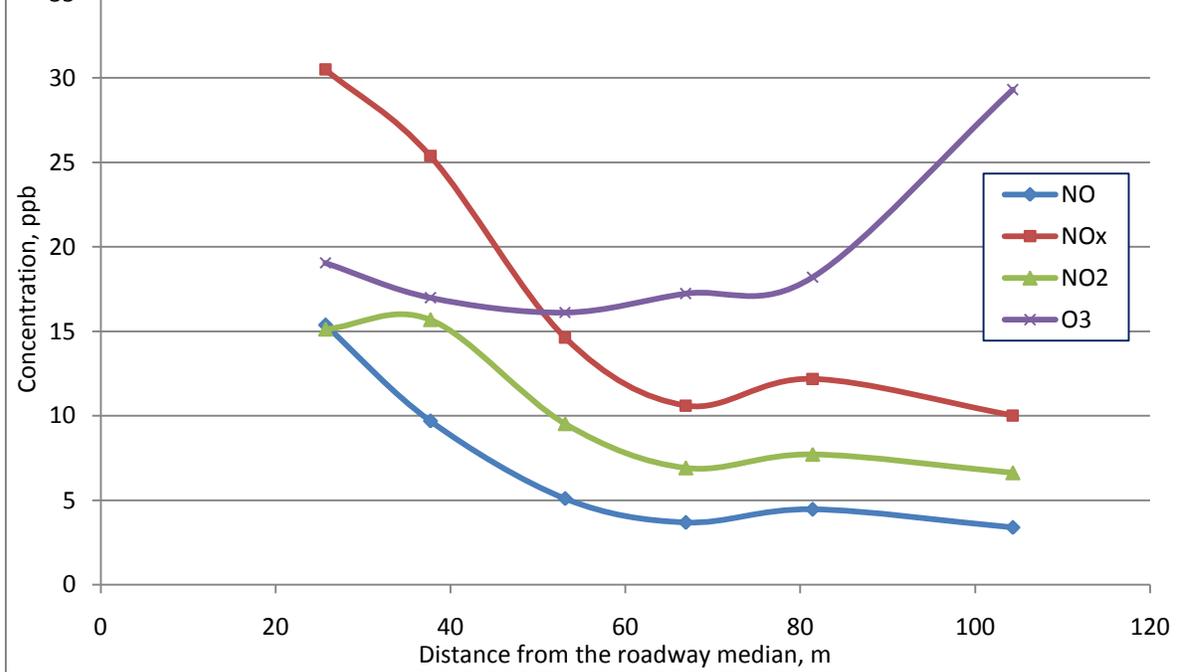
**Figure 9.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub>, and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=0.82 m/s, Wind direction= 82°, stability class=C



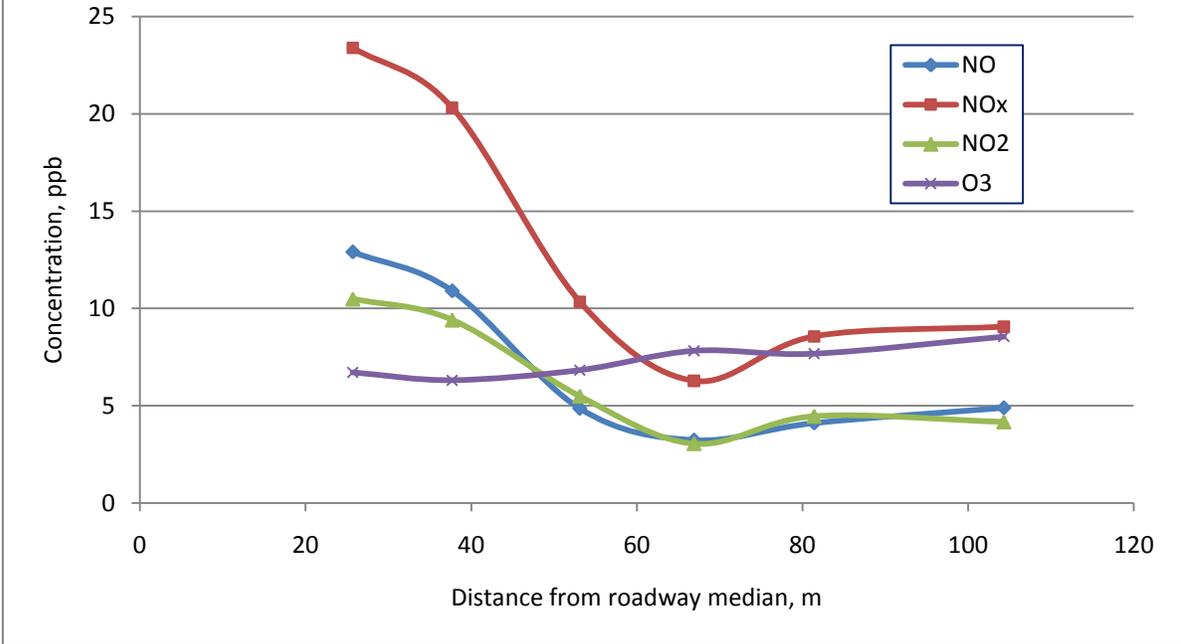
**Figure 10.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=0.82, wind direction=81°, stability class=A



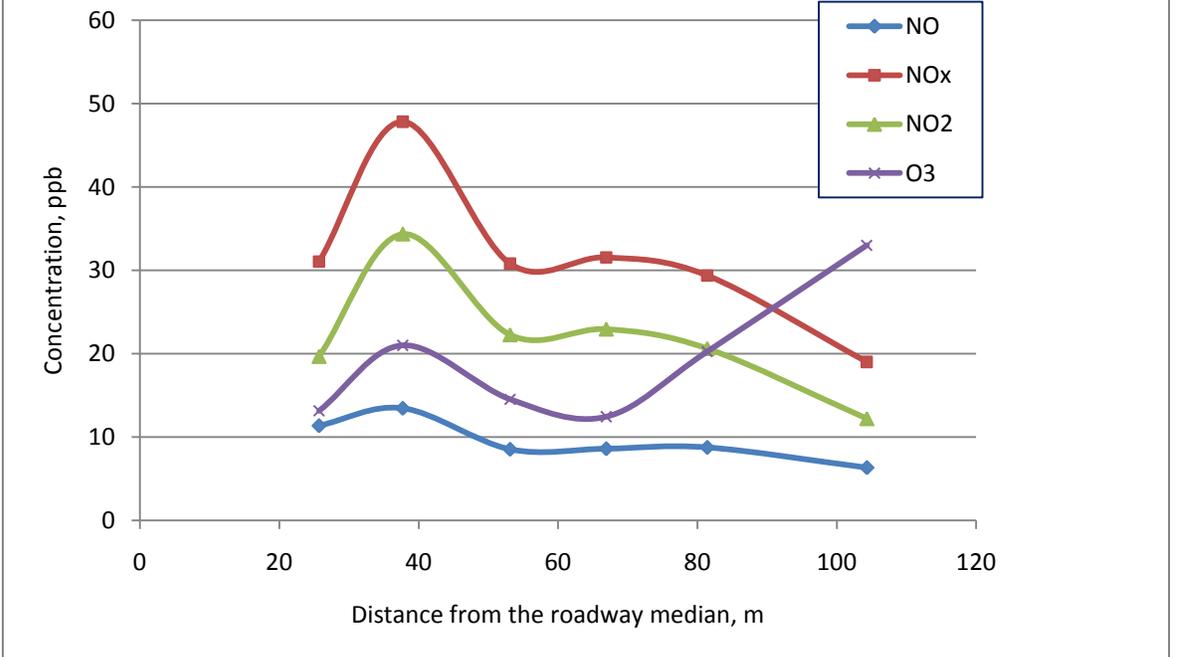
**Figure 11.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.63, wind direction=112°, stability class=A



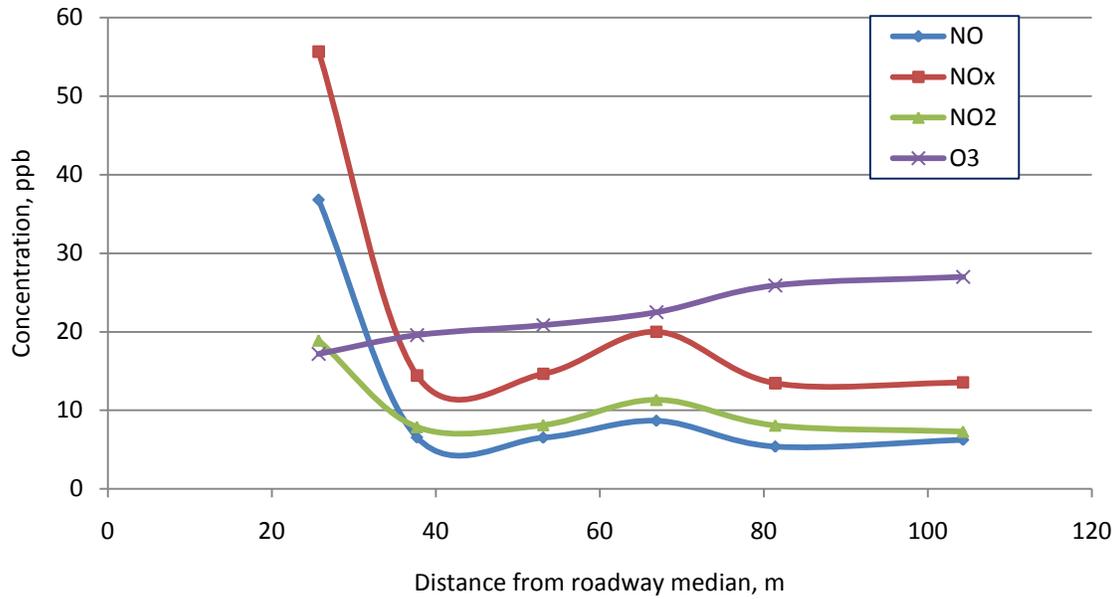
**Figure 12.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.97 m, wind direction=117°, stability class= A



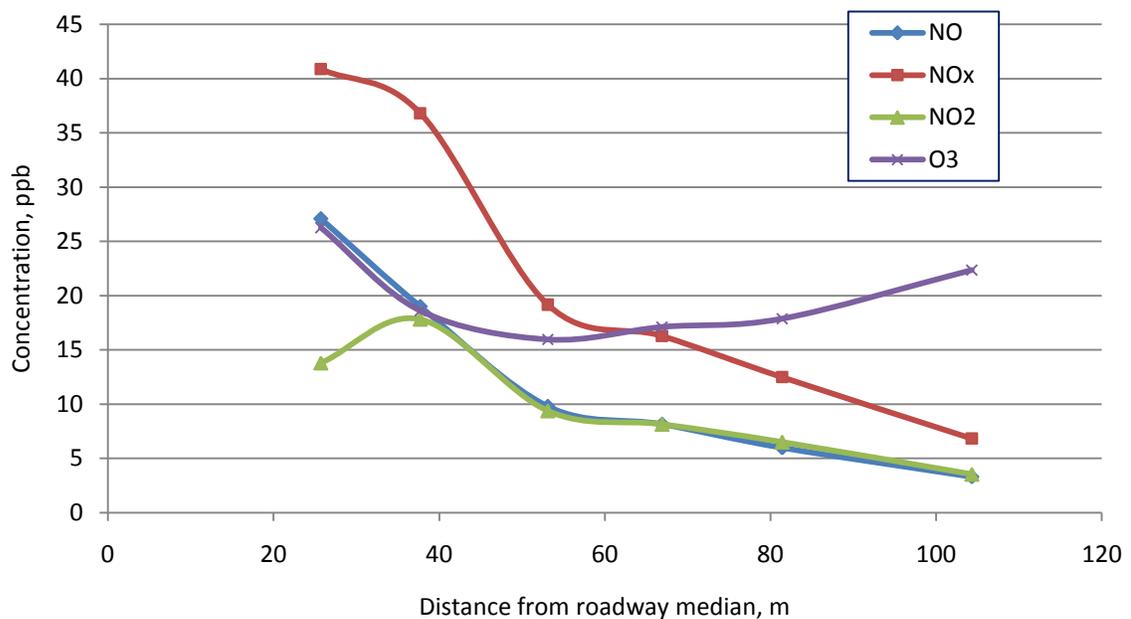
**Figure 13.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.27 m/s, wind direction=4°, stability class= A



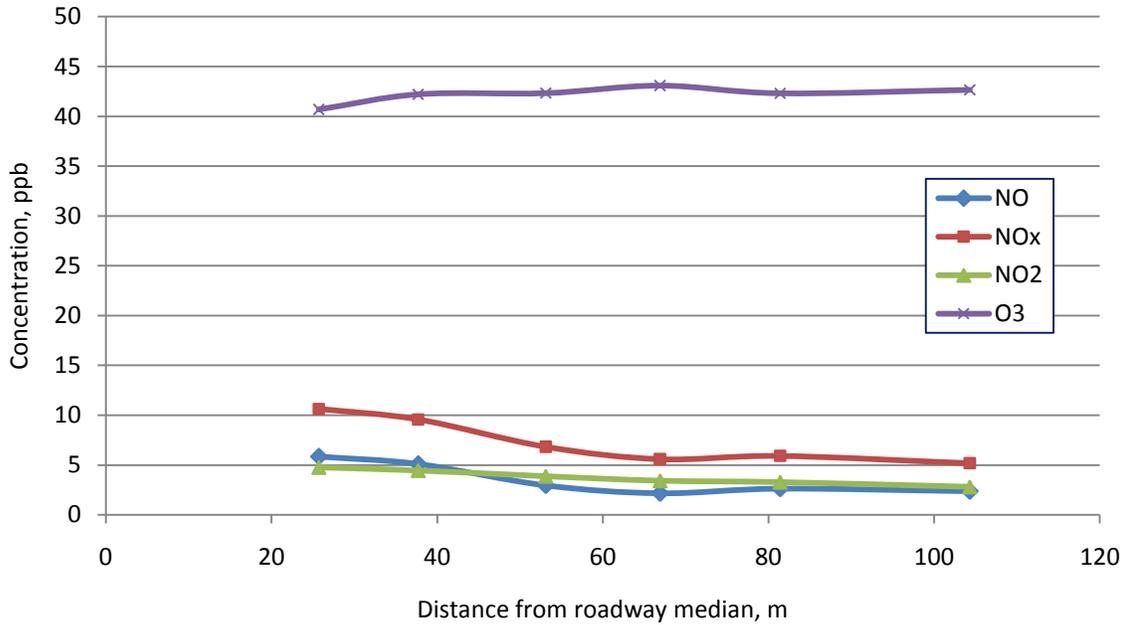
**Figure 14.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.32 m/s, wind direction=100°, stability class=A



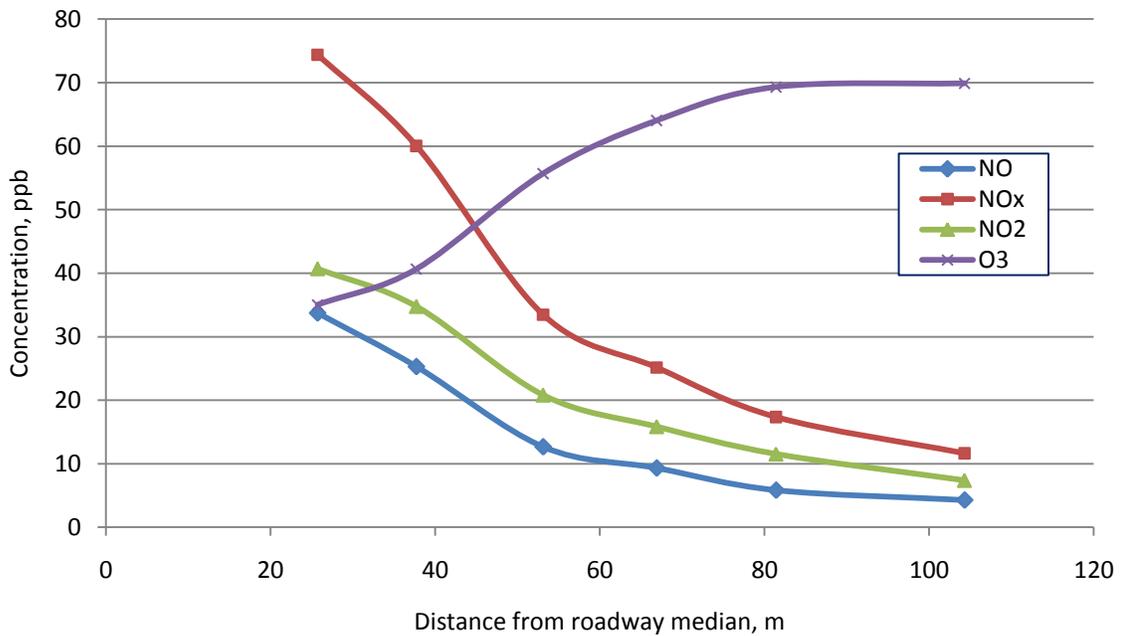
**Figure 15.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from Roadway Median. Wind speed=1.41 m/s, wind direction=96°, stability class=A

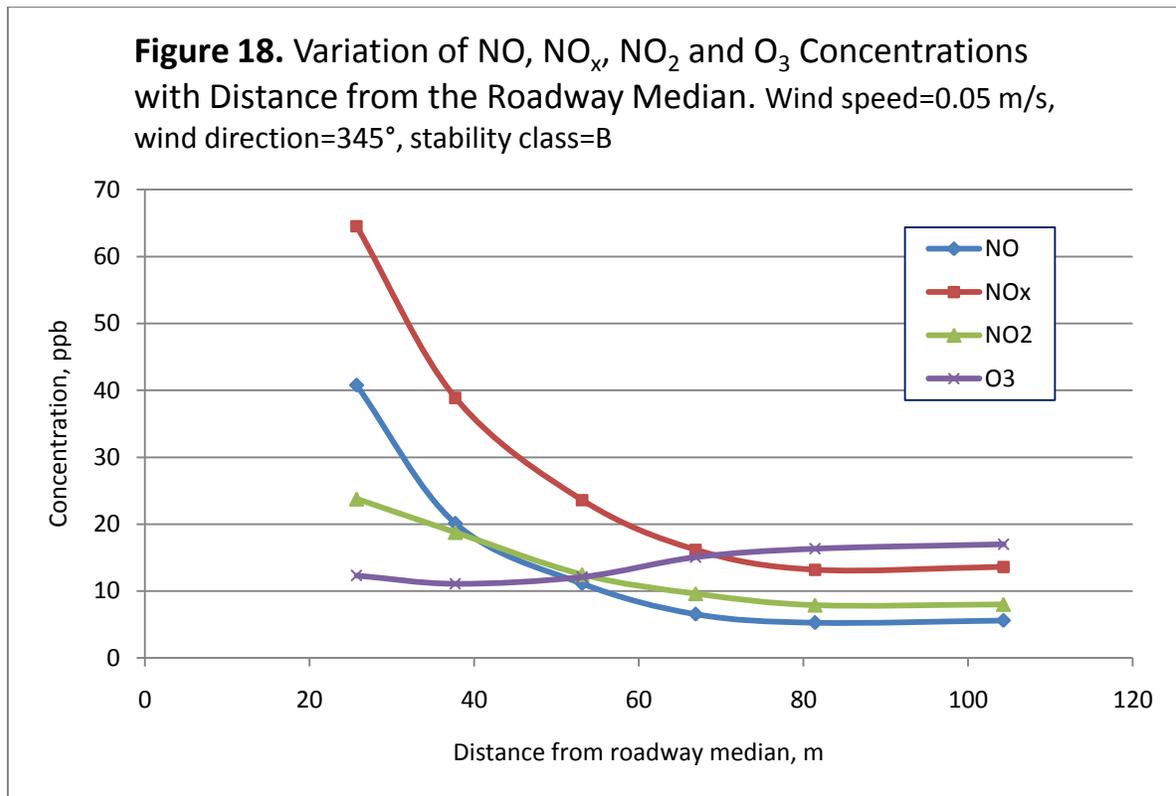


**Figure 16.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=2.13 m/s, wind direction=261°, stability class=A



**Figure 17.** Variation of NO, NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> Concentrations with Distance from the Roadway Median. Wind speed=1.25 m/s, wind direction=33°, stability class=A





Data shown in Figures 4 – 18 represent a large variety of weather conditions. Wind speeds were between 0.05 m/s to 2.13 m/s. Upwind, downwind, and parallel receptor locations and A, B, C stability classes were represented. Most traffic data were obtained before and after the concentration measurements. Before values were used for the first two receptor locations, average values were used for the next two locations, and the after values were used for the last two locations. For a few cases the traffic volumes could be observed during the concentration measurements and these showed some significant changes in traffic volumes including some short traffic stops. All these variables affect the NO<sub>x</sub> and ozone concentrations.

In most cases, NO<sub>x</sub> concentration decreases rapidly with the distance from the roadway, and then remains fairly constant for distances greater than about 100 m from the I-64 median. The reason for this decrease is atmospheric dispersion and conversion of NO<sub>x</sub> to other nitrogen-containing compounds. Close to the roadway, the majority of NO<sub>x</sub> is NO, which converts to NO<sub>2</sub> and other nitrogen compounds within 100 m from the median. The decrease in nitrogen dioxide concentration is significantly less. This seems to indicate the conversion of some NO to NO<sub>2</sub> through its reaction with ozone and subsequent reaction of NO<sub>2</sub> to form other nitrogen species as shown below:

#### Summary of NO<sub>x</sub> Reactions in the Atmosphere

- Nitrogen dioxide formation:  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

- Daytime nitric acid formation:  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$
- Nitrate radical formation:  $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$
- Dinitrogen pentoxide formation :  $\text{NO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M}$
- Nitric acid formation via surface reaction:  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} (\text{surface}) \rightarrow 2\text{HNO}_3$
- Nitrate removal:  $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$
- Renoxification by surface nitric acid:  $\text{NO} + \text{HNO}_3 (\text{surface}) \rightarrow \text{NO}_2 + \text{HONO}$

For a few cases (Figures 7, 8, 16) corresponding to high wind velocity and the receptors at the downwind position, the ozone concentration is relatively higher and the changes in species concentrations are lower compared to the other cases. Although the traffic volumes and ozone concentrations at the first receptor for those days were a little higher, due to the complexity of the processes taking place, we cannot cite these variables as the only reasons for these observations.

### Prediction of NO<sub>2</sub>

There are some limitations in using CALINE4 for the prediction of NO<sub>2</sub> concentrations. CALINE4 gives NO<sub>2</sub> results in increments of 10 ppb and only a few of the measured concentrations are at or above this value. Secondly, the location only permitted measurements up to about 100 meters and for some cases this was not sufficient to obtain accurate background values and needed the use of extrapolated values in the models. The estimated crosswind NO<sub>2</sub> values appear to be over predictions but due to the very low accuracy of CALINE4 at these low concentrations, this cannot be stated as a general conclusion (Figure 19).

**Figure 19.** A sample CALINE4 output

```

CALINE4: CALIFORNIA LINE SOURCE DISPERSION MODEL
      JUNE 1989 VERSION
      PAGE 1
      JOB: 1POSITION-1 EXP-05-25-10
      RUN: POSITION-1
      POLLUTANT: Nitrogen Dioxide
I. SITE VARIABLES
      U= 0.8 M/S      Z0= 100. CM      ALT= 6. (M)
      BRG= 97.1 DEGREES      VD= 0.0 CM/S
      CLAS= 1 (A)      VS= 0.0 CM/S
      MIXH= 1000. M      TEMP= 23.0 DEGREE (C)
      SIGTH= 38. DEGREES
NOX VARIABLES

```

NO2= 0.00 PPM NO= 0.00 PPM O3= 0.01 PPM KR= 0.004 1/SEC

II. LINK VARIABLES

```
LINK * LINK COORDINATES (M) * EF H W
DESCRIPTION * X1 Y1 X2 Y2 * TYPE VPH (G/MI) (M) (M)
-----*-----*-----
A. LI64WB1 * 9 86 10 0 * AG 2402 1.42 1.0 34.0
B. LI64WB2 * 10 0 13 -86 * AG 2402 1.42 1.0 34.0
C. LI64EB1 * -11 86 -10 0 * AG 2913 1.42 1.0 34.0
D. LI64EB2 * -10 0 -7 -86 * AG 2913 1.42 1.0 34.0
```

III. RECEPTOR LOCATIONS

```
* COORDINATES (M)
RECEPTOR * X Y Z
-----*-----
1. R1 * -26 0 1.0
```

IV. MODEL RESULTS (PRED. CONC. INCLUDES AMB.)

```
* PRED * CONC/LINK
* CONC * (PPM)
RECEPTOR * (PPM) * A B C D
-----*-----*-----
1. R1 * 0.14 * 0.02 0.02 0.04 0.06
```

**IX. Conclusions and Recommendations**

The predicted and measured nitrogen dioxide concentrations along with the corresponding values of major variables affecting the results are summarized in Table 1. Wind direction, wind speed, wind direction standard deviation, atmospheric stability, and traffic volume are taken as significant variables. Since the temperature for all experiments were in the upper 20's in °C, temperature was not included in the table. Similarly, other variables such as mixing height and NO<sub>2</sub> photolysis rate constant that are expected to affect the NO<sub>2</sub> concentrations did not differ between measurements and therefore not included in the table. Blank measurement cells in the table indicate runs where data is not available due to the malfunctioning of the weather station during the measurements. Blank cells in the predicted NO<sub>2</sub> column are for those runs for which the NO<sub>2</sub> levels were too low to give reasonable predictions.

Table 1. Summary of results. All concentrations are in ppm, wind direction is in degrees (wind angle definition is consistent with the CALINE4 definition), Wind speed is in m/s, and the traffic count is in vehicles/hour total in both directions.

Run No.	Pred. NO <sub>2</sub>	Meas. NO <sub>2</sub>	Meas. NO <sub>x</sub>	Meas. O <sub>3</sub>	wind ang.	wind spd	st. dev.	stability	Traffic Volm.
51910-1	0.17	0.008	0.025	0.02	159.6	1.013	19.4	A	4956
51910-2		0.008	0.035	0.005					
52410-1	0.02	0.011	0.048	0.015	104.8	0.72	30.8	C	5382
52410-2	0.02	0.009	0.038	0.01	114.2	0.628	21.8	C	5540
52410-3	0.02	0.005	0.018	0.015	87.8	0.792	42.2	C	5698
52410-4		0.003	0.011	0.016					
52510-1	0.137	0.008	0.03	0.019	97.1	0.789	38.2	A	5315
52510-2	0.087	0.005	0.025	0.011	111.1	0.852	35.2	A	5315
52510-3	0.037	0.005	0.015	0.015	87.9	1.21	51.1	A	5034
52510-4	0.027	0.003	0.01	0.014	56.8	1.941	35.3	A	5034
52510-5	0.027	0.003	0.008		83.1	1.453	37.5	A	4753
52510-6									
52710-1	0.002	0.018	0.045	0.018	209	1.22	16.1	B	6654
52710-2		0.018	0.039	0.016	222.2	1.938	10.8	B	
52710-3		0.014	0.028	0.014	222.1	2.262	7.42	B	
52710-4		0.016	0.026	0.014	225.3	2.1	9.29	B	
52710-5		0.016	0.025	0.025	218.9	2.023	7.12	B	
60210-1	0.05	0.003	0.007	0.028	228	1.654	14.4	A	7041
60210-2		0.002	0.005	0.031					8559
60210-3		0.002	0.007	0.026					6072
60210-4		0.002	0.005	0.026					5281
60310-1	0	0.002	0.004	0.025	237.3	2.073	18.9	C	6246
60310-2		0.002	0.004	0.028					6246
60310-3		0.002	0.005	0.026					6500
60310-4		0.001	0.004	0.029					6500
60310-5		0.001	0.004	0.029					6754
60310-6		0.002	0.004	0.029					6754
61410-1	0.1	0.003	0.023	0.018	98.7	0.82	32.6	A	
61410-2		0.003	0.011	0.021					

61410-3		0.002	0.011	0.015					
61410-4		0.003	0.011	0.014					
61410-5		0.003	0.008	0.015					
61410-6		0.004	0.01	0.025					
61510-1	0.09	0.01	0.038	0.02	114.4	0.807	29.7	A	4858
61510-2	0.08	0.01	0.036	0.013	120	0.707	20.5	A	4858
61510-3	0.06	0.006	0.018	0.008	118.9	0.429	32.6	A	5310
61510-4	0.06	0.006	0.017	0.01	102.5	0.633	31.2	A	5310
61510-5	0.05	0.006	0.013	0.011	47.8	1.285	36.9	A	5761
61510-6	0.04	0.005	0.009	0.027	83.3	1.131	45.8	A	5761
62510-1	0.15	0.015	0.03	0.019	70.5	0.753	43.1	A	6837
62510-2	0.11	0.016	0.025	0.017	102.8	0.7	40.5	A	6837
62510-3	0.08	0.01	0.015	0.016	95.9	1.256	43.7	A	7036
62510-4	0.03	0.007	0.011	0.017	40.1	2.063	31	A	7036
62510-5	0.02	0.008	0.012	0.018	39.2	2.532	19.6	A	7235
62510-6	0.02	0.007	0.01	0.029	58.5	2.44	22.1	A	7235
63010-1	0.01	0.024	0.065	0.012	194.9	0.05	41.5	B	6522
63010-2	0	0.019	0.039	0.011					6522
63010-3		0.012	0.024	0.012					6508
63010-4		0.01	0.016	0.015					6508
63010-5		0.008	0.013	0.016					6495
63010-6		0.008	0.014	0.017					6495
70210-1	0.2	0.01	0.023	0.007	147.4	0.9	36.1	A	8588
70210-2	0.1	0.009	0.02	0.006	53.6	1.58	41.5	A	
70210-3	0.04	0.005	0.01	0.007	28.1	2.3	30	A	
70210-4	0.05	0.003	0.006	0.008	65.1	2.26	25.3	A	
70210-5	0.02	0.004	0.009	0.008	36.8	2.21	25.4	A	
70210-6	0.02	0.004	0.009	0.009	45.7	2.7	24.4	A	
70610-1	0.05	0.02	0.031	0.013	201.6	0.97	32.5	A	6997
70610-2	0.13	0.034	0.048	0.021	110.4	0.7	51.8	A	6997
70610-3	0.03	0.022	0.031	0.015	178.4	0.818	54.1	A	6667
70610-4	0.03	0.023	0.032	0.012	160.5	1.059	40.7	A	6667
70610-5	0.01	0.021	0.03	0.02	201.7	1.982	16.9	A	6894
70610-6	0.01	0.012	0.019	0.033	201.1	2.076	12.6	A	6894
70810-1	0.04	0.019	0.056	0.017	89	0.682	35.3	B	5847

70810-2	0.03	0.008	0.014	0.02	63.4	1.335	34	B	5847
70810-3	0.03	0.008	0.015	0.021	69.8	1.165	42.5	B	5596
70810-4	0.03	0.011	0.02	0.022	88.5	1.294	41.2	B	5596
70810-5	0.02	0.008	0.013	0.026	69.6	1.775	26.4	B	7182
70810-6	0.02	0.007	0.014	0.027	99.6	1.719	24.1	B	7182
70910-1	0.14	0.014	0.041	0.026	116.2	1.119	18.9	A	6619
70910-2	0.12	0.018	0.037	0.019	113.1	0.719	25.1	A	6619
70910-3	0.09	0.009	0.019	0.016	115.3	0.867	45.7	A	6900
70910-4	0.05	0.008	0.016	0.017	69.9	1.338	50.3	A	6900
70910-5	0.04	0.007	0.012	0.018	64.9	1.544	37.8	A	7358
70910-6	0.02	0.004	0.007	0.022	60	2.169	28.8	A	7358
71410-1	0.0	0.005	0.011	0.041	279	2.133	23.7	A	7355
71410-2		0.004	0.01	0.042					7355
71410-3		0.004	0.007	0.042					7127
71410-4		0.003	0.006	0.043					7127
71410-5		0.003	0.006	0.042					6898
71410-6		0.003	0.005	0.043					6898
71510-1	0.12	0.041	0.074	0.035	175.9	1.293	18.7	A	6196
71510-2	0.12	0.035	0.06	0.041	126.7	0.853	39.9	A	6196
71510-3	0.06	0.021	0.033	0.056	143.6	0.913	49.4	A	6161
71510-4	0.06	0.016	0.025	0.064	130.1	1.088	24.58	A	6161
71510-5	0.04	0.012	0.017	0.069	72.9	1.485	32.8	A	6126
71510-6	0.03	0.007	0.012	0.07	111.3	1.815	24.6	A	6126

The measured NO<sub>x</sub> values at the receptors beyond 50 m from the roadway median were lower than the recently proposed EPA 1-hour NO<sub>2</sub> standard (between 80 and 100 ppb), the current average NO<sub>2</sub> standard (53 ppb) and the 24-hour emergency exposure guidance level (40ppb). The main health effects of nitrogen oxides are through their role in the formation of ground level ozone (smog) and nitrogen containing particulates. The measured ozone concentrations are also at levels below those that will pose a significant health risk. Particulate matter will be measured in the next research cycle and will provide information on the secondary species other than ozone.

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. 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.

Nitrogen dioxide concentrations at the receptor locations are strongly affected by the ambient ozone concentrations. Ozone plays a primary role in the generation of NO<sub>2</sub> from NO. It is also significant in the formation of secondary nitrogen-containing species, thus depleting NO<sub>2</sub>. The latter group of reactions is not considered in the estimation of NO<sub>2</sub> by CALINE4.

Table 1 indicates a significant over-prediction of the NO<sub>2</sub> concentrations under crosswind conditions. Wind angles larger than 180° correspond to conditions where the receptors are at upwind positions and as expected, the measured and calculated NO<sub>2</sub> concentrations are low. Wind angles around 180° (or 0°/360°) correspond to winds parallel to the roadway and under those conditions CALINE4 predictions are close to the measured values (e.g. run 70610 except at the second receptor position, which is close to a crosswind situation). In comparing the results, it needs to be considered that CALINE4 predictions are produced with ±0.005 ppm sensitivity. CALINE4 was reported to perform best under crosswind conditions with wind speeds greater than 1 m/s. So the over-prediction in our case under these conditions cannot be easily explained. Considering the complexity of the process, only few reasons for this observation may be suggested:

- Formations of secondary nitrogen species except NO<sub>2</sub> are not considered by CALINE4. We are planning to obtain simultaneous particulate matter measurements in the future, which could give some indication of the extent of the formation of aerosol and particulate species.
- The emission factor calculated by MOVES is based on the local average vehicle mix and may not correspond to the actual emission during the concentration measurements.
- The background concentrations used in predictions were taken as the values at a location about 100 m from the roadway median (at the farthest receptor location). At this point, if a steady state concentration value is not reached, extrapolation was used to obtain a rough estimate of the background concentration. Since both ambient NO<sub>x</sub> and O<sub>3</sub> concentrations strongly affect the predicted NO<sub>2</sub> concentrations, this could be a major source of error in the predictions. Obtaining better background concentration measurements may be difficult due to the limited area available at the current location.

To understand the obtained results better, statistical data analysis methods need to be used to identify the effects of the large number of variables affecting the process. More measurements will be made to produce more data for the statistical evaluation.