DISCLAIMER

VOC/NOx POINT SOURCE SCREENING TABLES

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Table of Contents

1.O INTRODUCTION

This document provide a simple screening procedure presented in tabular form to calculate the ozone increment due to a VOC dominated (i.e, VOC mass emissions greater than NOx emissions) point source. [Throughout this document, ozone increment refers to a calculated increase in ozone above an assumed ambient value due to the effect of a single point source.] The tables are based on a series of applications of the Reactive Plume Model-II (RPM-II), a Lagrangian based photochemical model. Anticipated applications would include evaluation of the impact on ambient ozone due to new or modified point sources emitting more than 25 tons/year NMOC (nonmethane hydrocarbons). The screening technique is presented as two separate tables intended for appilcation in urban and rural areas, respectively.

The user is directed to Section 3 of this report for appilcation procedures needed to conduct an ozone increment screening analysis. Required inputs for determining an ozone increment are limited to estimates of NMOC and NOx mass emissions rates. As a screening technique the procedure has been designed be both robust and simple to use, while maintaining several inherent assumptions which lead to conservative (high ozone)ozone increment predictlons. The user is not required to characterize ambient meteorology or source emission and ambient speciation profiles. This technique is not intended to to substituted for a realistic photochemical modeling analysis; rather it is to be used only in the context of a firt-step proecdure which potentially can preclude further resource intensive analyses. The ozone increment estimates produced from this analysis should be interpreted as conservative predictions which would exceed ozono formation produced by actual episodic events.

A description of the protocol and asumptions used in developlng the screening tables is given in Appendix A.

2.0 BACKGROUND

Estimations of impacts of point sources emitting ozone precursors (NOx and/or VOC emissions) on ambient ozone provide regulatory agencies with data to address air quality issues involving proposed new or modified sources. In theory many issues can be resolved by applylng a photochemical air quality model. However, two questions regarding model application must be resolved: (1) what is the most appropriate model for a particular application, and (2) how could that model be applied (i.e., how are model inputs developed and output interpreted)?

The Guideline on Air Quality Models (1986) recommends application of two photochemical models for addressing ozone air quallty issues, the Urban Airshed Model (UAM) or EKMA. The EKMA model is not desgined to handle point sources, as point source emissions are immediately spread into a broadly based urban mix and the individual contribution of a single point source is quenched by such broad spatial dilutlon. Although the UAM explicitly handles spatial resolutlon of point sources through spatially gridded cells, the degree of resolution typically offered by such gridding (4-5 km) is still insufficient to account for near-source behaviour. Also, the resources and input data required by the UAM are very extensive; consequently, it is an inefficient means for evaluating effects of individual sources.

The Reactive Plue Model-II (RPM-II) is an alternative air quality model whlch was developed in the late 1970's to address photochemically reactive plumes. The model's inherent flexibility accomodates recently developed chemical mechanisms; this work was based on use of the Carbon Bond Mechanism-Version IV (CBM-IV), which is consistent with oter, current EPA photochemical models (ROM, EXMA).

The RPM-II is an appropriate choice for case by case refined (i.e, not an initial screening estimate) modelling applications. However, the prospective model user faces the possibility of conducting an exhaustive compilation of meteorological and emissions source data. Consequently, use of photochemical models to assess individual point sources has been lmited. The development of a screening analysis may eliminate, in certain applicatlons, the nedd for a more intensive refined modeling analysis. Current modeling guidelines do not offer recommendatlons for screening of individual source impacts on ozone. The tables presented herein are intended to serve as a means for screening effects on ozone from individual point sources so that subsequent, more refined analyses can be focused on sources where it is warranted.

3.0 SCREENING TABLES

The interpretation or definition of a "rural" or "urban" area within the framework of this technique is intended to be rather broad and flexible. The rationale for having rural and urban tables stems from the need to account for the coupled effect of point source emissions and background chemistry on ozone formation. Background chemistry in the context of this procedure refers to a characterization of the ambient atmospheric chemistry into which a polnt source emits. The underlying model runs used to develop the rural table (Table 1) were performed with spatially invariant background chemistry representative of "clean" continental U.S. areas. Model runs used to develop the urban table (Table 2) are based on background chemistry incorporating daily temporal fluctuatlons of NOx and hydrocarbons asociated with a typical urban atmosphere (refer to Appendix A for details regarding background chemistry). Background chemistry is an important factor in estimating ozone formation; however, characterization of background chemistry is perhaps the most difficult aspect of reactive plume modeling because of data scarcity and the level of resources required to measure or model (temporally and spatially) the components necessary to charcterize the ambient atmospheric along the trajectory of a point source plume.

Recognizing the conflicting needs of using simple characterizations of background chemistries and applylng this screening technique in situations where sources are located in or impact on areas which can not be simply categorized, the following steps should be used to choose an appopriate table:

(1) If the source locatlon and downwind impact area can be decribed as rural and where ozone exceedances have never been reported, choose the rural area table.

(2) If the source location and downwind impact area are of urban characte, choose the urban area table.

(3) If an urban based source potentially can impact a downwind rural area, or a rural based source can potentially impact a downwind urban area, use the highest value obtained from applying both tables.

The VOC point source screninq tables (Tables 1 and 2) provided ozone increments as a function of NMOC (nonmethane organic carbon) mass emissions rates and NMOC/NOx emissions ratios. To determine an ozone impact the user is required to apply best estimates of maximum daily NMOC emissions rate, and estimated annual mass emissions rates of NMOC and NOx which are used to determine NMOC/NOx ratio for ascribing the applicable column in Table 1 or 2. The reasons for basing application on daily maximum NMOC emissions rates are (1) to avoid underestimates resulting from discontinuous operations and (2) the underlying modeling simulations are based on single day episodes. The NMOC emissions rates in Tables 1 and 2 are given on an annual basis; consequently the user must project daily maximum to annual emissions rates illustrated in the example

application given below. One purpose of the technique is to provide a simple, non-resource intensive tool; therefore, annual NMOC/NOx emissions ratios are used because consideration of daily fluctuations would require a screening application applied to each day.

Parameters describing background chemistry, episodic meteorology, and source emissions speciation affect actual ozone impact produced by a point source. However, as a screening methodology the application should be simple, robust and yield conservative (high ozone) values. Thus, only NMOC and Nox emissions rates are required as input to Tables 1 and 2.

Rural Example Application

A manufacturing company intends to construct a facility in an isolated rural location where ozone exceedances have never been observed. The pollution control agency requires that the company submit an analysis showing that operation of the proposed facility will not result in an ozone increment greater than X ppm in order to permit operation. The estimated daily maximum NMOC emissions rate is 9000 lbs/day. The annual estimated emissions rates for NMOC and NOx are 1000 tons/yr and 80 tons/yr, respectively. The company's strategy is to provide a screening analysis using the rural area table to prove future compliance. If the screening result exceeds X ppm, the company will initiate a detailed modeling analysis requiring characterization of source emissions speciation, ambient chemistry, and episodic meteorology.

Screening Estimate:

1 – Determine which column of Table (1) is applicable:

   The NMOC/NOx ratio is based on <u>annual</u> estimetes; thus, 1000/80 = 12.5 and middle column values are applied.

2 – Calculate annual NMOC emissions rates in tons/yr from maximum daily rate:

   (9000 lbs/day)(1 ton/2000 1bs)(365 days/yr) = 1643 ton~/yr

3 – Interpolate linearly between 1500 tons/yr and 2000 tons/yr to produce an interpolated column 2 ozone increment:

   (1643–1500)(3.84–3.05)/(2000–1500) + 3.04 = 3.27 pphm

   3.27pphm(1 ppm/100 pphm) = <u>0.0327 ppm</u>

If 0.0327 ppm is below the criterion value (X ppm), no further modeling analyis required and operation may be pemitted. Otherwise, the company wil1 procede with an additional case-specific modeling analysis.

Table 1.   Rural based ozone increment (pphm) as a function of NMOC emissions and NMOC/NOx ratios.

NMOC/NOx

TONS NMOC/TONS NOx
(PPMC/PPM)

NMOC EMISSIONS (TONS/YR)	> 20.7 (>20)	5.2–20.7 (5–20)	< 5.2 (< 5)
50	0.4	0.4	1.1
75	0.4	0.4	1.2
100	0.4	0.5	1.4
300	0.8	1.0	1.7
500	1.1	1.4	1.9
750	1.6	1.9	2.3
1000	2.0	2.4	2.7
1500	2.7	3.0	3.3
2000	3.4	3.8	3.7
3000	4.8	5.2	4.3
5000	7.0	7.5	4.8
7500	9.8	10.1	5.1
10000	12.2	12.9	5.4

• multiply pphm by 0.01 to obtain ppm

DRAFT

Table 2.   Urban based ozone increment (pphm) as a function of NMOC emissions and NMOC/NOx ratios.

NMOC/NOx

TONS NMOC/TONS NOx
(PPMC/PPM)

NMOC EMISSIONS (TONS/YR)	> 20.7 (>20)	5.2–20.7 (5–20)	< 5.2 (< 5)
50	1.1	1.1	1.0
75	1.2	1.1	1.1
100	1.3	1.2	1.1
300	1.8	1.6	1.9
500	2.2	2.0	2.8
750	3.3	2.6	3.9
1000	4.1	3.2	4.7
1500	5.8	4.2	4.9
2000	7.1	5.4	4.9
3000	9.5	7.8	6.5
5000	13.3	12.0	9.3
7500	17.3	16.7	12.5
10000	21.1	20.8	15.5

• multiply pphm by 0.01 to obtain ppm

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4.0 REFERENCES

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APPENDIX A

DEVELOPMENT OF SCREENING TABLES

RPM-II DESCRIPTON

Screening tables presnted in this report were derived using the Reactive Plume Model-II (RPM-II). RPM-II was originally developed by Systems Applications, Incorporated (SAI) under contract to EPA in the late 1970's. RPM-II is a Lagrangian based model which describes the downwind tranport and chemical behaviour of a plume emitted from a point source. Plume concontrations are a function of meteorological source emission and ambient air quality inputs. Downwind plume dimensions are either calculated through Gaussian dispersion formulae using Pasquill-Gifford stability classes, or dimensions are manually set. The plue is resolved lnto several well-mixed columns aligned transverely wlth the mean wlnd flow. Mass transfer of reactive species occurs across cell boundaries. As the plume expands it entrains backgound air which then is incorporated within the reactive plume mix. A thorough descrlption of the nodel formulation can be found in the RPM-II User's Guide (SAI, 1980). Listed below are general categories of model inputs used during RPM-II applications for developing the screening tables.

Model Inputs:

The followlng summary of model inputs addresses the major input data requirements used ln developing the screening tables; a comprehenslve list or required modeling inputs is found in the User's Guide. The RPM-II source code addresses a single input vhlch includes followlng:

Meteorological Coniderations - Required meteorological inputs include time-dependent values of wlnd speed and either stability class to determine horizontal and/or vertical plume dimensions or values reflecting user-determined plume depths and/or horizontal plume widths. The program has been modified to accept ambient temperature to adjust temperature dependent raaction rate constants.

Chemistry Considerations - The RPM-II was designed to accept different chemical mechanisms; a particular mechanism is entered as input data. The original RPM-II and subsequent variations have used an older mechanism, Carbon Bond 2 (CB2). The source code was modified to accept an array of eleven time-dependent photolysis rate constants so that the most recent version of the Carbon Bond-4 mechanism, which is also used in EKMA/OZIPM4 (EPA, 1988), could be applied. Additional code was installed to accept activation energies to determine temperature dependent reaction rates These code modifications and the operation of CB4 within RPM-II were evaluated by comparing RPM-ll predictions with EKMA/OZIPM4 Both models were run in batch reactor mode with identical sunlight, temperature and initial conditions over the course of a ton-hour run, both models produced nearly identical

time profiles for all species.

Air Quality Considerations – The model requires initialization of all CB4 surrogate and explicit species concentrations, and concentrations air of background air Time-variant concentrations off background air can be input manually, or the model will calculate temporal profiles of all species based on a user-supplied initial mix and diurnal variation in photolytic reaction rates.

Emissions Estimates – Principal emissions inputs are emissions rate of organic and inorganic species. Although any species included in thee CB4 mechanism can be declared as an emissions input, typical inputs include NO; NO2; CO; CB4 surrogate organic groups – parrafins (PAR), olefins (OLE), higher aldehydes (ALD2) and explicit organic groups – formaldehyde (FORM), ethylene (ETH), toluene (TOL) and xylene (XYL).

DERIVATION OF SCREENING TABLE

The concept of a screening procedure for ozone precursors is immediate with an immediate contradiction: A screening tool must be simple to apply and robust, but the inclusion of photochemical phenomena in a modeling analysis typically is complicated and case specific. A major difficulty in applying a model such as RPM-II is specifying background concentrations because the model is particularly sensitive to ambient air quality. Hydrocarbon and NOx composition vary spatially and temporally throughout any region. A thorough refined modeling exercise would require temporal profiles of all dominant inorganic and organic species in the CB4 mechanism. Such data are scarce for even a single location. The problem is handled explicitly in grid modeling (e.g., UAM application) by assimilating appropriate emissions inventories and generating ambient air quality estimates (in combination with invoking reasonable assumptions regarding initial and boundary conditions). Similarly, it is feasible to generate ambient air quality data with a trajectory model like RPM-II, with appropriate placement of emissions sources. However, that approach is cumbersome within the model framework as well as application specific and, consequently, not amenable to developing a robust screening tool. To overcome this difficulty, simplifying assumptions regarding background chemistry quality must be invoked. Such assumptions should yield conservative answers (i.e., high ozone generation) and, as a consequence of building in "conservatism" via air qualitiy assumptions, the need for case-specific representativeness diminishes. Accordingly, these screening tables are based on "prototypical", assumed characterizations of background chemistries, representing rural and urban locations. The following discussions outline the procedures used to develop base cave meteorological and chemical inputs so that conservative estimates of ozone formation would be produced from model runs performed with the various source emissions scenarios incorporated in the screening tables.

DEVELOPMENT OF REASONABLE WORST-CASE MODEL INPUTS (RURAL)

Background Air Chemistry

Ambient concentrations of all CB4 species (Table A1) assumed for rural background air are identical to those utilized in rural ozone modeling studies (PEI, 1988) performed with EPA's Regional Oxidant Model (ROM). Those concentrations were generated by applying the CBM-RR chemical mechanism (a more detailed version of the carbon bond mechanism) in a batch reactor mode under sequential 12-hour alternating periods of full sunlight and darkness until a relatively aged, steady state mixture was produced. Initial concentrations of NOx, CO, and NMOC were derived by EPA's Atmosphorlc Science and Research Laboratory (Schere, 1988).

The ambient NOx and hydrocarbon concentrations in Table A1 reflect generally low ozone precursor concentrations which might suggest a minimum of ozone forming potential, relative to a more concentrated urban mix. Although sonewhat counter-intuitive results derived from running various emissions mixes (VOC don$nated) with rural or urban background concentrations showed a greeter ozone increment with rural background air, under equivalent emission rates. This might simply be explained by considering that ozone forming potential already exists in urban air due to a large mass of pollutants implied in urban background concentrations. In contrast, ozone forming potential in rural air may be lacking key ingredients (NOx, reactive VOC) which when supplied results in a larger increment Also, low NO concentrations in rural air probably results in less ozone scavenging through direct titration.

Meteorological and Source Speciation Inputs

A prospective user of the screening tables would select an appropriate mass emission rate and NMOC/NOx emissions ratio to determine the ozone increments due to individual VOC/NOx sources. The tables have no provisions for specifying values of meteorological variables (such rigidity is common for most screening analyses). Furthermore, adjustment of the mix of emitted hydrocarbon fractions is not permitted, again keeping within reasonable restrictions imposed by a screening technique.

A base-case input file incorporating a single set of base-case values for meteorological parameters and one emissions reactivity mix was developed with the intention of providing conservative (worst case) ozone formation estimates. The screening tables represent runs based on those meteorological parameters with selected adjustments in emissions rates.

The set of meteorological parameters were chosen by running the model over a range of discrete values for one variable, while holding all other variables constant. A true factorial analysis of all possible combinations of wind speed plume dimensions, starting time and temperature was not performed because of the range, continuous nature and number of variables involved.

The procedures used to determine base-case meteorological

inputs are listed below and followed by a discussion of the results from that analysis. For clarity, throughout the discussion "standared value" refers to the value which each variable is maintained while other variables are varied; the "standard value" should not be confused with "base-case" value, the determination of which was the object of this exercise.

Background Air – Concentrations of CB4 species representative of rural, continental U.S. locations as presented in Table A1 were held constant throughout each modeling run.

Emissions – A continuous mass emission rate of 10,000 tons/year NMOC was used for all runs designed to produce base-case values for meteorological variables. The NMOC/NOx; NOx/NO; CO/NMOC and hydrocarbon speciation partitioning were based on EKMA default values (EPA, 1988):

PPM CO/PPMC NMOC – 1.2

PPMC NMOC/PPM NOx – 10

PPM NOx/PPM NO   –   4

CB4 group fraction on PPMC basis

ETH 0.037
OLE 0.035
ALD2 0.052
FORM 0.021
TOL 0.089
XYL 0.117
PAR 0.564
NR   0.085

Additional related issues involving emissions scenarios are discussed below within the context of reactivity.

Location – In terms of model inputs, location only translates to diurnal variation of solar zenith angle. The EKMA default location of Los Angeles, California (Lat. 34.058; Long. 138.256; 6/21/75) was used in all runs, virtually no sensitivity resulted from varying latitude.

Starting Time – Starting times (i.e., plume emergence were incremented hourly from 0600 to 1200 LST (0800 standard start).

Wind Speed – Wind speeds were incremented by 1 m/s over a range from 1 m/s to 4 m/s. The standard wind speed for all rune was 4 m/s.

Plume Width – Spatially variant downwind plume widths were generated by specifying standard Pasquill-Gifford stability classes 1-5 with class 3 used as the standard stability class.

Plume Depth – Plume depths were incremented 200 m over a range from 300 m to 1500 m (500m standard depth).

Temperature – Temperatures were incremented 8 K over a range from 287 K to 311 K (303 K was standard).

Emissions NMOC Mix – In addition to the standard EKMA mix with a NMOC/NOX of 10, runs were performed with single-component NMOC emissions representing each CB4 class (except isoprene) and different NMOC/NOx ratios. To overcome numerical problems requiring excessive computational time for olefins, a mix of 70% olefins end 30% parafins was used in place of pure olefins.

These single-component emissions were run with mass emissions rates of CO and NOx that were identical to those applied for the standard EKMA emissions mix. Consequently, NMOC/NOx (PPMC/PPM basis) ratios varied somewhat due to differences in effective molecular weights among the emissions scenarios. All NMOC emissions were based on the standard mass emission rate of 10,000 tons/year. Also, additional NMOC/NOx ratios of 5 and 2 (based on standard EKMA mix) were applied for all emissions mixes.

RESULTS AND DISCUSSION

Meteorology:

     Sensitivities of maximum ozone increments within a point
source plume due to independent variation of several
meteorological parameters are presented in Figures 1-5. Based on
13 these results and consideration of consistency among
meteorological variables, the following values based on the
subsequent analysis were chosen for base-case meteorological
inputs to provide conservative ozone increment estimates:

                    wind speed - 1 m/s
                    horizontal stability - class C
                    plume depth - 700 m
                    ambient temperature - 311 K
                    start time - 1000 LST (NMOC/NOx > 5)
                               - 0700 LST (5 > NMOC/NOx > 1)
                               - 0600 LST (NMOC/NOx < 1)

Starting Time - Only minor sensitivity was attributed to varying
starting time from 0600 to 1200 LST for standard mix with
NMOC/NOx = 10 (Figure 1). Sensitivity to starting time increased
as NMOC/NOx ratio decreased; at lower NMOC/NOx ratios earlier
starting times produced larger ozone increments (Figures 2-3).
     Sensitivity to starting time is strongly coupled to
optimizing both NO to NO2 conversion and prividing adequate
reactive VOC. At highNMOC/NOx, NO titration of ozone is not
dominant and exposure of high incident radiation to concentrated
NMOC (short time after start-up) produces large ozone increments.
In contrast, at low NMOC/NOx ratios NO titration is a problem and
the plume requires extended time to reach optimum ozone forming
potential. Accordingly, an earlier start time which provides
intense incident radiation upon segments sufficiently downwind
such that a substantial percentage of NO has been converted (as
well as diluted).

Wind Speed - Wind speed variations impart the greatest degree of
sensitivity on maximum ozone increments (Figure 4). Successively
smaller decreases in ozone impacts occur as wind speed increases
from 1 to 5 m/s; a reasonable response since, in effect, a 2-fold
increase in wind speed represents a 50% decrease in the effective
emissions rate injected into a plume segment. In addition, a
dilution effect due to increased dispersion near the source
accompanies elevated wind speeds.

Stability Class (Horizontal dispersion) - Ozone formation
increased as stability classes were changed from Class A(1) to
Class E(5) (Figure 5), an expected response related to
successively less downwind dilution when proceeding through
higher stability categories. In the context of this analysis
Class D and E stabilities yield large ozone increments; but these
classes are clearly inconsistent with other optimal ozone forming
conditions (full sunlight, light winds). In following a
conservative approach consistent with any screening protocol
selection of Class C stability is appropriate. Actually, the

selection of a more stable dispersion scenario is consistent with the notion of plume meander whereby plume dispersion calculated from standard dispersion parameters encompasses a complete crosswind profile due to plume meander, yet the effective crosswind plume dimension (where reactions occur) is governed by an instantaneous crosswind dimension. While plume meander certainly increases areal exposure to a particular plume, reactivity is dependent on actual crosswind dimensions at a point in time.

Plume depth – The ozone formation response to plume depth (held constant throughout time) is similar to that for wind speed (Figure 6), an apparent dilution phenomenom. The selection of 700 m maximum plume depth is, admittedly, somewhat arbitrary. Certainly an upper bound must be imposed to account for low mixing heights, otherwise a plume would grow indefinitely, and rather rapidly, over time. While the existence of 700 m mixing heights is not uncommon, the occurrence of such a low mixing height under optimal ozone forming conditions is not likely in many locations. Nevertheless, an upper bound must be imposed and, as illustrated in Figure 6, the difference in maximum ozone increments between 700 mand 900 m is about 15 %. Furthermore, observed summertime, afternoon measurements of plume depths taken from the Tennessee Plume Study (Ludwig et a1., 1981) show plume depths typically ranging from 500 m to 700 m.

Temperature – Ozone formation increased with increased temperature (Figure 7), a result consistent with observed correlations among high temperature and high ozone levels. The selection of 311 K (100 $^\circ$F) is not unreasonably high.

VOC Emissions Reactive Mix

The apportioning of emissions by CB4 classes would typically be set by a particular source profile for a refined modeling application. Since screening tables are designed to provide a simple and robust screening procedure, out of necessity the emissions mix becomes a bariable which must be addressed when developing a worst-case baseline input file. A robust method conceivably should bracket the limitless variety of VOC mixes, a rather encompassing objective. To that end a crude attempt at bracketing a range of all possible VOC point source emissions was developed by running the RPM-II with single-component NMOC emissions for each CB4 category.

Results of this analysis ara shown in Figures 8-10 for three different NMOC/NOx ratios. All VOC emissions rates were held at 10,000 tons/year, and NMOC/NOx and NMOC/CO ratios were based on the standard EKMA mix. The large NMOC emissions rate of 10,000 tons/year was not intended to be representative; the rate was used to better indentify trends which otherwise might have been lost in numerical noise. The ratios varied slightly among the different mixes because of differences in VOC molecular weights. To provide consistency all mass rates for NOx (at a given NMOC/Nox ratio) and CO were identical for different mixes (the NMOC/NOx ratio is volume based). Consequently, different NMOC molar emissions rates existed among mixes, with higher molar

emission rates for lower weight classes (e.g. paraffins). The
decision to base this analysis on mass emissions is based on the
expectation that the anticipated users of this screening
technique will address permitting issues based on mass emission
rates.

As shown in Figures 8-10, variation in ozone increments
predicted for different CB4 components range up to about 1.5
times the ozone increment obtained with a standard EKMA urban
mix. Accordingly, the EKMA mix is retained for all screening
analyses and application will requre a scale-up factor of 1.5.
It should be noted that a 70 % olefln mix is unrealistic as most
olefin-named compounds are composed of chains dominated by
paraffin bonds. At first glance the magnitude of differences
among various mixes is surprising within the context of k-OH
values for the various CB4 groups (listed bolow) - thls topic is
pursued further in a later section regarding urban table
development.

CB4 Class	k-OH (min^{-1})
ETH	5824
OLE	20422
ALD2	11833
FORM	15000
TOL	1284
XYL	4497
PAR	1203
EKMA MIX	3180

Rural Area Screening Tables

Results from a matrix of runs covering a range of VOC emission rates and NMOC/NOx emissions ratios are presented in Table A2. In order to maintain a consistent basis for data evaluation, all Table A2 results are based on a 1000 LST start time. Several trends exist among the data in Table A2:

* At NMOC ratios greater than 3, any increase in NMOC loading leads to an increased ozone maximum

* As VOC loading rate increases an optimal NMOC/NOx emissions ratio exists, and this ratio shifts to lower values as NMOC source size increases.

* At NMOC/NOx emissions ratios less than 3, VOC loading increases can lead to relative decreases in ozone maximums as wall as oxone deficits during one solar day.

A simplified version of Table A2 is presented as the rural area screening table in section 3.0 (Table 1). The effects of NMOC/NOx ratios have been attenuated somewhat by presenting three broad NMOC/NOx ratios. The results under each range reflects a scale-up factor of 1.5 and are based on the most conservative (maximum ozone producing) NMOC/NOx ratio each rango > 20 (NMOC/NOx = 20); 5-20 (12 - see Figure 11); < 5 (5). In addition the results in Table 1 are based on optimal starting times for different NMOC/NOx ratios and adjusted by using a reactivity scale-up factor of 1.5.

DEVELOPMENT OF REASONABLE WORST-CASE MODEL INPUTS (URBAN)

Unless listed below, all model inputs used to develop urban screening tables were identical to those used for rural tables. Specifically, these similar inputs include plume geometry, wind speed and ambient temperature.

Background Air Chemistry

A diurnal concentration and composition profile for background air chemistry was prepared by conducting 8 A.M.-6 P.M.

20

simulations using the ambient mode option (batch reactor) in RPM-II followed by a plume simulation using a 10,000 ton/yr VOC emissions source with composition described above in the rural table development secton. The ambient mode sumulation develops background profiles for all CB4 species (inorganics, intermediates, precursors and sinks). In turn, the background air devoloped by the ambient simulation can become entrained (and available for reaction) within the source emissions plume during the subsequent plume simulation.

A rather crude attempt at determining a "reasonable worst-case" background profile consisted of running various simulations using different precursor levels to identity a set of precursors which produces 1) a relative maximum ozone increment during the plume simulation and 2) a background profile characteristic, in a broad sence, of urban air quality. Initial concentrations of precursors used to drive tho ambient simulation were based on starting with OZIPM4 default values (listed below) for NMOC, NOx and CO composition and concentration, and scaling those values downward and across-the-board (i.e., reducing total precursor concentration yet retaining default composition) such that conditions 1) and 2) were achieved. The downward scaling is required because the ambient mode option in RPM-II has no provision for adjusting mixing height; consequently, a set of precursors which might produce a realistic profile with typical diurnal dilution yields highly concentrated, unrealistic cancentrations with a constant reactor volume constraint.

```
                     OZIPM4 DEFAULT PRECURSOR INPUTS

     NMOC Total    1.0     ppmc    OLE 0.0175          ppm
     Nox Total0.1  ppm     ETH 0.0185  ppm
     NO2           0.025 ppm FORM    0.021          ppm
     NO            0.075 ppm TOL 0.0127    ppm
     CO            1.2     ppm ALD2    0.026          ppm
     PAR           0.564 ppm NR       0.085          ppm
     XYL           0.146 ppm H2O 20,000    ppm
```

The results of several simulations are presented in Figure
12. The OZIPM4 default set of precursors without reduction
produces an excessively high peak background ozone concentration
of 46.4 pphm. subsequent simulations with across-the-board
precursor reductions resulted in successively larger ozone
increments and lower peak ambient ozone concentrations. The set
of precursor inputs corresponding to 16 % of default values
produced the largest ozone increment while achieving ambient
ozone above 12 pphm. Accordingly, that set of precursors were
used for developing the urban screening tables (unadjusted –
Table A3, adjusted – Table 2, main text).

Starting Time

The precursor concentrations reflect 6-9 A.M. values. Thus,
to provide consistency with precursor composition, all
simulations started at 8 A.M. LST.

VOC Emissions Reactive Mix

Results of modal runs conducted with single-component CB4
mixes at different NMOC/NOx ratios show substantial differences
on formation of ozone increments (Figure 12). These results
contrast sharply with the analogous set of rural based
simulations (Figures 8-10). The urban based ozone increment due
to olefins is more than five times that of the EKMA mix at an
NMOX/NOx ratio of 10, whereas only a 50 % increase occurred in
the rural analysis. Differences among the more reactive urban
mixes and the EKMA mix diverge further at lower XMOC/NOx ratios.
Also, a large dependence on NOx which produces a shift from
reactive to much less reactive (high to low NMOC/NOx ratio)

occurs with formaldehyde.

For the purpose of preparing a "single" urban screening
table, a scale-up factor of 3 was applied to the results in Table
A3 (urban area increments as a function of VOC emissions rates
and NMOC/NOx emissions ratios) to derive the urban screening
table (Table 2). The value of 3 is not entirely arbitrary.
Based on the results in Figure 13, a scale-up factor of 5 might
be more appropriate. However, because so much conservatism is
built in to the meteorological and, to a certain degree, the
background chemistry inputs, collecting the most reactive mixes
for scale-up would probably result in a screening out of nearly
all VOC point sources. The factor 3 was determined by surveying
the weighted k-OH values of VOC species profiles in the Air
Emissions Speciation Manual (EPA, 1988). The weighted k-OH of
the 90th percentile (about 9000 min-1) was nearly three times
that of the standard EKMA mix used in formulating Table A3
(Baugues, 1988). Considering that the highest weighted k-OH
values for the VOC species profiles exceeded 20,000 min-1,
scaling by 3 might be viewed as a less drastic approach.

CONCLUDING REMARKS

These reactivity-sensitivity simulations suggest that
background chemistry is a limiting factor in determining ozone
increments due to ozone precursor emissions - hardly a surprising
outcome. Such dependency on source composition, especially
within urban atmospheres, infers that a single scale-up factor,
as used for the rural table, is not adequate. One can always
resort to more refined source specific analyses. Ideally, a
thorough refined analysis would formulate background chemistry
with the best available modeling techniques and let a source
plume entrain those concentrations - the basic concept of the
PARIS model which imbeds RPM-II within the Urban Airshed Model
(UAM), which can utilize available meteorological, air quality
and emissions (all categories) information to formulate
background chemistry profiles. Such an exercise is highly
resource intensive, and thus a motivation for developing a usable
screening approach. _

Clearly, a need exists for accommodating variations in point
source VOC speciation within the context of a screening analysis.
It is suggested that the concept of an extended screening
approach which allows source specific emissions speciation inputs
be pursued. a possible approach could utilize the apparent,
conservative meteorological inputs developed for these tables
(and/or from additional efforts) as default inputs to RPM-II in
combination with best estimates of the composition of a specified
source. This approach would eliminate the major difficulties in
operating a model such as RMP-II - characterization of
meteorology and background chemistry.

Table A1. Background species concentrations (ppm) taken to be representative of "clean" atmospheric conditions

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ALD2	9.005E-5	NO	5.054E-5
H2O2	1.084E-3	OH	2.947E-7
MGLY	1.529E-6	PHO	4.124E-9
O	1.496E-10	XYL	1.296E-9
PAR	3.224E-3	ETH	1.681E-5
XO2	1.171E-5	HO2	2.496E-5
C2O3	7.389E-7	NO2	1.491E-4
N2O5	1.723E-9	OLE	4.676E-9
O3	3.193E-2	FORM	1.148E-3
PHEN	4.286E-5	ISOP	0.000E+0
XO2N	1.417E-6	NO3	2.041E-8
CO	9.873E-2	PAN	5.167E-5
HNO3	1.646E-3	TOL	1.219E-5

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from (PEI, 1988)

Table A2. Rural based ozne increment (pppm) as a function of NMOC emissions and NMOC/NOx emissions ratios.

NMOC EMISSIONS (TONS/YR)	ALL VOC	30	20	NMOC/NOx (PPMC/PPM) 15	12	10	5	3	1
50	0.21	0.23	0.24	0.25	0.25	0.27	0.35	0.42	0.70
75	0.21	0.24	0.25	0.27	0.29	0.32	0.42	0.53	0.83
100	0.20	0.27	0.28	0.31	0.34	0.36	0.49	0.63	0.92
300	0.19	0.44	0.53	0.60	0.69	0.72	0.94	1.09	1.14
500	0.18	0.63	0.76	0.88	0.96	1.02	1.25	1.36	0.87
750	0.16	0.85	1.05	1.17	1.29	1.32	1.55	1.55	0.39
1000	0.15	1.08	1.33	1.46	1.57	1.59	1.80	1.68	0.12
1500	0.15	1.47	1.82	2.01	2.03	2.15	2.20	1.70	–
2000	0.15	1.86	2.24	2.48	2.56	2.65	2.44	1.61	–
3000	0.15	2.63	3.20	3.39	3.46	3.54	2.87	1.29	–
5000	0.15	3.93	4.65	4.88	5.00	4.97	3.22	0.90	–
7500	0.14	5.49	6.52	6.63	6.73	6.63	3.40	0.75	–
10000	0.13	6.83	8.11	8.22	8.57	8.06	3.62	0.65	–

– indicates no discernible ozone enhancement

Table A3. Urban based ozone increment (pphm) as a function of NMOC emissions and NMOC/NOX ratios.

NMOC EMISSIONS (TONS/YR)	ALL VOC	NMOC/NOx (PPMC/PPM)						
		30	20	15	10	5	3	1
50	0.38	0.27	0.36	0.36	0.36	0.34	0.32	0.21
75	0.39	0.39	0.38	0.38	0.38	0.3S	0.32	0.20
100	0.42	0.40	0.40	0.40	0.39	0.3S	0.32	0.22
300	0.59	0.57	0.54	0.52	0.51	0.42	0.34	0.62
500	0.74	0.71	0.68	0.68	0.62	0.46	0.48	0.93
750	1.09	0.90	0.87	0.85	0.78	0.61	0.65	1.31
1000	1.38	1.08	1.07	1.02	0.91	0.74	0.89	1.56
1500	1.93	1.61	1.41	1.36	1.21	1.02	1.27	1.64
2000	2.35	2.07	1.80	1.68	1.48	1.33	1.63	1.24
3000	3.16	2.81	2.59	2.28	2.00	1.95	2.17	0.14
5000	4.43	4.31	4.01	3.43	3.11	2.99	3.09	–
7500	5.34	5.76	S.56	4.92	4.37	4.17	3.64	–
10000	5.90	7.03	6.93	6.31	5.49	5.17	3.55	–

– indicates no discernible ozone enhancement

Figure 1. Starting Time
NMOC/NOx = 10

OZONE INCREMENT (PPHM) vs STARTING TIME
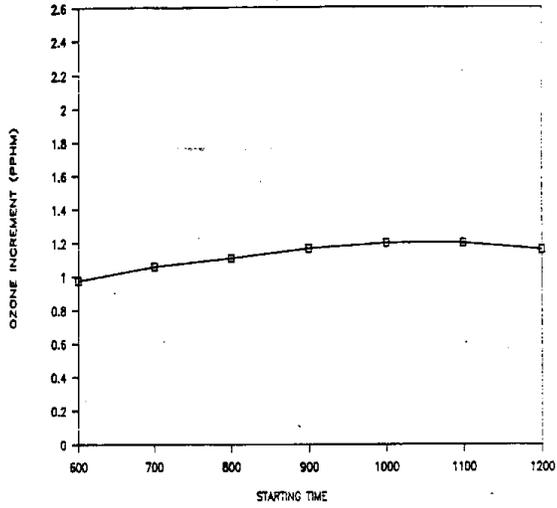
Figure 2. Starting Time
NMOC/NOx = 5

OZONE INCREMENT (PPHM) vs STARTING TIME
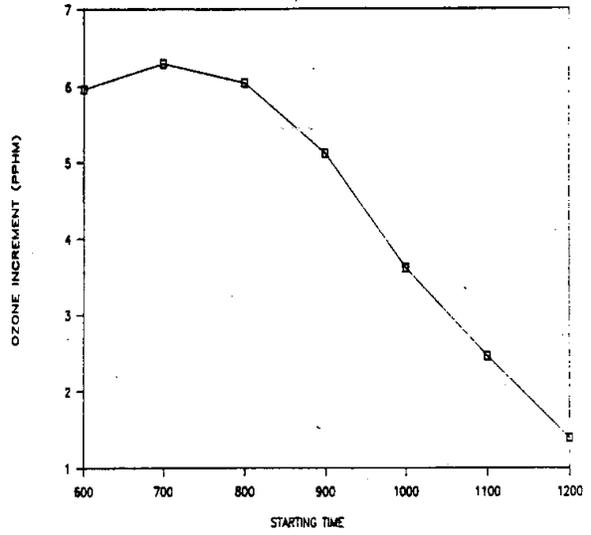
Figure 3. Starting Time
NMOC/NOx = 1

OZONE INCREMENT (PPHM) vs STARTING TIME

Figure 4. Wind Speed

OZONE INCREMENT (PPHM) vs WIND SPEED (M/S)
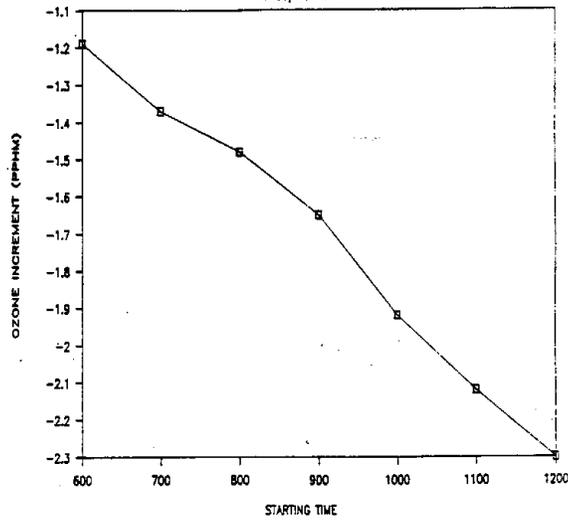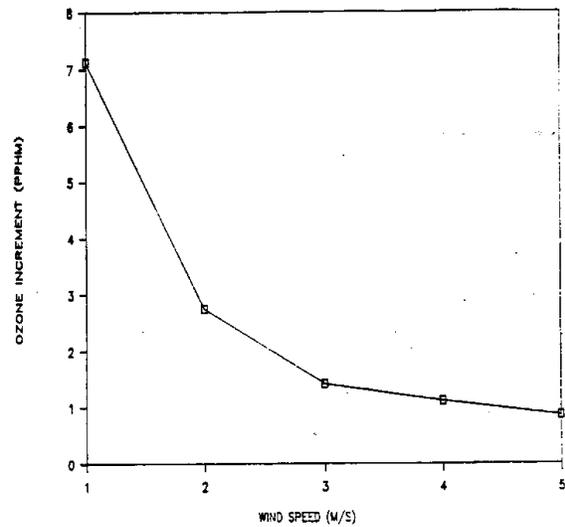
Figure 5. Stability Class

OZONE INCREMENT (PPHM) vs STABILITY CLASS (WIDTH)

Figure 6. Plume Depth

OZONE INCREMENT (PPHM) vs CONSTANT PLUME DEPTH (M)

27
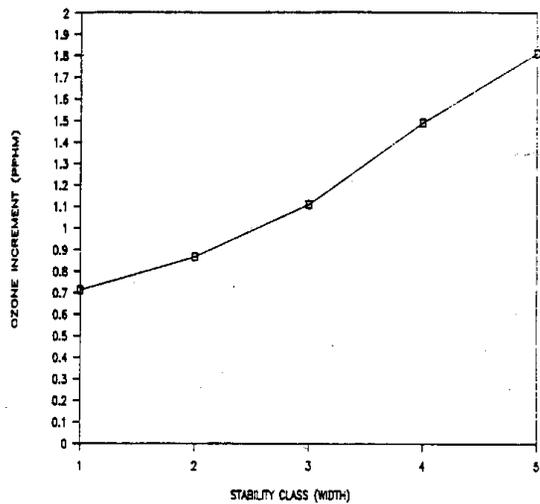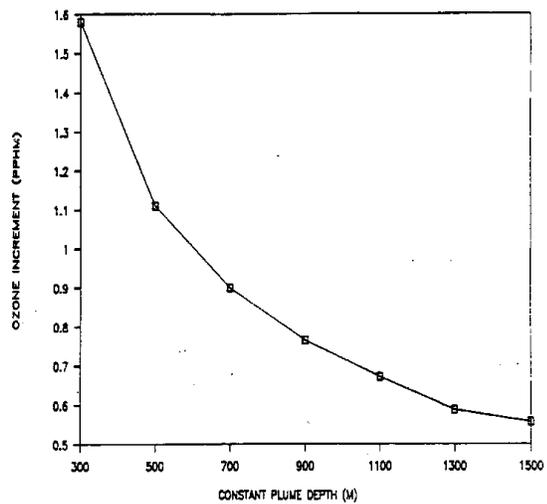
Figure 7. Temperature
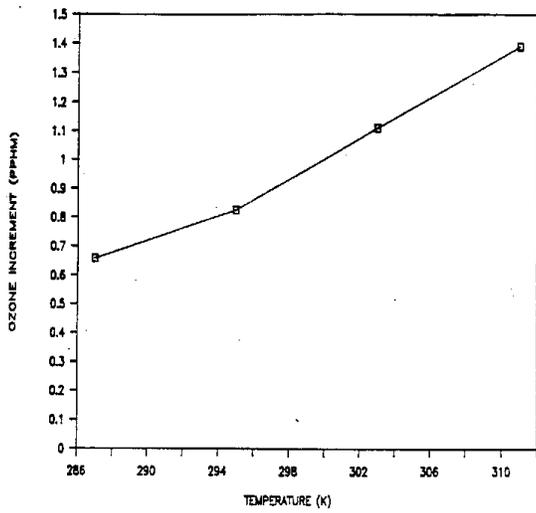
Figure 8. Single component CB4 emissions
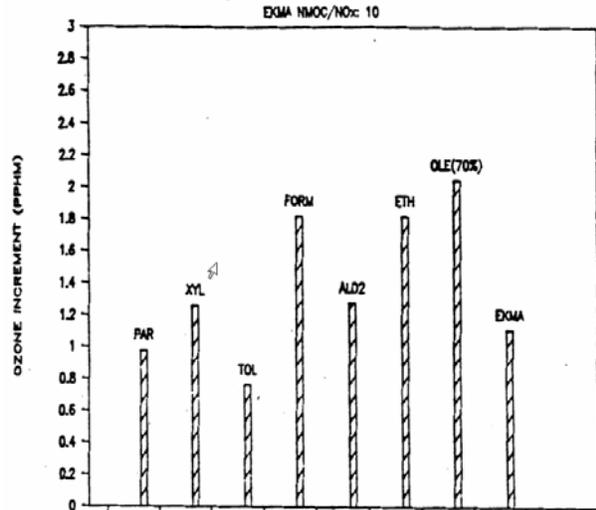
Figure 9. Single component CB4 emissions
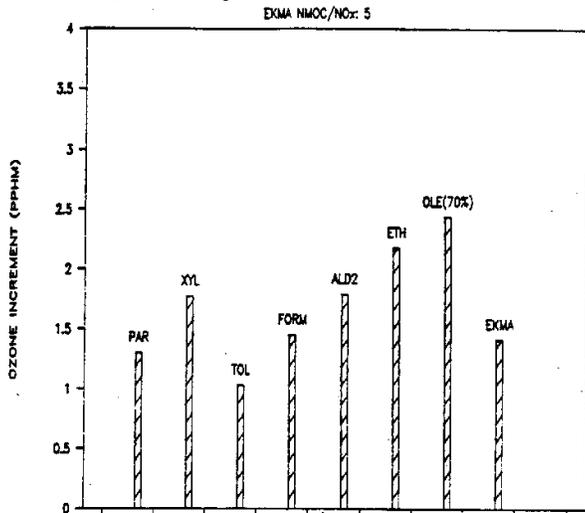
Fig. 10. Single component CB4 emissions
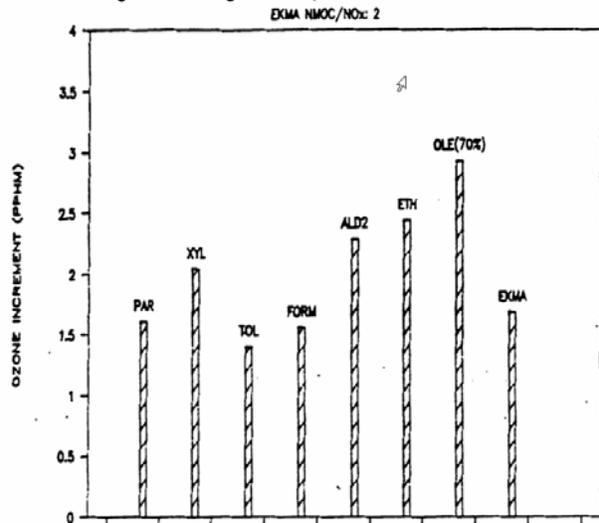

Figure 11. NMOC/NOx effect on ozone
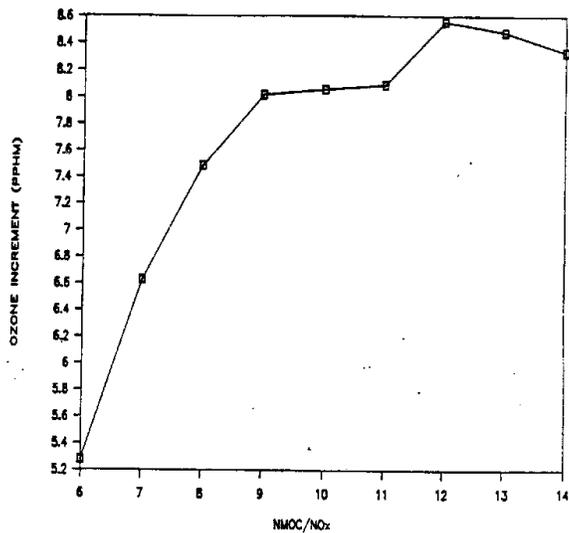

Figure 12. Effect of Urban Precursor Levels on Ozone Increment

28

Fig. 13. Single Component CB4 Emissions

EKMA NMOC/NOx 2,5,10 (Urban)

Legend: NMOC/NOx 2 — NMOC/NOx 5 — NMOC/NOx 10