

W-24-50
W-25-30

Preliminary Evaluation of the US EPA Proposed Ozone Precursor Point Source Screening Technique

Report on Task 1 of the Comprehensive Evaluation Plan

API PUBLICATION NO. 4488
HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
DECEMBER 1988

American Petroleum Institute
1220 L Street, Northwest
Washington, DC 20005



Preliminary Evaluation of the US EPA Proposed Ozone Precursor Point Source Screening Technique

**Report on Task 1 of the
Comprehensive Evaluation Plan**

**Prepared for the American Petroleum Institute
1200 L Street, NW
Washington, DC 20005
and
Chemical Manufacturer's Association**

**Prepared under contract by:
Panos G. Georgopoulos and John H. Seinfeld
California Institute of Technology
Pasadena, California 91125**

December 1988

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET DUTIES OF EMPLOYERS; MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

Preliminary Evaluation of the US EPA Proposed Ozone Precursor Point Source Screening Technique

EXECUTIVE SUMMARY

A preliminary evaluation of the *US EPA Proposed Ozone Precursor Point Source Screening Technique* is presented here, for the purpose of providing comments to the EPA regarding the technical validity of this technique.

The technique under consideration relies on the use of two screening tables, for rural and urban conditions respectively. These tables give directly the increment of ambient ozone levels (in pphm) due to emissions of non-methane organic compounds (NMOC) and nitrogen oxides (NO_x) given the maximum daily NMOC mass emission rate, expressed on an annual basis (tons/yr), and the range of the magnitude of the annual NMOC/ NO_x mass emissions ratio. This ratio is classified as high (> 20), moderate (5-20), and low (< 5). The screening tables do not allow for adjustment for different ambient conditions or reactivity (i.e. speciation) of emissions in computing the ozone increment.

The ozone increments in the screening tables were calculated using a modification of the Reactive Plume Model II (RPM-II). This modified version of RPM-II employs the Carbon Bond IV chemical mechanism (rather than the "standard" Carbon Bond II). The inputs for the calculations comprised a set of "base case" meteorological, air quality, and emissions speciation parameters. These inputs were selected based on the results of a sensitivity analysis so as to represent a "reasonable worst-case" scenario leading to conservative estimates of ambient impact.

Three main issues are addressed in assessing the validity of this screening technique:

- the validity of the basic concept of the technique and of its proposed implementation;
- the validity of the procedures applied in computing the ozone increments in the screening tables; and
- the validity of the refined modeling scheme (based on the modified RPM-II) that was used in deriving the screening tables, and the general requirements for proper reactive plume modeling.

The study of the above issues in the present report leads to the following conclusions and recommendations:

- The proposed screening technique exhibits unacceptable sensitivity with respect to low-to-moderate values of the NMOC/NO_x emissions ratio. The parameterization scheme adopted in the present version of the technique must be modified for this sensitivity to be reduced.
- Limitations of the applicability of the screening technique must be identified explicitly and methods for extending this applicability must be developed. A detailed protocol ensuring application of the technique within the limits of its validity as well as the proper calculation of emissions related inputs must be developed.
- The expected degree of conservatism of the technique in relevance to actual applications must be explicitly quantified. In situations where the degree of overestimation seems unacceptable modifications of the technique will be needed to provide a meaningful screening test.
- It is necessary to identify criteria guiding the selection of "base case" inputs (that ensure conservatism in the construction of the screening tables) to "near-optimal" values. These criteria should reflect compromises among the various conflicting factors (need for realism, simplicity, generality, etc.) governing the result of such a selection. The approach followed in selecting the base case inputs has not identified such criteria and, furthermore, has not fully justified many of the ad hoc assumptions that were used in the sensitivity studies. Also, the procedures followed in performing the sensitivity study that produced the base case inputs do not ensure the universal validity of the sensitivity analysis results and they leave unresolved questions regarding the degree of conservatism that is incorporated in the screening technique.
- RPM-II must be validated for applications relevant to the screening technique (emissions with high VOC levels). General validation studies of the RPM version that incorporates CB-IV are also required.
- The limitations of RPM-II (and of other similar trajectory models) in describing atmospheric mixing and chemistry in both the near field and the far field must be recognized and specific protocols must be developed for their application, to ensure that these limitations are not ignored. Further research is needed to improve the state of the art of atmospheric photochemical plume modeling. Development of a "new" comprehensive reactive plume model that will incorporate recent advances in our understanding of atmospheric transport and mixing processes rather than a partial modification of RPM-II (or of a similar existing model) may be necessary. Only when this model has been properly evaluated can it then be used as the basis of a screening technique.

The evaluation and the recommendations that were summarized here represent the outcome of Task 1 of a comprehensive, two-task evaluation plan focusing on the screening technique and its implications. Task 2 of this evaluation plan is intended to expand on the problems identified in Task 1, perform case studies relevant to problems actually encountered in practice, and analyze in more detail the shortcomings and strengths of the Reactive Plume Model (RPM-II) on which the screening technique is based.

1. INTRODUCTION

The U.S. EPA has proposed a screening technique for predicting the impact of point sources of ozone precursor emissions, i.e. volatile organic compounds (VOC) and nitrogen oxides (NO_x) on ambient ozone concentrations. To ensure simplicity and ease of application this technique introduces two *screening tables*, for rural and urban conditions respectively, that give directly the increment of ambient ozone levels due to emissions of non-methane organic compounds (NMOC) and NO_x . The only information required to use these tables is the maximum daily NMOC mass emission rate and the range of the magnitude of the annual NMOC/ NO_x mass emissions ratio (high, moderate, low); ambient meteorological and air quality conditions and composition of emissions are assumed the same for all rural or urban cases, corresponding to "base case inputs." The ozone increments in the screening tables were calculated using a modification of the Reactive Plume Model II (RPM-II) with base case inputs that were selected so as to guarantee conservatism in the results.

There are three main issues that must be addressed in assessing the validity of this screening technique:

- (i) the validity of the basic concept of a screening technique that associates directly a single point source of VOC and NO_x with an ambient ozone increment level using only minimal information about the source and the location under consideration;
- (ii) the specific procedures applied in developing the screening tables employed in implementing the above technique, i.e. the procedures applied in computing the ozone increments in the screening tables; and
- (iii) the validity of the refined modeling scheme – based on a modification of the Reactive Plume Model, version II (RPM-II) – used in deriving the screening tables. Discussion of refined modeling is relevant here not only because its validity is a necessary condition for the validity of the specific screening technique under consideration but also due to the implication that further modeling (based on RPM-II) will be required, either as part of a suggested "extended screening approach" (Scheffe, 1988, p. 19), or for refined calculations using case-specific inputs if screening indicates the possibility of unacceptable ambient ozone increments.

This report is organized according to the above three points. After a brief description of the proposed screening technique the discussion focuses in turn on the three issues outlined above, i.e. the basic concept underlying the proposed technique, the derivation of the screening tables, and the problems relevant to valid refined modeling. Brief concluding remarks are presented after the discussion of each issue. The conclusions of each section have also been summarized together in the Executive Summary.

2. BRIEF DESCRIPTION OF THE SCREENING TECHNIQUE

As it was mentioned in the Introduction, the volatile organic compounds and nitrogen oxides (VOC/NO_x) point source screening technique, described in Scheffe (1988), relies on the use of two screening tables, for rural and urban conditions respectively. These tables give directly the increment of ambient ozone levels (in pphm) due to sources of non-methane organic compounds (NMOC) and NO_x. The "input column" in each table consists of the maximum daily NMOC mass emission rate expressed on an annual basis (ranging from 50 to 10,000 tons/year). The three "output columns" in each table are the ambient ozone increments in pphm for three ranges of the annual NMOC/NO_x mass emissions ratio, high (> 20), moderate (5-20), and low (< 5). The screening tables do not allow for adjustment for different ambient conditions or reactivity (i.e. speciation) of emissions in computing the ozone increment.

The ozone increments in the screening tables were calculated through a procedure that employed a modification of the Reactive Plume Model, version II (RPM-II) and a set of "base case" meteorological, air quality, and emissions speciation partitioning inputs that were intended to represent a "reasonable worst-case" scenario resulting in conservative estimates.

The modified version of RPM-II that was used in the calculations employs version IV of the Carbon Bond chemical mechanism (CB-IV) (*).

The base case inputs were derived from a series of single-parameter sensitivity calculations with the modified RPM-II that identified the values of each input producing maximum ozone increments when all other inputs assume a priori selected "standard values."

In the calculations performed with the modified RPM-II the composition of NMOC emissions was assumed to be the same in all cases, corresponding to the EKMA default values. However, to ensure conservatism for the cases of emissions that

* Note: The standard version of RPM-II, described in the 1986 EPA Guldellne on Air Quality Models (Revised) and designated as an *alternative* model (computer tape available from NTIS with accession number PB83-154898), employs version II of the Carbon Bond Mechanism (CB-II) with certain steady state assumptions (see Appendix A for details). The modified version of RPM-II (employing CB-IV) was developed specifically for the purpose of deriving the screening tables and has not been evaluated against field data. No information has been given regarding the availability of this version.

are more reactive than the standard EKMA NMOC mix, the ozone increments in the screening tables were calculated by multiplying the estimates derived from the modified RPM-II (using a standard EKMA emissions mix) with a scaling factor that was equal to 1.5 for the rural case and to 3.0 for the urban case.

More specifically, the modified RPM-II, employing a standard EKMA emissions mix and the "base case" inputs, was used to estimate the (maximum) ozone increment – for the rural and urban cases – for NMOC/NO_x emissions ratio equal to 1, 3, 5, 10, 12 (for the rural case only), 15, 20, 30, and for "all VOC" emissions, for thirteen values of the NMOC emissions rate (ranging from 50 to 10,000 tons/yr). Then, for each emission rate an upper bound was determined for the ozone increments corresponding to high, moderate, and low values of the NMOC/NO_x ratio. Finally, these upper bounds of ozone increments were multiplied by scaling factors to produce the values listed in the screening tables. Scaling factors equal to 1.5 for the rural case and to 3.0 for the urban case were selected on the basis of a sensitivity analysis performed for EKMA NMOC/NO_x = 2, 5, and 10. This analysis compared results from calculations (with the modified RPM-II) that assumed standard EKMA mix emissions with results corresponding to emissions consisting entirely of each of the seven reactive organic components of the EKMA mix (except for the olefin component where a 70% olefin mix is assumed rather than all olefin emissions).

3. PROBLEMS RELEVANT TO THE CONCEPT OF THE PROPOSED SCREENING TECHNIQUE

In the document describing the proposed technique it is recognized that "the concept of a screening procedure for ozone precursors is beset with an immediate contradiction: A screening tool must be simple to apply and robust, but the inclusion of photochemical analysis typically is complicated and case specific" (Scheffe, 1988, p. 10). Nevertheless, the proposed method employs a most drastic conceptual simplification, essentially eliminating most of the case specific aspects of a particular application.

First, the entire spectrum of meteorological and ambient air quality conditions that can be encountered in practice is reduced to two general cases (urban and rural) that must be representative of "reasonable worst case" conditions for all U.S. locations. Then, only one input, the maximum daily mass emission rate of NMOC, is allowed to vary over a relatively large set of values. The only additional information on the emissions required in applying the screening technique is the identification of the range of the annual NMOC/NO_x mass emission ratio. This ratio is classified as high (> 20), moderate (5-20), or low (< 5). The composition of NMOC emissions is assumed to be the same in all cases (with two different scaling factors – to ensure conservatism – for the results of chemistry calculations, corresponding to the rural and urban cases). Therefore, the proposed screening tables are based on an essentially single parameter approach that allows only for the value of the total NMOC emissions rate to correspond directly to actual data, while it lumps all the other parameters of the problem into a very limited number of choices (rural/urban location, high/moderate/low NMOC/NO_x emissions ratio).

While these simplifications make the screening technique easy to apply, they fail to guarantee the robustness of the procedure. This is obvious when the screening tables are presented in graphical form. Figures 1A and 2A correspond to Tables 1 and 2 of Scheffe (1988, pp. 6 and 7) giving the rural and urban based ozone increments respectively as a function of NMOC emissions and NMOC/NO_x emissions ratios. The coordinates of these figures represent ozone increments (in pphm) versus NMOC emissions (tons/yr). The three curves in each of these figures correspond to high, moderate, and low NMOC/NO_x emissions ratios respectively. Figures 1B and 2B correspond to Tables A2 and A3 of Scheffe (1988, Appendix A) and represent the results of the actual calculations with RPM-II over the full range of the

NMOC/NO_x emissions ratio values that were used in the sensitivity analysis performed to identify the base case inputs corresponding to maximum ozone increments and therefore conservative screening estimates. The maximum values of ozone increments – separately for the ranges of high (>20), moderate (5-20), and low (<5) values of the NMOC/NO_x emissions ratio – from the sets of curves in Figures 1B and 2B have been multiplied by 1.5 and 3.0 respectively to produce the results of Figures 1A and 2A, i.e. the ozone increments of the screening tables. From Figures 1A and 2A one sees immediately that the sensitivity of calculated ozone increment to the NMOC/NO_x emissions ratio is clearly unacceptable for values of this ratio near 5. Indeed, in both the rural and the urban cases, the screening tables give differences of more than 5 pphm in ambient ozone increments when the annual NMOC emissions (based on a daily maximum rate) are in the range of 8,000 to 10,000 tons/year and the NMOC/NO_x ratio is slightly lower than 5 (e.g., it is equal to 4.9) than when it is slightly above 5. In the rural case this corresponds to total ozone increments differing by a factor > 2. These differences are in general substantial for values of annual NMOC emissions above 4,000 tons/year. Given the existing uncertainty regarding the actual value of the NMOC/NO_x ratio to be used in a given application, it is clear that this unphysical behavior of the screening technique in the low-to-moderate range of NMOC/NO_x ratios will unavoidably lead to serious problems in applications.

From a more general perspective, it should be noted that, given the complexity of the atmospheric phenomena affecting ozone formation, one cannot expect that a bounding estimate can be calculated via a "quasi-single parameter approach" for classes of applications that correspond to wide ranges of actual variations of inputs, *unless no practical limit is imposed on the allowed degree of overestimation*. On the other hand, setting some desirable upper limit to the degree of overestimation of ambient ozone increments, while retaining the same definitions of classes of applications, will limit the validity of the screening technique.

Thus, there arises the need for any simple screening procedure, to provide, on one hand, estimates of the expected degree of conservatism, or of the expected range of bounding factors, and on the other hand, to identify explicitly conditions for the validity of the technique. The proposed method under consideration here needs to be studied extensively with respect to both the above aspects. A more realistic correspondence to actual application situations will in general require incorporating more parameters in the screening procedure, such as, e.g., ambient temperature, solar radiation intensity, ambient air quality measures, etc. The specific, "optimal"

sets of parameters (corresponding to maximum simplicity of the technique) and their range and resolution of variation can only be identified through systematic sensitivity studies. For example, a direction towards the improvement of the rural case based screening technique would be to consider different "reasonable worst case" scenarios based on conditions of ambient air quality and meteorology prevalent in broad geographical areas of the U.S. (for example, the Western, Central, and the Eastern U.S.). For the urban case it may be necessary to treat some measure of ambient air quality and the ambient NMOC/NO_x ratio as inputs to the screening calculations in addition to the emission inputs. Furthermore, in this case the speciation partitioning of the emissions NMOC is expected to be even more important than in the rural case. It is obvious that examining the improvement of the proposed screening technique along such lines will require considerable amount of study.

Additional remarks concerning the concept and the implementation procedure of the proposed screening technique follow. These remarks are relevant not only to the specific screening tables and their use as described in Scheffe (1988) but also to any modifications, extensions, and improvements that would conform to the same general philosophy embodied in the proposed technique.

- The applicability of the refined modeling method (reactive plume model) used to derive the screening tables limits the applicability of the tables. This fact should be explicitly expressed and checks for confirming the applicability of the procedure should be incorporated in the standard use of the screening tables.
- Modifications or extensions of the proposed screening technique may be needed in cases where NMOC and NO_x are not mixed together in the emissions (e.g., NO_x is emitted aloft from stacks and fugitive VOC emissions are near ground level). Development of alternative refined modeling schemes may be required for the construction of screening tests relevant to these cases.
- The estimated impact on ambient ozone is not associated with the downwind distance from the point source in the proposed technique. In addition to the usefulness of correctly identifying the downwind dependence of the impact, especially in cases where the source under consideration is not an isolated one, the location of the maximum ambient concentration increments should be consistent in all cases with the range of the validity of the refined modeling method (reactive plume model) used to derive the screening tables.
- The proposed technique considers only sources with emission rates of VOC that are greater than the NO_x emission rates. However, emissions with low VOC levels and high NO_x levels, when located upwind of urban areas, have