

A
QC
880
A4.
no.82

Environmental Research Laboratories

Air Resources

Atmospheric Turbulence and Diffusion Laboratory

Oak Ridge, Tennessee

APPLICATION OF A SIMPLE MODEL OF PHOTOCHEMICAL SMOG

Steven R. Hanna

ATDL Contribution File No. 82

U. S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

A
QC
880
A4
no. 82

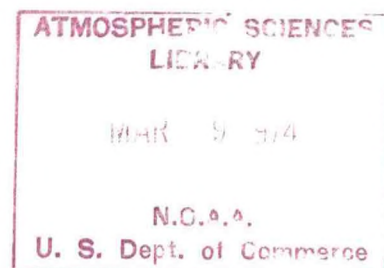
APPLICATION OF A SIMPLE MODEL OF PHOTOCHEMICAL SMOG

//

Steven R. Hanna
Air Resources
Atmospheric Turbulence and Diffusion Laboratory
National Oceanic and Atmospheric Administration
Oak Ridge, Tennessee

Published in the proceedings of the 3rd Clean Air Congress
of the International Union of Air Pollution Prevention
Association, held in Dusseldorf, Germany, Oct. 8-12, 1973.

74 1142



Application of a Simple Model of Photochemical Smog

by Steven R. Hanna

Air Resources

Atmospheric Turbulence and Diffusion Laboratory

National Oceanic and Atmospheric Administration

Oak Ridge, Tennessee

Abstract

The simple ATDL dispersion model is extended to predict concentrations of chemically reactive pollutants. The concentrations in the governing equations are non-dimensionalized by using as a scaling factor the concentration predicted by the simple model for inert pollutants. As a result, the influence of any given set of reactions on the system, however complex, can be easily analyzed by examining a set of dimensionless parameters. If these parameters are all less than about 0.1, then chemical reactions are not important and the simple model prediction is valid. The relative importance in any pollution problem of wind speed, source strengths, and atmospheric stability can be assessed. The model is used to estimate hourly concentrations of CO, NO, NO₂, and reactive hydrocarbons at eight stations in the Los Angeles basin for the time period 6 a.m. - 12 noon on 30 September 1969. It is seen that the estimates of CO, NO, and reactive hydrocarbons agree fairly well with observations (correlation coefficients range from .43 to .99), but that the estimates of NO₂ are inconsistent with the observations (correlation coefficients range from -.80 to .78).

Application of a Simple Model of Photochemical Smog

by Steven R. Hanna
Air Resources

Atmospheric Turbulence and Diffusion Laboratory
National Oceanic and Atmospheric Administration
Oak Ridge, Tennessee

1. Derivation of General Equation for the Time Variation of Reactive Pollutants

An application of the simple ATDL model of photochemical smog to a specific day in Los Angeles is given in this paper. In the simple ATDL model for chemically inert substances, such as carbon monoxide or suspended particles, surface concentration [C] (ppm) is proportional to the local area source strength Q (cm³/m²sec) and inversely proportional to the wind speed U(m/sec):

$$[C] = A \frac{Q}{U} \quad (1)$$

The constant parameter A is calculated from the basic theory¹ to equal about 50, 200, and 600 for unstable, neutral, and stable conditions, respectively. For average annual conditions, data from many cities² verify that A equals 225. In the absence of significant removal processes, such as dry deposition or chemical reaction, eq. (1) successfully estimates the magnitude and space and time variation of urban pollution.

To analyze chemical reactions in the atmosphere, it is first convenient to define an atmospheric volume within which pollutant concentrations can be assumed uniform. Since eq. (1) is in effect a box model, then the constant A is equivalent to $\Delta x/Z$. The distance Δx is the region length and the height Z is the average depth of the pollution cloud over the region. For a typical urban region, the height Z equals approximately 2000, 150, and 40m for nonstable, neutral, and stable conditions, respectively.¹ We therefore assume that

the volume within which pollutant concentrations are uniform has length Δx and height Z . The equation describing the time rate of change of concentration $[C_i]$ in this volume is the following:

$$Z \Delta x \frac{\partial}{\partial t} [C_i] = Q_i \Delta x - Z U [C_i] - Z \Delta x \sum_{m=1}^r \alpha_{im} [C_i]^{a_{im}} \prod_{j \neq i} [C_j]^{a_{jm}}. \quad (2)$$

The terms on the right hand side describe the gain of pollutant due to source input, the loss due to advection, and the change due to chemical reactions. The constant α_{im} is proportional to the rate constant for the m th chemical reaction involving species i , and the constant a_{jm} is the stoichiometric coefficient for reactant j in the m th balanced chemical reaction equation. The concentration symbol $[C_j]$ refers to the j th reactive species. There are p species and a total of r reactions.

The key step in our analysis is our method of making eq. (2) dimensionless^{3,4}. All concentrations $[C]$ are normalized by the scaling concentration AQ/U , which is the predicted steady-state concentration for non-reactive pollutants. Time is normalized by the scaling time $\Delta x/U$, which is the time required for the air to pass through the region. The dimensionless parameters $[C_i]^*$ and t^* are defined:

$$[C_i]^* = \frac{[C_i]U}{Q_i A}, \quad t^* = \frac{tU}{\Delta x}. \quad (3)$$

Using these definitions and the identity $A = \Delta x/Z$, eq. (2) takes the dimensionless form:

$$\frac{\partial}{\partial t^*} \ln [C_i]^* = \frac{1}{[C_i]^*} - 1 \quad (4)$$

$$- \sum_{m=1}^r \left[\prod_{j \neq i} [C_j]^*{}^{a_{jm}} \right] \left[\alpha_{im} \frac{\Delta x}{U} \prod_{j \neq i} \left(\frac{Q_j}{U} A \right)^{a_{jm}} \left(\frac{Q_i}{U} A \right)^{a_{im}-1} \right] [C_i]^*{}^{a_{im}-1}.$$

Thus the dimensionless numbers in the square brackets completely determine the solution. If these numbers are all much less than unity, then chemical reactions are not important in a system. From these results, it is easy to determine the effects of meteorological variables on chemical processes.

2. A Specific System for Estimating Photochemical Smog Concentrations.

The equation outlined above is quite general and can be applied to a wide variety of chemical pollutants. As an illustration of the application of the theory, the kinetic mechanism proposed by Friedlander and Seinfeld⁵ is used in the last term of eq. (4). The following dimensionless equations for the time variation of dimensionless concentrations of nitrous oxide, $[\text{NO}]^*$, nitrogen dioxide, $[\text{NO}_2]^*$, and reactive hydrocarbons, $[\text{RH}]^*$, are obtained:

$$\frac{\partial}{\partial t} \ln [\text{NO}]^* = \frac{1}{[\text{NO}]^*} - 1 - D_1 [\text{NO}_2]^* [\text{RH}]^* \quad (5)$$

$$\frac{\partial}{\partial t} \ln [\text{NO}_2]^* = \frac{1}{[\text{NO}_2]^*} - 1 + D_2 [\text{NO}]^* [\text{RH}]^* - D_3 [\text{NO}_2]^* [\text{RH}]^* \quad (6)$$

$$\frac{\partial}{\partial t} \ln [\text{RH}]^* = \frac{1}{[\text{RH}]^*} - 1 - D_4 [\text{NO}_2]^* - D_5 [\text{NO}_2]^* / [\text{NO}]^* \quad (7)$$

The five dimensionless governing parameters D_1 through D_5 are defined by the identities:

$$\begin{aligned} D_1 &= \alpha Q_{\text{NO}_2} Q_{\text{RH}} A^3 Z / U^3 & D_2 &= \alpha Q_{\text{NO}} Q_{\text{RH}} A^3 Z / U^3 \\ D_3 &= \lambda Q_{\text{NO}_2} Q_{\text{RH}} A^3 Z / U^3 & D_4 &= \theta Q_{\text{NO}_2} A^2 Z / U^2 \\ D_5 &= \mu (Q_{\text{NO}_2} / Q_{\text{NO}}) A Z / U, \end{aligned}$$

where the rate constants α , λ , μ , and θ equal $1.7 \times 10^{-3} \text{ ppm}^{-2} \text{ sec}^{-1}$, $3.3 \times 10^{-4} \text{ ppm}^{-2} \text{ sec}^{-1}$, $4.0 \times 10^{-6} \text{ sec}^{-1}$, and $3.3 \times 10^{-5} \text{ ppm}^{-1} \text{ sec}^{-1}$, respectively⁵.

It is assumed that the reaction rates are constant. Consequently we use this technique only for the morning and early afternoon, since the sun does not set in this model.

Based on source data reported by Roth et al.⁶ and Weisburd et al.⁷, it can be assumed that the ratios $Q_{\text{NO}_2} / Q_{\text{RH}}$ and $Q_{\text{NO}} / Q_{\text{RH}}$ equal .2 and .3, respectively. The governing parameters then become:

$$D_1 = 3.3 \times 10^{-4} Q_{RH}^2 A^3 Z/U^3 \quad D_2 = 1.5 D_1 \quad D_3 = .2 D_1$$

$$D_4 = .02 D_1 U/A Q_{RH} \quad D_5 = 2.8 \times 10^{-6} AZ/U$$

where Q_{RH} has the units $\text{cm}^3/\text{m}^2\text{sec}$, Z has the units m , and U has units m/sec .

3. Application to Smog Data from Los Angeles on September 30, 1969

Hourly values of pollutant concentrations and wind speeds for six days in Los Angeles were kindly supplied by R. Sklarew and D. B. Turner. September 30, 1969, is chosen for this application because it is the subject of a similar study by Sklarew et al⁸, who estimate smog concentrations using the "PICK" diffusion model. Since their model is considerably more complex than ours and requires the use of a digital computer, it is interesting to compare their results with ours.

Average hourly concentrations of CO , RH , NO_2 , and NO were calculated for the period 6 a.m. to noon at 8 monitoring stations in the Los Angeles basin. Area source strengths for a 64 km^2 area around each station were determined from source patterns given by Roth et al⁶. Based on the average wind speed during the 6 hour period, and assuming that A equals 200 and Z equals 150m, the constants D_1 through D_5 are calculated for each station. Relevant source data, wind speeds, and values of the constants are given in Table 1.

Table 1
Source Strengths, Wind Speeds, and Constants, $D_1 - D_5$ for Selected Stations in the Los Angeles Basin for 6 a.m. - 12 noon, 30 Sept. 1969

Station	Q_{RH} ($\text{cm}^3/\text{m}^2\text{sec}$)	U (m/sec)	D_1	D_2	D_3	D_4	D_5
Downtown L.A.	.0080	2.0	3.2	4.8	.64	.080	.042
Whittier	.0016	1.2	.60	.40	.12	.045	.070
Reseda	.0018	.8	2.5	3.7	.50	.11	.105
Pomona	.0005	1.2	.060	.090	.012	.014	.070
Azusa	.0010	1.4	.14	.21	.028	.020	.060
Burbank	.0041	1.6	1.7	2.5	.34	.067	.053
West L.A.	.0027	.7	8.3	12.4	1.66	.22	.12
Long Beach	.0032	1.2	2.4	3.6	.48	.092	.070

Eqs. (5) - (7) are used to estimate the variation of $[RH]^*$, $[NO]^*$, and $[NO_2]^*$ with t^* . Eq. (1) is used to estimate the concentration of carbon monoxide. It is assumed that dimensionless concentrations of all substances equal unity at 6 a.m.; i.e., the simple model given by eq. (1) is valid before the sun rises. Dimensional concentrations $[C]$ are recovered by multiplying $[C]^*$ by $[C]$ at 6 a.m. times the ratio of the hourly wind speed at 6 a.m. to the hourly wind speed at the times of interest. Real time is recovered by multiplying t^* by the region length, 50 km, and dividing by the six hour average wind speed. Correlations between the resulting estimates and observed hourly concentrations are given in Table 2.

Table 2

Correlations between Estimated and Observed Hourly Concentrations for Selected Stations in the Los Angeles Basin for 7 a.m. - 12 noon, 30 September 1969.

Station	r_{CO}	r_{RH}	r_{NO_2}	r_{NO}
Downtown L.A.	.97	.99	-.80	.99
Whittier	.92	--	-.45	.88
Reseda	.71	--	.78	.89
Pomona	.43	--	.46	.40
Azusa	.98	.72	.72	.94
Burbank	.48	--	-.75	.92
West L.A.	.63	--	.48	.98
Long Beach	.88	--	.55	.99

From this table it is clear that the ATDL model is fairly successful in the prediction of hourly variations of CO, RH and NO. However, the model is inconsistent in its predictions of NO₂. But the correlation between predictions of NO₂ by the PICK model by Sklarew *et al.*⁸ and observations at the Downtown L.A. station for this period is -.97. The correlations between his RH and NO predictions and observations are .98 and .88, respectively. Thus when our model fails, so also does the PICK model. This failure is probably due to insufficient knowledge of the reaction mechanism for NO₂.

4. Conclusions

A simple model for estimating concentrations of chemically reactive pollutants is derived and applied to Los Angeles smog. Hourly variations of CO, RH, and NO are estimated fairly well by the model. However, this model, as well as other models, fails to provide satisfactory estimates of hourly variations of NO₂.

Acknowledgement

This research was performed under an agreement between the National Oceanic and Atmospheric Administration and the Atomic Energy Commission.

References:

1. Hanna, S. R., "A Simple Method of Calculating Dispersion from Urban Area Sources," J. Air Poll. Control Assoc., 21, 774-777 (Dec. 1971).
2. Gifford, F. A., and S. R. Hanna, "Modelling Urban Air Pollution," Atmos. Envir., 7, 131-136 (Jan. 1973).
3. Hanna, S. R., "A Simple Model for the Analysis of Photochemical Smog," Proceedings A.M.S. Conference on the Urban Environment, Philadelphia, 31 Oct. - 2 Nov. 1972, 4 pp.
4. Hanna, S. R., "A Simple Dispersion Model for the Analysis of Chemically Reactive Pollutants," to be published in Atm. Envir.
5. Friedlander, S. K., and J. H. Seinfeld, "A Dynamic Model of Photochemical Smog," Envir. Sci. and Technol., 3, 1175-1181 (Nov. 1969).
6. Roth, P. M., S. D. Reynolds, P. J. Roberts, and J. H. Seinfeld "Development of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants," Final Rept. under contr. no. CPA-70-148 by Systems Applic., Inc., Beverly Hills. Calif. 90212 for Air Poll. Cont. Off., EPA, Durham, N.C. 27701, 55 pp + 6 appen. (1971).
7. Weisburd, M., L. G. Wayne, R. Danchick, and A. Kokin, "Development of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants," Final Rept. under contr. no. CPA-70-151 by Systems Development Corp., 2500 Colorado Ave., Santa Monica, Calif. 90406, for Air Poll. Cont. Off., EPA, Durham, N.C. 27701, ix + 191 pp (1971).
8. Sklarew, R. C., A. J. Fabrick, and J. E. Prager, "Mathematical Modeling of Photochemical Smog Using the PICK Method," J. Air Poll. Control Assoc., 22, 865-869 (Nov. 1972).