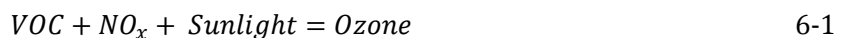




6.0 OZONE MODELLING

Ground level ozone is a secondary pollutant that forms photochemically (i.e. a reaction caused by sunlight) in the troposphere (lowest portion of the atmosphere) due to the presence of nitrogen oxides (e.g., NO and NO₂) and volatile organic compounds (VOCs). The emission rates of these precursor compounds are regulated to minimize the formation rate of ozone and the other photochemical reaction products. The general formulation is given below.



When nitrogen dioxide (NO₂) is exposed to the ultraviolet radiation in sunlight, the NO₂ molecule splits into nitric oxide (NO) and a single atom of oxygen (O).



The oxygen atom quickly combines with oxygen (O₂) that is normally in the atmosphere to produce ozone (O₃).



Where M is a third body (such as N₂, O₂, etc.) that absorbs energy from the reaction to stabilize the ozone. When two nitrogen dioxide molecules are exposed to sunlight, they produce two separate oxygen atoms that combine with oxygen to produce two more ozone molecules. This process continues to produce ozone molecules until ultraviolet energy (sunlight) is no longer available.

The ozone molecule would normally react with the nitric oxide (NO) to produce NO₂



Near strong emission sources of NO_x, where there is an abundance of NO, ozone is “scavenged” as it reacts with NO to form NO₂.(Equation 6-4) As a result ozone concentrations are often low in busy urban centres and higher in suburban and adjacent rural areas. However, ozone is also transported long distances in the atmosphere and is therefore considered a transboundary problem.



Organic gases (VOCs) affect the rate at which this reaction takes place. In other words, VOCs slow down the conversion of ozone to NO_2 thus keeping the levels of ozone in the atmosphere elevated. Organic gas concentrations in the atmosphere have a significant effect on ozone levels. These organic gases also react in the presence of sunlight to produce other components of smog.

NO_x and VOCs come from natural sources as well as human activities. About 95% of anthropogenic NO_x comes from the burning of fossil fuels (i.e., coal, gas, oil, etc) in motor vehicles, homes, industries and power plants. VOCs from human activity come mainly from gasoline combustion and marketing, upstream oil and gas production, residential wood combustion and from the evaporation of liquid fuels and solvents. Significant quantities of VOCs also originate from natural (biogenic) sources such as coniferous forests.

Ozone can also form in apparently clean rural environments. In these areas, the "pollutants" are apparently low levels of organic compounds emitted from trees and vegetation and low levels of nitrogen oxides emitted from natural biological activity. The photochemical reactions are similar to those in polluted urban areas; however, the concentrations of rural ozone are limited by the very low concentrations of nitrogen oxides that are usually available. Rural ozone is considered natural.

Although CALPUFF is not a photochemical model which could estimate the levels of ozone (O_3) created in a region, the results of CALPUFF can be used to estimate the levels of ozone, indirectly with the aid of an alternative approach.

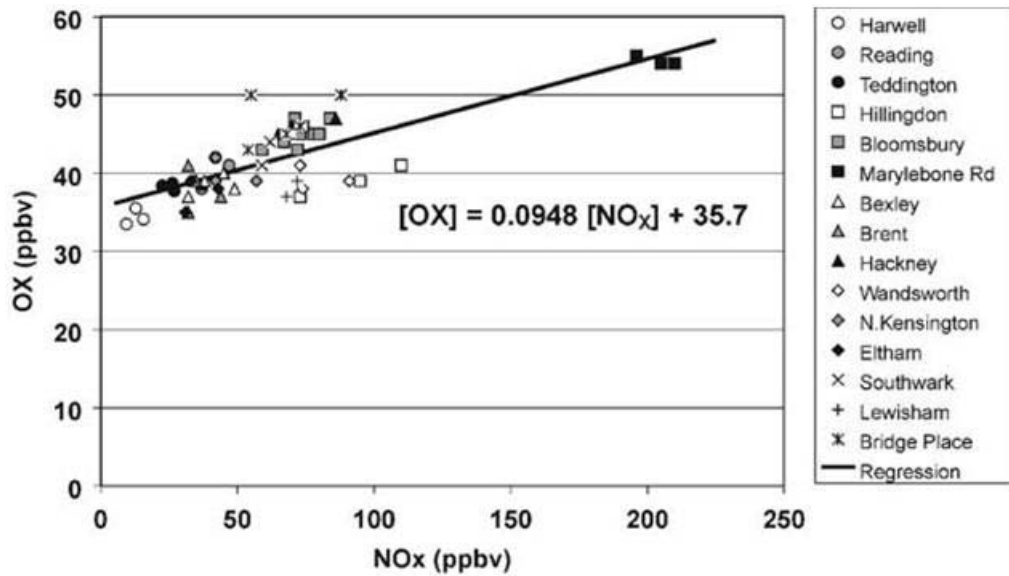
6.1 Modelling Approach

Golder investigated a number of observation based models (OBM) and identified Clapp and Jenkins (2001) approach as suitable for estimating annual ozone concentrations. Clapp and Jenkin (2001) study indicated that the level of OX ($\text{O}_3 + \text{NO}_2$) at a given location is made up of NO_x -independent and NO_x -dependent contributions. The former is effectively a regional contribution, which equates to the regional background O_3 level, whereas the latter is effectively a local contribution, which correlates with the level of primary pollution. The study analysed NO , NO_2 and O_3 monitoring data from several monitoring stations collected between 1992 and 2000. Figure 6-1 shows the variation of annual mean OX ($\text{O}_3 + \text{NO}_2$) mixing ratio with NO_x ($\text{NO} + \text{NO}_2$) obtained as the result of this study.

The empirical model was previously used and evaluated by Golder in Halton Airshed Modelling Study (Golder, 2009) where it showed very good predictability. Following this approach, an analysis of NO , NO_2 and O_3 monitoring data in the GTA was carried out and a similar correlation for OX and NO_x concentrations was also found.



Figure 6-1: Variation of annual mean OX (O₃ + NO₂) mixing ratio with NO_x



Since no ambient air monitoring stations from MOE or NAPS network were identified within the study area, monitoring data from the closest monitoring location were used as surrogates for the air quality in the Neighbourhood; namely the MOE monitoring station located in Downtown Toronto (station ID: 31103) at the intersection of Bay St. and Wellesley St. West. Linear regression of the daily average monitored data from 2006 at this location resulted in the following dependence.

$$OX = 0.1404[NOx] + 38.06$$

6-5

It should be noted that this correlation is valid and appropriate to use when correlating annual concentrations and trends only. It is not expected to vary considerably on a year-to-year basis, however it may vary significantly from season to season due to inherently different rates in photochemical conversion and episodic O₃ concentrations between summer/warm and cold months.



6.2 Evaluation of OBM Model

Using the derived ozone model based on 2006 data, local average monthly O₃ concentrations were calculated and compared with those monitored. By substituting [OX] with [O₃]+[NO₂] and [NO_x] with [NO]+[NO₂] and by rearranging the 2006 model equation, ozone concentrations can be calculated as:

$$O_3(ppb) = 0.1404 NO (ppb) - 0.8596 NO_2(ppb) + 38.06 \quad 6-6$$

Table 6-1 summarises average monthly monitored NO and NO₂ values from Toronto Downtown station used to calculate modelled [O₃] and compares the modelled concentrations with those measured at the same monitoring location. As it can be seen the modelled vs. monitored ratio varies between 0.66 (in summer season) and 1.97 (in winter). As noted previously, this is to be expected due to the fact that background O₃ (i.e. intercept) derived on an annual basis is under-predictive of higher background O₃ levels in summer and over-predictive of those in winter. However, on an annual-average basis it can be seen that the model prediction is excellent with modelled to monitored ratio of 1.0.

Table 6-1: Modelled Vs. Monitored O₃ Concentrations in Toronto Downtown for 2006

Month	Monitored NO (ppbv)	Monitored NO ₂ (ppbv)	Modelled O ₃ (ppbv)	Monitored O ₃ (ppbv)	Modelled to Monitored Ratio
January	11.1	22.4	20.4	12.3	1.66
February	8.0	22.3	20.1	20.4	0.98
March	7.7	23.7	18.8	25.0	0.75
April	5.0	19.9	21.7	29.0	0.75
May	5.6	21.2	20.6	31.4	0.66
June	4.4	16.5	24.5	30.8	0.79
July	3.6	15.2	25.5	35.1	0.73
August	3.8	14.8	25.9	26.4	0.98
September	6.1	14.8	26.2	19.7	1.33
October	8.5	17.8	24.0	15.5	1.55
November	13.3	22.1	20.9	10.6	1.97
December	6.3	19.4	22.3	14.5	1.53
Annual Average	6.9	19.1	22.6	22.6	1.00

In view of a very good performance of the empirical O₃ model and absence of reliable time varying emission rates over the large domain within and outside the study area, O₃ modelling was carried out using this method. Modelled annual average O₃ in the SRLB was obtained using Equation (6-6) using the modelled NO and NO₂ concentrations, where cumulative concentrations were obtained from the CALPUFF results.



6.3 Determination of Background and Cumulative NO and NO₂ Concentrations

Since CALPUFF is not capable to model or predict thermodynamic and photochemical inter-conversion between NO and NO₂, the speciation of the transboundary NO_x into NO and NO₂ was determined based on 2006 monitored data in the vicinity of the study area. Five MOE monitoring location surrounding the Tier 3 domain were chosen as surrogates for background NO and NO₂ concentrations in the City of Toronto area depending on the prevailing wind direction. Those were Newmarket station (during north winds), Oshawa (east), St. Catherines (southeast-south winds), Oakville (southwest) and Brampton (west winds).

Table 6-2 shows the wind sectors associated with each of the stations used to determine hourly background NO and NO₂ concentrations in the study area.

Table 6-2: Wind Sectors Used To Determine Transboundary NO And NO₂ Concentrations In The City Of Toronto Region

MOE Station	Associated Wind Sector [°]
Newmarket	325 - 40
Oshawa	40 - 90
St. Catherines	90 - 215
Oakville	215 - 260
Brampton	260 - 325

Background/transboundary NO and NO₂ concentrations, indicative of the contribution of NO_x sources from Tier 1 and Tier 2, were obtained by averaging hourly values obtained using the method described above. Cumulative concentrations were obtained by superimposing background and local components, where the local NO and NO₂ concentration contributions were obtained from the CALPUFF model itself, based on Tier 3 sources (only) contribution. Table 6-3 shows the annual mean background, local and cumulative NO and NO₂ concentrations used in ozone modelling.

Table 6-3: Annual mean background concentrations of NO and NO₂ in the GTA

Pollutant	Annual Mean Background concentration [ppbv]	Annual Mean Modelled concentration [ppbv]	Annual Mean Cumulative concentration [ppbv]
NO	3.89	21.55	25.44
NO ₂	10.04	1.60	11.64



6.4 Modelling Results

As noted, the applicability of this ozone model is limited to the analysis of annual average values, therefore ozone modelling results are reported and discussed in that context only.

Annual average ozone concentration in the SRLB neighbourhood was calculated from Equation (6-6) and cumulative NO and NO₂ concentrations summarized in Table 6-4. The predicted annual ozone concentration in the neighbourhood is presented on Table 6-5.

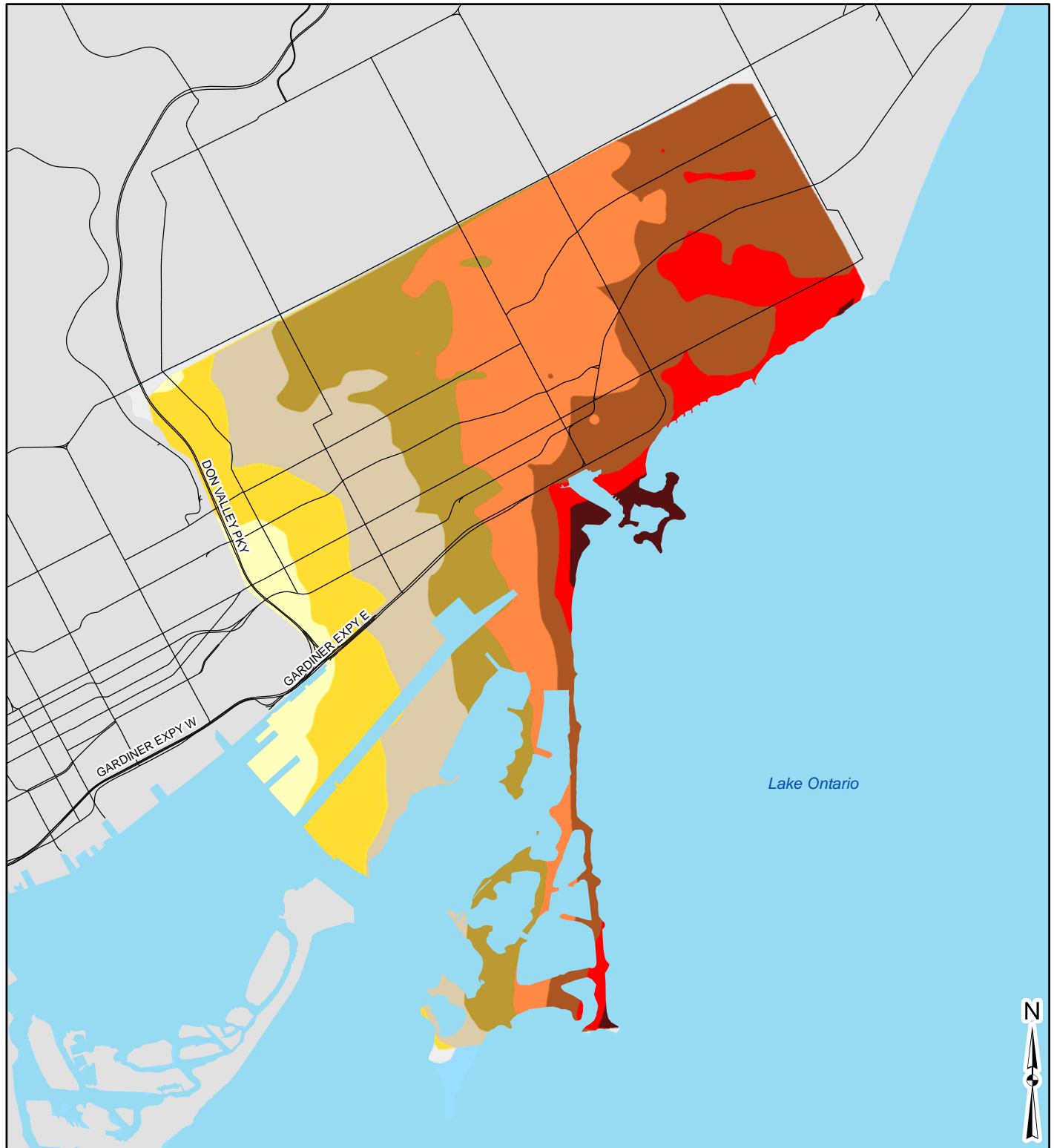
Table 6-4: Predicted versus Monitored O₃ Concentrations SRLB Neighbourhood

Location	Cumulative NO (ppb _v)	Cumulative NO ₂ (ppb _v)	Modelled O ₃ ¹ (ppb _v)
SRLB Neighborhood	19.0	18.1	25.2

Notes: All modelled values are based on annual average NO and NO₂ concentrations

The isopleths for annual average O₃ concentrations are shown in Figure 6-2. It is apparent that O₃ concentration in the region is to a large extent dominated by the regional background O₃ level. While on a shorter time scale (hourly and daily) locally generated ozone can exert positive contribution to the regional background level, local NO_x levels are such that in overall (on annual average basis) they lead to the depletion of background ozone, particularly in the areas with increased NO_x levels such as around major highways.

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LEGEND

— Road	O3 (ppb)	16.99 - 17.96
■ Toronto	6.66 - 10.75	17.96 - 18.64
	10.75 - 13.61	18.64 - 19.11
	13.61 - 15.60	19.11 - 19.8
	15.60 - 16.99	

REFERENCE

Base Data - MNR NRVIS, obtained 2004, CANMAP v2008.4
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 Projection: Lambert Conformal Conic Datum: NAD 83 Coordinate System: US EPA LCC



PROJECT		TORONTO AIRSHED MODELLING	
TITLE		ISOPLETH OF ANNUAL AVERAGE O3 CONCENTRATIONS FROM ALL SOURCES	
 Golder Associates Mississauga, Ontario	PROJECT NO.	08-1112-0148	SCALE AS SHOWN
	DESIGN	PRM 16 Nov. 2009	REV. 0.0
	GIS	PP 15 Nov. 2010	FIGURE: 6-2
	CHECK	BCo 15 Nov. 2010	
REVIEW	AC 15 Nov. 2010		