MATHEMATICAL MODELS FOR ESTIMATING WORKPLACE CONCENTRATION LEVELS: A LITERATURE REVIEW

Prepared for:

Economics and Technology Division
U.S. Environmental Protection Agency
401 M. Street, N.W.
Washington, D.C.

Prepared by:

Clement Associates, Inc.
1010 Wisconsin Avenue, N.W.
Washington, D.C. 20007

EPA Contract No. 68-01-6065

Project Officer: Kin F. Wong

October 22, 1981

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. MATHEMATICAL MODELS OF WORKPLACE CONCENTRATION LEVELS	6
A. Mass Balance Models	6
1. Simple Models	8
2. Simple Equilibrium Models	12
3. Complex Models	22
4. Summary of Models	30
B. Miscellaneous Models	32
1. Schroy Model	33
2. Davis Model	37
III. DISCUSSION	40
TECHNICAL APPENDIX: Assignment of Numeric Values to Models' Input Variables	
Methods for Determining Vapor Generation Rates	A-1
Workplace Mixing Factor--k	A-23

LIST OF TABLES

		Page
Table I.	Input Parameters Found in Models	4
Table II.	Measured and Predicted Concentrations of Benzene Using Equation (8)	14
Table III.	Measured and Predicted Concentrations of Hexane Using Equation (8)	15
Table IV.	Measured and Predicted Concentrations of Toluene Using Equation (8)	16
Table V.	Summary of Mass Balance Equations	31
Table VI.	Values of $1/2\pi\sigma_y\sigma_z$ for Equation (40)	34

LIST OF FIGURES

		Page
Figure I.	Mass Balance in an Enclosed Space	7
Figure II.	Graphical Solution of Equation (4)	10
Figure III.	Graphical Solution of Equation (7)	11
Figure IV.	Proposed Method of Relating Plant Volume to Production Volume	20
Figure V.	Graphical Solution of Equation (17)	21
Figure VI.	Comparison of Experimental Results with Results Predicted from Equation (22)	25
Figure VII.	Comparison of Experimental Results with Results Predicted from Equation (25)	26
Figure VIII.	Limits of Validity of Equation (40)	36
Figure IX.	Comparison of Experimental Results with Results Predicted from Equation (45)	39

I. INTRODUCTION

Exposure to a physical, chemical, or biological agent occurs when the agent comes into contact with an individual or group of individuals. The magnitude of this exposure is determined by the amount of the agent in contact with the body and the duration and frequency of contact. Estimations of the magnitude of an exposure are known as "exposure assessments." Exposure assessments are often combined with environmental and health effects data to determine the risk associated with a substance.

Exposure assessments are usually based, in part, on monitoring data. For example, monitoring data are collected to quantify the amount of an agent in food, air, or water. Humans come into contact with these media, which may contain these agents at levels determined by sampling data. Other information, including the duration and frequency of exposure to the agent, is used to complete an exposure assessment.

Monitoring data are not always available or attainable for some situations that require exposure or risk assessments. This typically occurs during the evaluation of premanufacturing notifications (PMNs) of new chemical substances because the chemical has not been manufactured or used prior to or during this evaluation period. However, since the evaluation of a PMN substance requires an assessment of the risk associated

with that substance, some estimate must be made of likely levels of exposure.

In situations such as these where no monitoring data exist, environmental levels of a chemical can be predicted by mathematical modeling. One definition of a mathematical model is "an abstract, simplified mathematical construct related to a part of reality and created for a particular purpose" (Bender 1978). In other words, a mathematical model is an equation (or series of equations) that quantitatively mimics the relevant features of a situation and computes a desired output. Mathematical models have been developed that predict the generation, dispersion, and fate of environmental agents in a variety of different media such as food, air, and water (Drake 1979, Miller 1978).

Exposure to a PMN chemical substance will occur chiefly in an industrial setting during its manufacture or use through contamination of the airspace. Airborne concentrations of a chemical substance are generally determined by industrial air samples, but since the PMN chemical will not have been manufactured or used during the evaluation period, no air sampling data will be available. However, mathematical models can be used to predict airborne concentration of a PMN substance during its subsequent manufacture or use. The following paper is a summary of published models used to predict airborne contaminant concentrations in an industrial setting. To keep the models consistent with each other, the variables have been

standardized for all the modeling equations. For example, some published models represent "concentration" with the variable X. Others use the variable C. As a result, the equations given here may appear to be different from those given in the referenced published version. However, the physical meanings of the variables and the units have not been changed. The variables found in the models are listed in Table I.

A technical appendix, which describes how to assign numeric values to the models' input variables, is attached.

TABLE I

INPUT PARAMETERS FOUND IN MODELS

Variable	Meaning	Units	Found in Models (eqn. no.)
C	Concentration	mass/volume	all
C_a	Average concentration		
C_i	Concentration in infiltration air		20,23,25
C_o	Initial concentration		
C_{eq}	Equilibrium Concentration		8,10,31
C_{max}	Maximum concentration at a distance downwind from the source		32,40
Q	Ventilation Flow Rate	volume/time	2,4,7,8, 10,20
Q_i	Volume flow of infiltration air		23,25
Q_R	Volume flow of recirculated air		23,25
Q_{eff}	Volume flow of effective ventilation rate		10
V	Volume of Room or Enclosure	volume	2,4,7,20, 23,25
t	Elapsed Time	time	2,4,7,20, 23,25
G	Generation Rate (source strength)	mass/time	7,8,10, 20,23,40
G_j	Source strength of the jth source		25,26
$G_{(t)}$	Time dependent source strength		37
k	Mixing Factor	(unitless)	4,7,10, 20,23,25
k_j	Mixing factor of the jth source		26

TABLE I (Continued)

Variable	Meaning	Units	Found in Models (eqn. no.)
E	Efficiency of Air Cleaning Filter	(unitless)	23,26
P	Production Rate	mass/time	17
Vel	Velocity of Workplace Ambient Air Passing Point of Contaminant Release	distance/time	40
J	Time Necessary for Each Source to Complete a Contaminant Generation Cycle	time	26

II. MATHEMATICAL MODELS OF WORKPLACE CONCENTRATION LEVELS

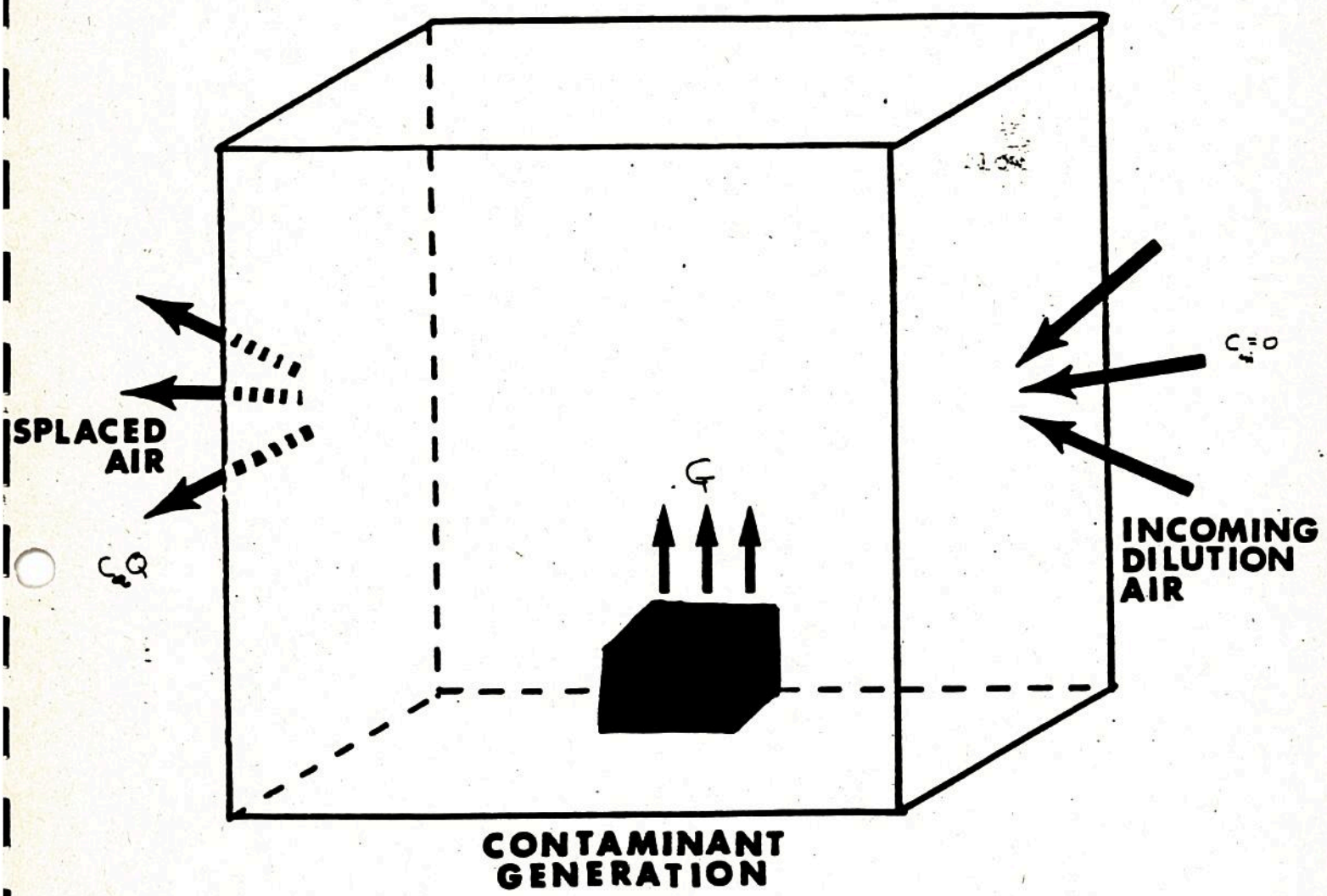
A. Mass Balance Models

The method most commonly used for modeling contaminant concentrations in an industrial environment is an equation describing the mass balance of the contaminant as it is generated in and removed from an enclosed space. This concept is visually illustrated in Figure I. A contaminant will be released into an enclosed space at a given rate, G. This release can be instantaneous, constant, or a function of time. The contaminant can also be released from one or more sources. Simultaneous with the release of the contaminant, a fixed flow of air, Q, will enter the room, diluting and mixing with the contaminated air. To prevent a buildup of positive pressure in the room, the same flow, Q, of contaminated air will leave the room. As a result, the concentration of a contaminant will be continuously changing with time because of the combined effects of contaminant generation, and mixing and dilution with clean ventilation air.

Mass balance models are most applicable for contaminants in the gaseous or vapor states because they follow normal air currents and are not subject to gravitational forces. The concentration of small particles with diameters less than 10-20 microns can also be approximated by mass balance models because the particles are carried with air currents, and their settling rate is negligible.

FIGURE I

MASS BALANCE IN AN ENCLOSED SPACE



$$C_2 V - C_1 V + C_{avg} Q \Delta t = G \Delta t$$

$$C_2 Q t_2 - C_1 Q t_1$$

$$\boxed{V \frac{dc}{dt} = G - CQ} \quad + C_i Q$$

additional term for contaminated air incoming air

other terms

① filtration of incoming air containing contaminants with removal efficiency E

CEQ_v

At $t = 0$ $\quad C = C_0$

1. Simple Mass Balance Models

The simplest equation to describe the mass balance of a contaminant in an enclosed space is:

$$V \frac{dC}{dt} = -CQ. \tag{1}$$

V is the volume of the room, the ventilation air flow is represented by Q, and C is the contaminant concentration. The contaminant release is instantaneous, generating an initial concentration of C_o. The solution of equation (1) is:

$$C = C_o \, e^{-(Q/V)t}. \tag{2}$$

Equation (2) will satisfy mass balance only under ideally mixed conditions. If k[1] is less than 1, implying that the mixing of ventilation air with contaminated air was not complete, the condition of mass balance will be met by equation:

$$V \frac{dC}{dt} = -kQC \tag{3}$$

and the solution of equation (3) is given by:

$$C = C_o \, e^{-k(Q/V)t}. \tag{4}$$

---

[1] See Technical Appendix, Section B, for a discussion of the k-factor or mixing factor.

Equation (4) has been referenced (Bridbord et al. 1975) and is illustrated graphically in Figure II for different values of k.

The contaminant may be released at a constant rate of G (mass/time). The mass balance equation given in equation (1) can be rewritten as:

$$V \frac{dC}{dt} = G - CQ \tag{5}$$

or, if nonideal mixing is assumed:

$$V \frac{dC}{dt} = G - kQC \tag{6}$$

The solution of equation (6) is given as:

$$\boxed{C = G/Q + (C_o - G/Q)e^{-k(Q/V)t}} \tag{7}$$

and is illustrated graphically in Figure III. Equation (7) has also been discussed by several authors (Roach 1977).

FIGURE II

GRAPHICAL SOLUTION OF EQUATION (4)

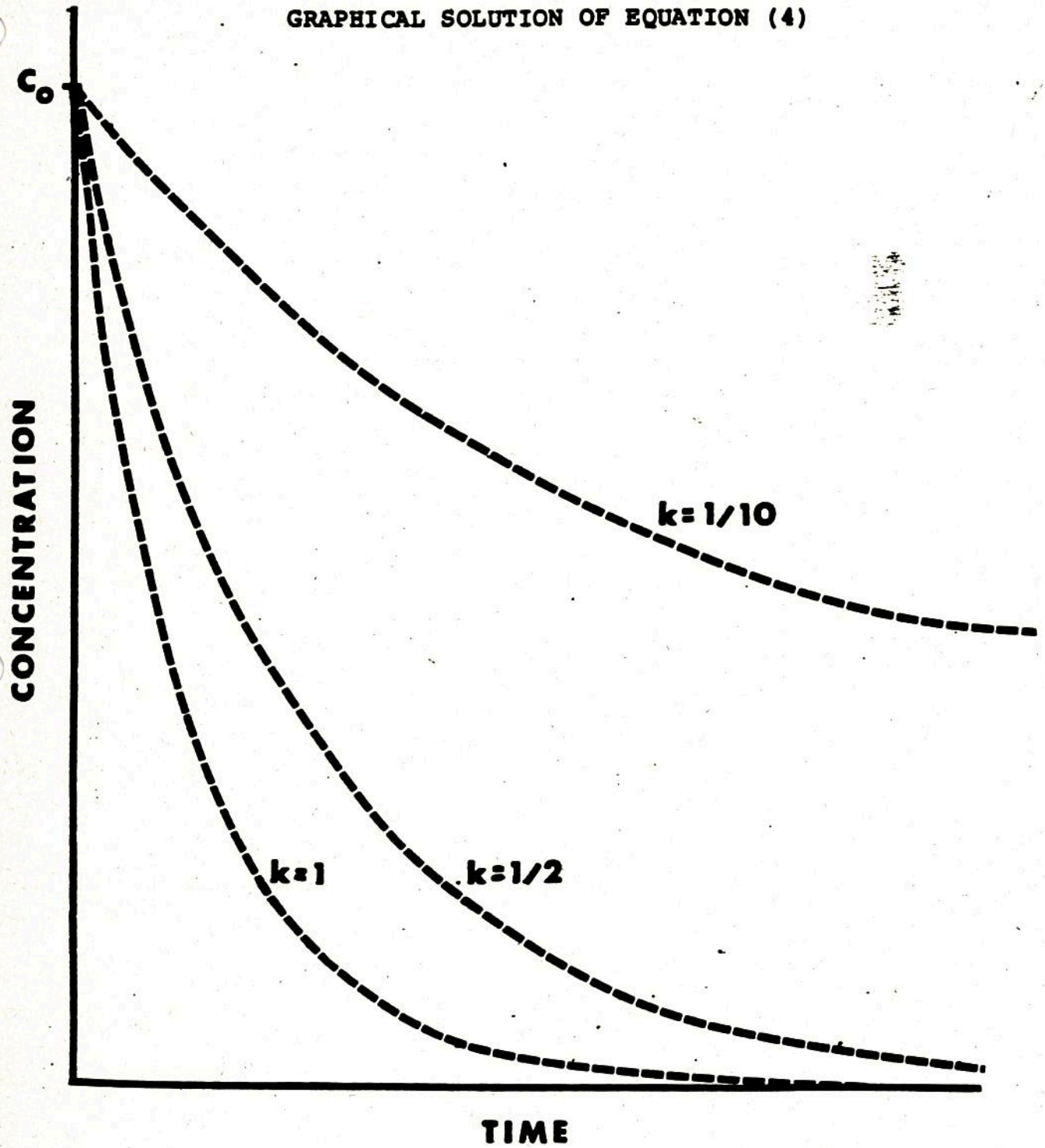
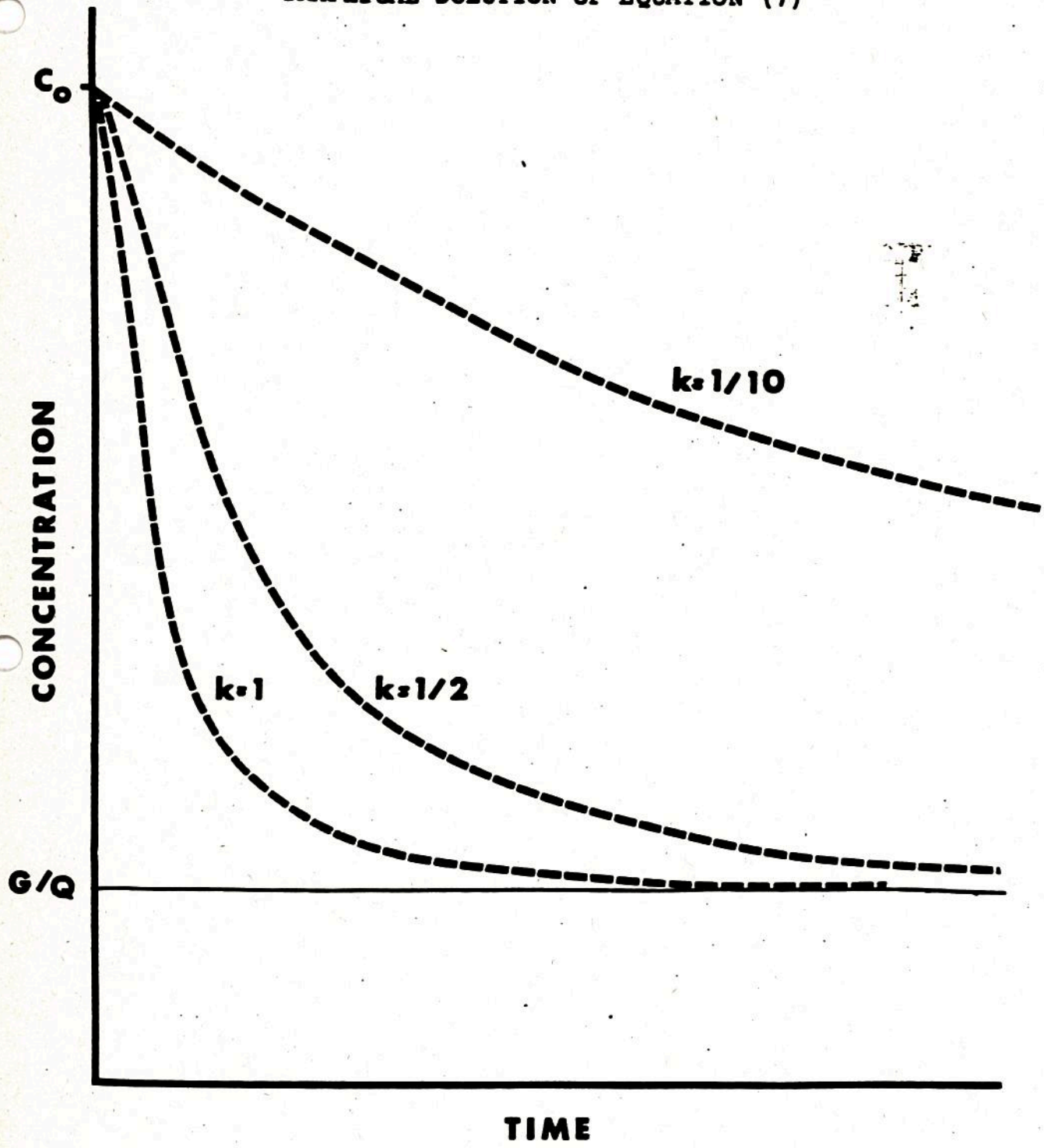


FIGURE III

GRAPHICAL SOLUTION OF EQUATION (7)



2. Simple Mass Balance Equilibrium Models

As t increases, equation (7) will reach an equilibrium concentration, C_{eq}:

$$C_{eq} = G/Q. \tag{8}$$

Several authors have used equation (8) as a model to predict contaminant concentration (Baker 1977, Becker et al. 1979). It is perhaps the easiest model to use because it is not time dependent and requires only two input parameters.

Baker (1977) tested this model for its ability to predict solvent vapor concentrations in three rooms of a tire manufacturing plant. The values for Q in the three different rooms were either directly measured, estimated from measurements taken at other parts of the plant, or taken from company records. The methods used to determine Q in the Baker study can only be used in a predictive model to estimate exposure to a PMN substance if the relevant information is supplied by the submitter.

The method for determining G used in the Baker study was based solely on solvent evaporation rates. (For a discussion of estimating G, see the Technical Appendix, Section A).

Tables II through IV summarize the solvent concentrations in the three rooms of the tire factory that were both measured by air sampling and predicted by equation (8). Two or three predicted concentrations are given for each work area because

different methods were used to estimate Q; each estimate of Q generated a different predicted contaminant concentration.

The measured concentration usually exceeded the predicted concentration by up to a factor of 10. The author concluded that the measured or actual ventilation rate, Q, was greater than the effective ventilation rate, Q_E, due to incomplete mixing, which occurred even at equilibrium. Q is related to Q_E by the k factor as shown in the following equation:

$$Q_E = kQ. \qquad k < 1 \qquad (9)$$

Therefore, equation (8) can be rewritten as:

$$C_{eq} = G/kQ. \qquad (10)$$

(Typical values of k are given in Section B of the Technical Appendix.)

eqn (10) $C_{eq} = G/kQ$

$k = G/C_{meas}Q$

TABLE II

MEASURED AND PREDICTED CONCENTRATIONS
OF BENZENE USING EQUATION (8)

Area	Measured	Predicted (eqn (8))	k (eqn (10))
Tire Building	.33 ppm	.30 ppm[a]	.9
		.10 ppm[a]	.30
		.15 ppm[a]	.45
Final Finish	.13 ppm	.046[b]	.36
		.026[c]	.43
Cement House	.66	.067[b]	.10
		.047[c]	.07

[a] Q estimated

[b] Q measured

[c] Q determined from company records

(Baker 1977)

TABLE III

MEASURED AND PREDICTED CONCENTRATIONS
OF HEXANE USING EQUATION ~~(8)~~ (10)

Area	Measured	Predicted	k
Tire Building	8.3 ppm	11.69[a]	1.4 ? k<1 ?
		3.74[a]	.45
		5.89[a]	.71
Final Finish	1.29 ppm	1.01[b]	.77
		.57[c]	.43
Cement House	10.2 ppm	3.39[b]	.33
		2.41[c]	.24

[a] Q estimated

[b] Q measured

[c] Q determined from company records

(Baker 1977)

TABLE IV

MEASURED AND PREDICTED CONCENTRATIONS OF TOLUENE USING EQUATION ~~(8)~~ (10)

Area	Measured	Estimated	k
Tire Building	.40 ppm	.42[a]	1.01
		.13[a]	.32
		.21[a]	.52
Final Finish	.65 ppm	.31[b]	.48
		.18[c]	.28
Cement House	.53 ppm	.099[b]	.18
		.071[c]	.13

[a] Q estimated

[b] Q measured

[c] Q determined from company records

(Baker 1977)

Equation (13) can be rewritten as:

$$V(M^3) = 4.67\ P(kg/day) + 5{,}660. \qquad (14)$$

A graph of equation (14) is given in Figure IV. The authors did not fully explain the rationale behind this equation, and its accuracy is questioned.

The final assumption made in the model is that industrial ventilation will always be 10 air changes per hour. In other words, a volume of ventilation air equal to 10 times the room volume will flow through the room in 1 hour. The assumed room ventilation rate, $Q(mg^3/hour)$, will be:

$$Q(m^3/hour) = 10V\ (m^3)/hour. \qquad (15)$$

If the room volume is a function of maximum daily production, then ventilation flow will also be a function of production. Combining equations (14) and (15) produces the following expression:

$$Q(m^3/hour) = \frac{10[4.67 \times P(kg/day) + 5{,}660]\,m^3}{1\ hour}. \qquad (16)$$

If the in-plant concentration is defined by the ratio of $G(mg/hour)$ to $Q(m^3/hour)$, then the ratios of equations (12) and (16) can be written as:

$$\boxed{C(mg/m^3) = \frac{4.167 \times P(kg/day)}{4.67 \times P(kg/day) + 5{,}660}.} \qquad (17)$$

Becker model

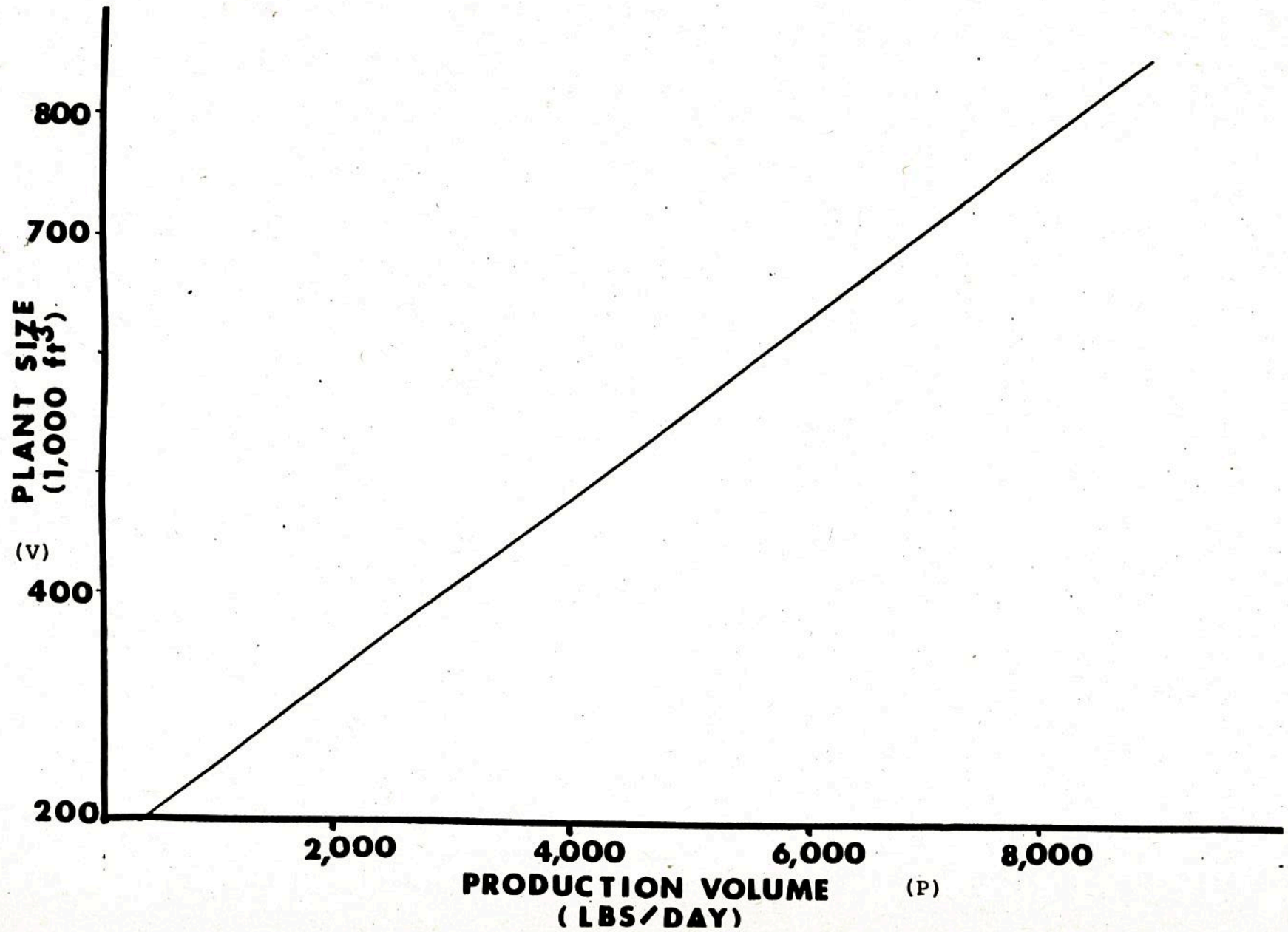
not realistic!

Equation (17) is the model given by Becker et al. (1977). Its graphical solution is given in Figure V. Although the only input into the Becker model is P, maximum daily production, the model is still based on equation (8). The Becker model multiplies the numerator of equation (17) with a variable, R. R is defined as "persistence" (R = 1.0 for a gaseous contaminant and 3.0 for a nonvolatile). No further explanation of R nor the derivation of its values was given.

The derivation of the Becker model, as given in this section, was not presented by Becker et al. (1979). Further, the model and its three assumptions, given by equations (12), (14), and (15), were not verified experimentally in that paper.

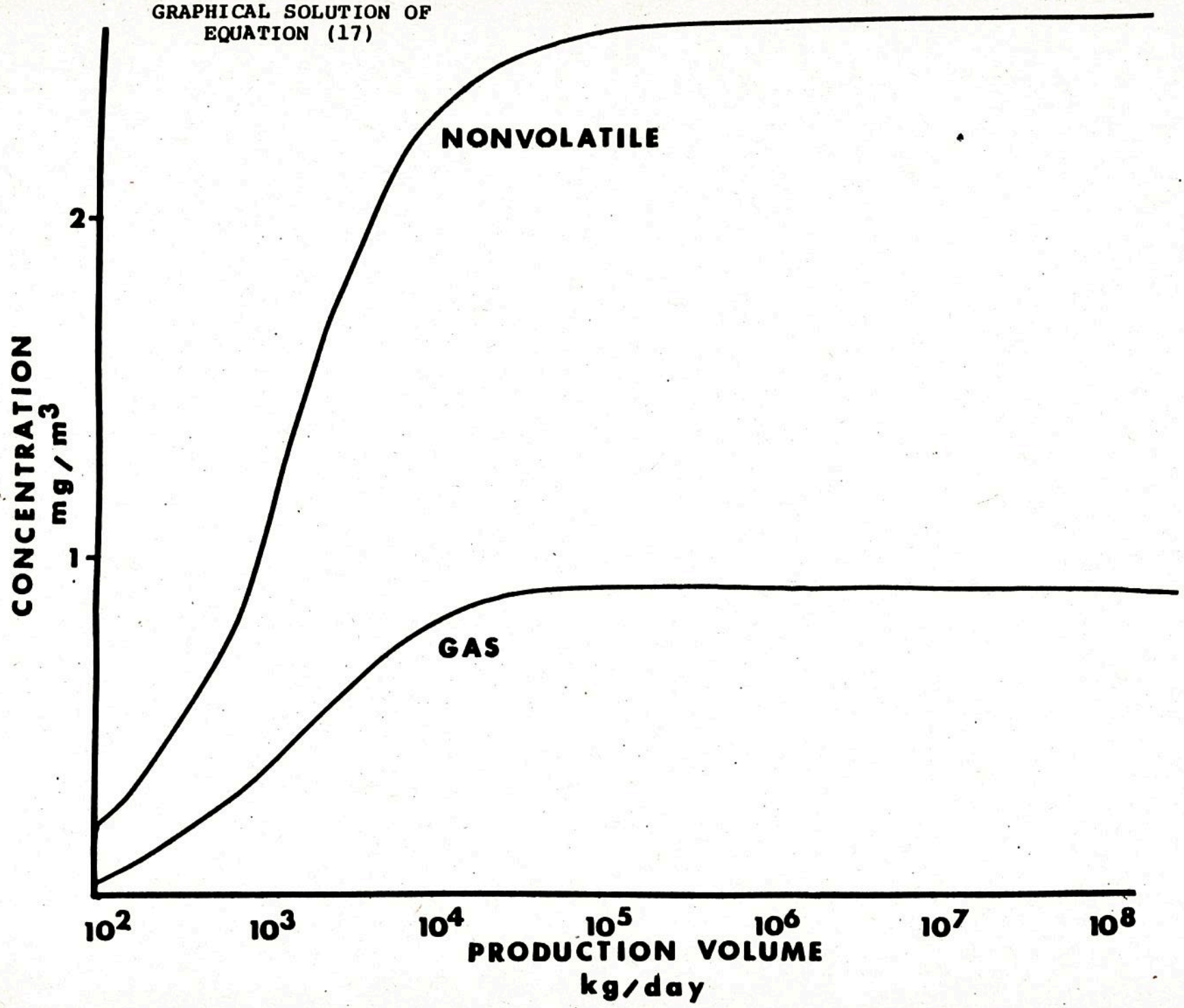
FIGURE IV

PROPOSED METHOD OF RELATING PLANT VOLUME TO PRODUCTION VOLUME



FIGURE

GRAPHICAL SOLUTION OF EQUATION (17)



3. Complex Mass Balance Models

Any terms that describe the generation or removal of a contaminant from an enclosed space can be respectively added or subtracted from the simple mass balance equations (2) and (5). For example, the contaminant can be generated from many sources or can be characterized as a function of time. The contaminant can also enter the room if it is contained in the ventilation air.

Although the mass balance equations that contain the additional terms are not complicated, the integrated solutions to these equations are. The equations are also more difficult to use because they require more input parameters. However, if an industrial setting is sufficiently well characterized and all the necessary inputs to the model are known, these equations may give more accurate estimates of actual concentrations.

Harris et al. (1979) described a mass balance model that contains an additional term for the concentration of contaminant in the incoming dilution (infiltration) air. The equation is given by:

$$V \frac{dc}{dt} = G + QC_i - QC. \qquad (18)$$

Integration of equation (18) yields:

$$C_t = C_o e^{-(Q/V)t} + (C_i + G/Q)(1 - e^{-[Q/V]t}). \qquad (19)$$

If the mixing factor is considered in equation (18), its integration will be rewritten as:

$$C_t = C_o\, e^{-k[Q/V]\,t} + (C_i + C/Q)(1 - e^{-k[Q/V]\,t}). \qquad (20)$$

Turk (1963) also presents a model that accounts for the presence of the pollution in infiltration air. However, his model assumes that some of the contaminated air in the room will be recirculated after it is passed through a filtering device with a known efficiency, E. The mass balance equation for a workplace in which the contaminated air is filtered and recirculated will be written as:

$$V\,\frac{dc}{dt} = G + C_iQ_i - CQ_i - CEQ_r. \qquad (21)$$

The solution of equation (21) is written as:

$$C = C_o\, e^{-([Q_i+EQ_r]/V)\,t} + \frac{C_iQ_i+G}{Q_i+EQ_r}\,(1 - e^{[(Q_i+EQ_r)/V]\,t}). \qquad (22)$$

If the k factor is considered, equation (22) will be written as:

$$C = C_o\, e^{-k([Q_i+EQ_r]/V)\,t} + \frac{C_iQ_i+G}{Q_i+EQ_r}\,(1 - e^{-k[(Q_i+EQ_r)/V]\,t}). \qquad (23)$$

Ishizu (1980) noted that since k describes a difference between the actual and effective ventilation flows (k = Q effective/Q actual), his published model modifies equation (21) as follows:

should k be here?

$$V \frac{dc}{dt} = G + C_i k Q_i - C k Q_i - C k E Q_r . \qquad (24)$$

The integration of this equation produces:

$$C = C_o \, e^{-k([Q_i+EQ_r]/V)t} + \frac{kC_iQ_i+G}{(kQ_i+EQ_r)} \left(1 - e^{-k[(Q_i+EQ_r)/V]t}\right). \qquad (25)$$

To verify his model, Ishizu compared the concentrations predicted by equations (22) and (25) with the actual smoke concentration in a room containing smouldering cigarettes with a known rate of contaminant release. The room volume and ventilation rate were also known. The results of these comparisons are given in Figures VI and VII. The results of this experiment show that equation (25) was better able to predict the concentration of smoke in a test chamber.

FIGURE VI

COMPARISON OF EXPERIMENTAL RESULTS WITH RESULTS PREDICTED FROM EQUATION (22)

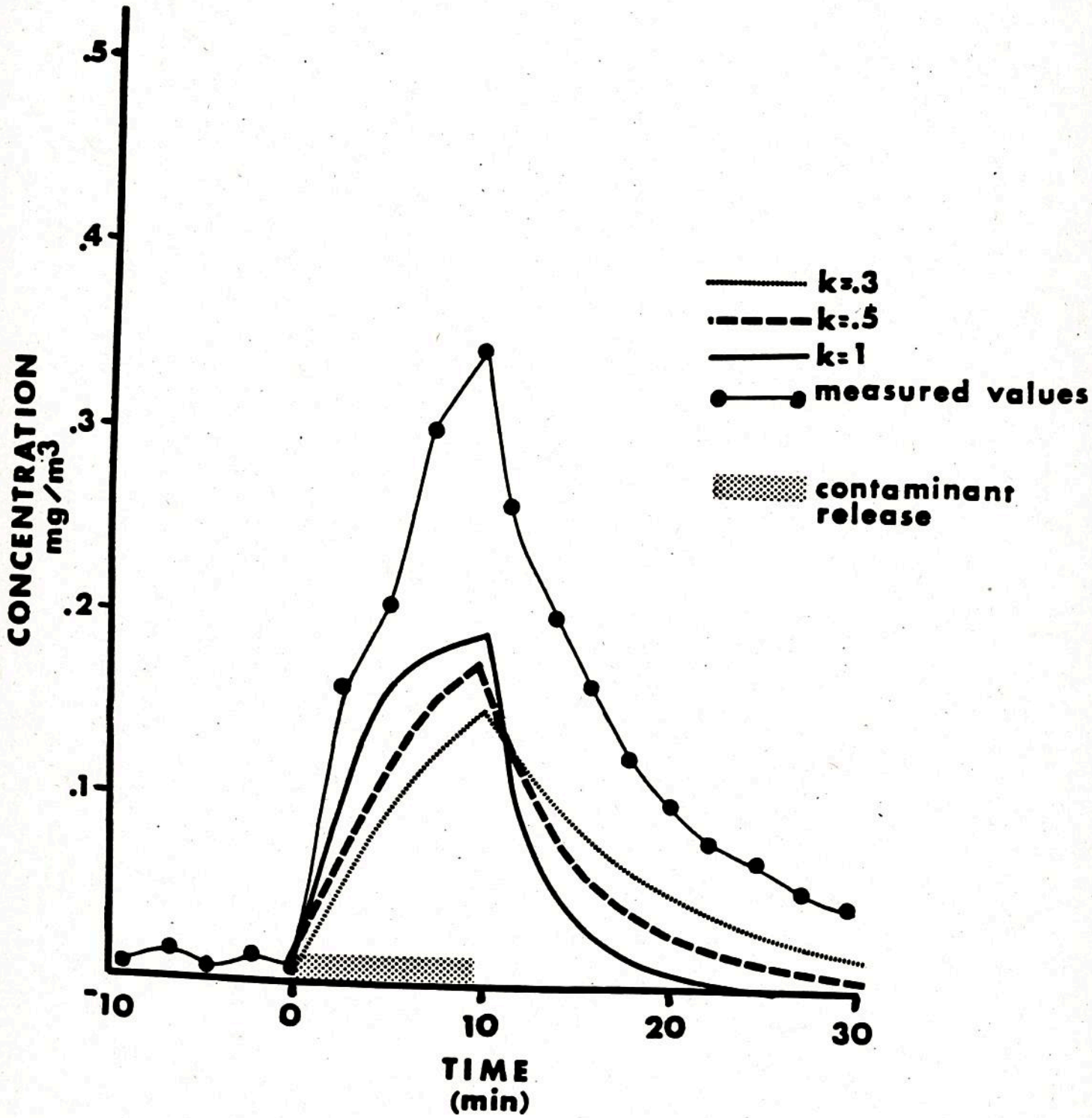
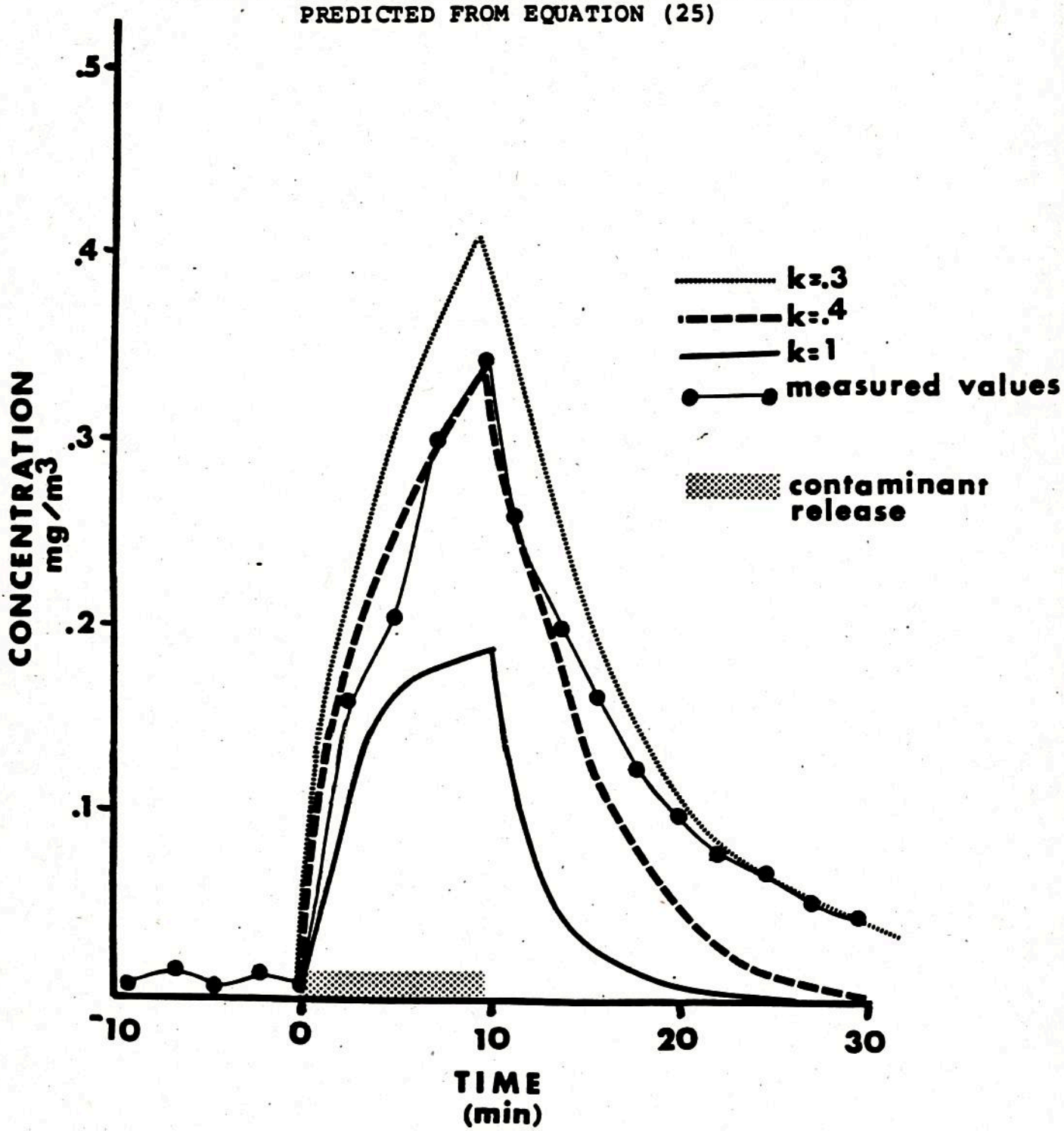


FIGURE VII

COMPARISON OF EXPERIMENTAL RESULTS WITH RESULTS PREDICTED FROM EQUATION (25)



Esman (1978) published the most complex mass balance model used for predicting contaminant concentration in enclosed spaces. His model accounts for multiple sources in which each source has its own generation rate and mixing factor. Further, each source will be periodic and will only be releasing contaminant for part of a cycle; it will be inactive the remainder of the time. The duration of the cycle for each source will be contaminant J_i. During α_i fraction of time J_i, the contaminant will be released, and for the remaining fraction of time, $1-\alpha_i$, the source will not release contaminant.

The solution of the mass balance equation for the completion of n cycles will be:

$$C(t) = C_{in}\exp(-\beta_o t) + \frac{Q_o C_o}{Q_o + EQ_R}[1 - \exp(-\beta_o t)] + \sum_{j=1}^{m}\sum_{i=1}^{n_j}(B_{ij}R_{ij} + B_{ij}P_{ij}) \qquad (26)$$

where:

$$\beta_{ij} = \frac{k_{ij}(Q_o + EQ_R)}{V} \qquad (27)$$

$$P_{ij} = 1 - \exp(-\beta_{ij}\alpha_{ij}J_{ij}) \qquad (28)$$

$$R_{ij} = [\exp -\beta_{ij}(t - \sum_{1}^{i-1} J_{ij})][1 - \exp(-\beta_{ij}\alpha_{ij})] \qquad (29)$$

$$\beta_{ij} = \frac{G_{ij}}{k_{ij}(Q_o + EQ_R)}. \qquad (30)$$

The subscript "i" is the time interval index and "j" is the source index.

Because all of the parameters for each individual cycle are not likely to be known, even for the most well-studied environments, one can estimate the average concentration and the peak concentration for plants with multiple contaminant sources. These quantities have been derived as:

$$C_{eq} = \frac{Q_i C_i}{Q_i + EQ_R} + \sum_{j=1}^{m} B_j \alpha_j \tag{31}$$

and:

$$C_{max} = \frac{Q_i C_i}{Q_i + EQ_R} + \sum_{j=1}^{m} Bj \; \frac{1-\exp\,(-B_j \alpha_j J_j)}{1-\exp\,(B_j J_j)}. \tag{32}$$

Ishizu (1980) considered the mass balance equation given in equation (24) in which G was a function of time. Thus far, G has always been considered to be constant. When G is time variant, equation (24) is rewritten as:

$$V \frac{dC}{dt} = G(t) + C_i k Q_i - CkQ_i - CkQ_r E \tag{33}$$

Rewriting equation (33) yields:

$$dC/dt + PC = Q \tag{34}$$

where:

$$P = \frac{k(Q_i + EQ_r)}{V} \tag{35}$$

$$Q = \frac{G(t) + C_i kQ_i}{V}. \tag{36}$$

Since equation (34) is a linear equation of the first order, it can be solved as:

$$C = e^{-Pt}\left(\int_o^t e^{Pt} Q\, dt + C_0\right) \tag{37}$$

When G(t) is expressed by power functions as:

$$G(t) = at^n$$

where a is a constant and n is an integer (0,1,2,3,...), then:

$$C = \frac{a}{V}\left[\frac{t^n}{P} - \frac{nt^{n-1}}{P^2} + \frac{n(n-1)t^{n-2}}{P^3} - \ldots + (-1)^{n-1}\frac{n!t}{P^n} + (-1)n\frac{n!}{P^{n+1}}\right] + \frac{C_i kQ_i}{VP} + C_o - \frac{a + C_i kQ_i}{VP} e^{-Pt}. \tag{38}$$

When G(t) is expressed by sine functions as:

$$G(t) = b \sin (ct)$$

where b and c are constants, then:

$$C = e^{-Pt}\left[\frac{b}{V}\frac{e^{Pt}(P\sin[ct] - c\cos[ct]) + c}{P^2 + c^2} + \frac{C_i k Q_i e^{Pt} - 1}{V \quad P} + C_o\right] \tag{39}$$

Other forms of G(t) can be solved by referring to a table of integrals.

4. Summary of Mass Balance Models

Table V summarizes and compares all of the mass balance equations found in Section II-A, Mass Balance Models. This table illustrates that all the models are essentially similar and only differ by factors added to or subtracted from the mass balance equation. Other mass balance models can be derived for any industrial setting in which a contaminant is generated in and removed from an enclosed space.

TABLE V
MASS BALANCE MODELS

Mass Balance Equation	Solution
$V \frac{dC}{dt} = - CQ$	$C = C_o e^{-(Q/V)t}$
$V \frac{dC}{dt} = - kCQ$	$C = C_o e^{-k(Q/V)t}$
$V \frac{dC}{dt} = G - CQ$	$C = G/Q + (C_o - G/Q) e^{-(Q/V)t}$
$V \frac{dC}{dt} = G - kCQ$	$C = G/Q + (C_o - G/Q) e^{-k(Q/V)t}$
$V \frac{dC}{dt} = G + C_iQ - CQ$	$C = C_o e^{-(Q/V)t} + (C_i + G/Q)(1 - e^{-(Q/V)t})$
$V \frac{dC}{dt} = G + kC_iQ - kCQ$	$C = C_o e^{-k(Q/V)t} + (C_i + G/Q)(1 - e^{-k(Q/V)t})$
$V \frac{dC}{dt} = G + C_iQ_i - CQ_i - CEQ_r$	$C = C_o e^{-((Q_i + EQ_r)/V)t} + \frac{C_iQ_i + G}{Q_i + EQ_r}(1 - e^{-((Q_i + E_r)/V)t}$
$V \frac{dC}{dt} = G(t) + kC_iQ_i - kCQ_i - kCEQ_r$	Variable -- depends on the function G(t)

B. Miscellaneous Models

Two other models that estimate contaminant concentrations have been described in the literature. These models are not based on the principles of mass balance, dilution, and mixing as were the models discussed previously. One model characterizes the behavior of an airborne substance in terms of Gaussian diffusion; the other relates the behavior of airborne particles to aerosol mechanics. The former model is most applicable to substances manufactured or used in rooms with large volumes; the latter is applicable to large, heavy particles whose airborne behavior will be affected by gravitational settling.

1. Schroy Model

Schroy (1979) developed a modeling procedure that utilizes both emission rate (source strength) and Gaussian diffusion. Gaussian diffusion is a probabilistic phenomenon in which particles engage in "random walks" in space, gradually and predictively moving away from a source. Gaussian dispersion models are generally used to model air pollution (Turner 1969). Gaussian models are generally more applicable to contaminants generated in rooms with large volumes or to chemicals manufactured or used outdoors.

The model is designed to predict the maximum downwind concentration of the contaminant as a function of distance from the source. It can calculate the expected workplace concentration at a given point either from one source or from a number of sources.

The air dispersion equation for maximum downwind concentrations at a given distance from the source is given as:

$$C_{max} = 57.715 \times G\ (1/Vel)\,(1/2\pi\sigma_y\sigma_z)_d. \qquad (40)$$

The variables σ_y and σ_z are defined as diffusion coefficients (in meters), which are functions of the distance, d, from the contaminant. The quantity $1/(2\pi\sigma_y\sigma_z)$ is also a function of distance. Values of $1/(2\pi\sigma_y\sigma_z)$ as a function of distance, d, are given in Table V. G must be expressed in grams per hour, and velocity is expressed in feet per minute.

standa devia of the profi in y or pla

$$C = \frac{Q \leftarrow \text{gen rate}}{2\pi\sigma_y\sigma_z \underset{\uparrow \text{vel}}{u_0}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right)\left(\left[\exp - \frac{(z-h)^2}{2\sigma_z^2} + \exp - \frac{(z+h)^2}{2\sigma_z^2}\right]\right)$$

for x, y, z point away from stack of height h

TABLE VI

VALUES OF $1/2\pi\sigma_y\sigma_z$ FOR EQUATION (40)

DISTANCE, d		VALUE OF	DISTANCE, d		VALUE OF	DISTANCE, d		VALUE OF
Feet	Meters	$(1/(2\pi\sigma_y\sigma_z))$	Feet	Meters	$(1/(2\pi\sigma_y\sigma_z))$	Feet	Meters	$(1/(2\pi\sigma_y\sigma_z))$
1.5		0.1458	12.0		0.07431	65.6	20	0.01989
1.64	0.5	0.1447	13.12	4.0	0.07074	98.4	30	0.01255
2.0		0.1420	14.0		0.06844	131.0	40	0.00938
3.0		0.1347	16.0		0.06324	164.0	50	0.00793
3.28	1.0	0.1326	16.41	5.0	0.06217	196.8	60	0.00642
4.0		0.1259	18.0		0.05873	229.7	70	0.00553
5.0		0.1166	19.69	6.0	0.05507	262.5	80	0.00463
6.0		0.1072	20.0		0.05451	295.3	90	0.00426
6.56	2.0	0.1020	25.0		0.04912	328.1	100	0.00372
7.0		0.09929	26.25	8.0	0.04528			
8.0		0.09288	29.53	9.0	0.04188			
9.0		0.08653	30.0		0.04131			
9.84	3.0	0.08120	32.80	10.0	0.03789			
10.0		0.08069	35.0		0.03521			

Workplace concentrations can be calculated for any location by summing the concentrations due to n individual sources:

$$(C_{max})_{total} = \sum_{i=1}^{n} (C_{max})_i . \tag{41}$$

The limits of the model's validity are shown visually in Figure VIII. The model is only valid downwind from an unconfined plume for points lying in an x,y plane. The plane is defined by two vectors, the air velocity vector and a vector perpendicular to the floor. Further, the limits of validity are bounded on the x-axis of the plane by the distance:

tan 8.6° = 0.1512

$$X = h(\tan 8.6°). \tag{42}$$

min ?

It is bounded on the y-axis by the coordinates:

$$y_{lower} = h - d(\tan 8.6°) \tag{43}$$

and

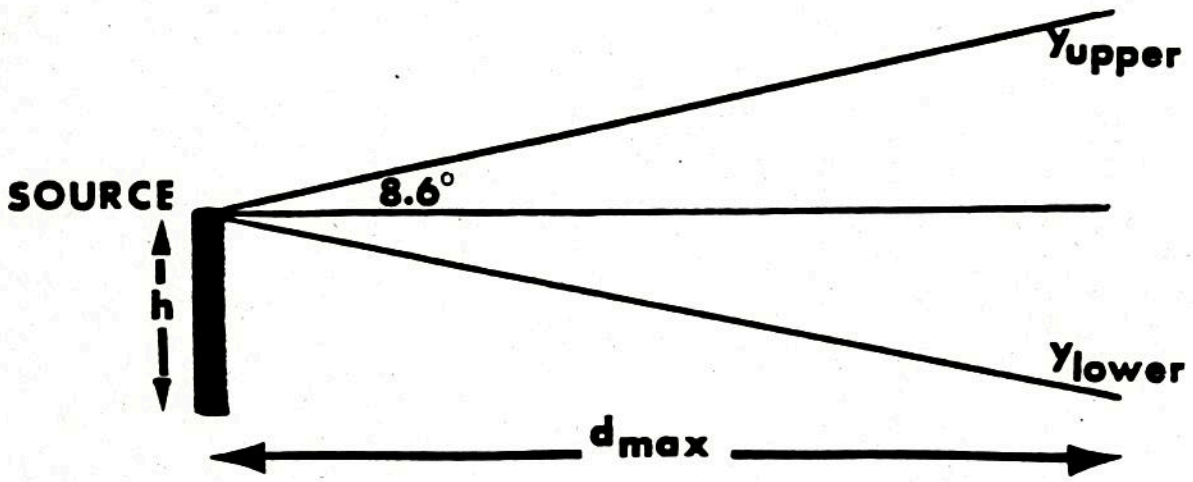
$$y_{upper} = h + d(\tan 8.6°). \tag{44}$$

The variable h is defined as the height of the source on the y-axis, and d is the distance from the source on the x-axis.

No experimental verification of the model was given in the paper.

FIGURE VIII

LIMITS OF VALIDITY OF EQUATION (40)



2. Davis Model

Davis (1971) developed a model that calculated aerosol concentration in a closed vessel. The model was based on the properties and mechanics of airborne particles such as particle generation, coagulation, and settling velocity. The theory on which the model is based is very complicated; thus, the model's derivation (given in the paper) is not repeated. The equations in the model are also complicated, and it is advisable to use the model on a computer.

The following variables and physical constants are inputs into the model:

N_o = initial particle number concentration (no./cm^3)

ρ = particle density (g/cm^3)

V_{min}, V_{max} = minimum and maximum particle volumes (cm^3)

G = mass generation rate (g/cm^3-sec)

h = height of source (cm)

K = coagulation rate constant
= 3×10^{-10} cm^3/particle-sec

g = acceleration due to gravity
= 980 cm/sec^2

η = viscosity of air
= 1.81×10^{-4} gm/cm-sec

g = mean free path of molecules in air
= 0.07 mm = 7×10^{-6} cm.

Each of these input variables and constants is used in the equation to determine aerosol number concentration (number particles/cm^3) at a given time t:

$$N_t = - \frac{K' + R + (K' + R)\ e^{-Rt}}{2K(1 - Qe^{-Rt})} \tag{45}$$

where:

$$K' = VC/h \tag{46}$$

$$V = (3/4\pi)^{2/3}\ (2\rho g/9\eta)\,AE \tag{47}$$

$$A = (1/V_{min} - 1/V_{max})^{-1} \tag{48}$$

$$E = 3(V_{min}^{-1/3} - V_{max}^{-1/3}) \tag{49}$$

$$C = 1 + (3A\lambda/2E)\,(4\pi/3)^{1/3}\ (V_{min}^{-2/3} - V_{max}^{-2/3}) \tag{50}$$

$$R = [(K')^2 + 4KK'']^{1/2} \tag{51}$$

$$K'' = GB/A\rho \tag{52}$$

$$B = 1/\ln\ (V_{max}/V_{min}) \tag{53}$$

$$Q = \frac{2KN_o + K' - R}{2KN_o + K' + R}\ . \tag{54}$$

The calculated value of N_t can be converted to a mass concentration at a given time t by the equation:

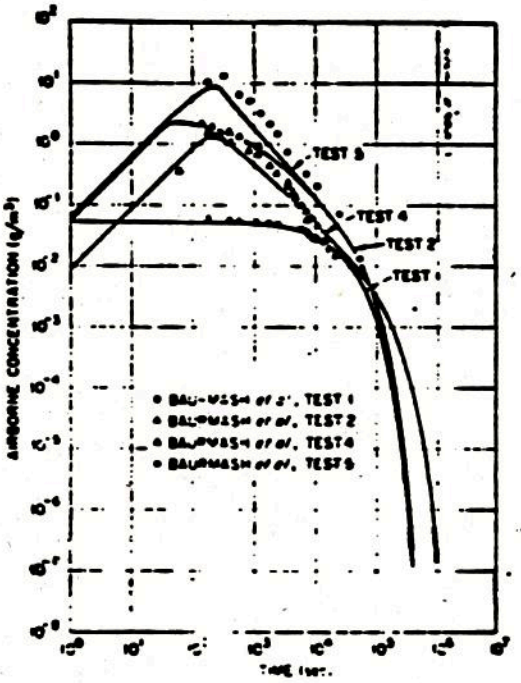
$$M_t = N_t\ \rho\ A/B. \tag{55}$$

This model has been verified experimentally in a test chamber. Figure IX shows the comparison of the calculated and observed concentrations as a function of time. The input parameters were controlled by the author.

FIGURE IX

COMPARISON OF EXPERIMENTAL RESULTS WITH RESULTS

PREDICTED FROM EQUATION (45)



III. DISCUSSION

The most commonly used modeling methodology for determining exposure to a substance in an enclosed space consists of mass balance equations. These equations describe the change in contaminant concentrations over time as the contaminant simultaneously enters and leaves the space.

The simplest mass balance equation approaches an equilibrium concentration of:

$$C_{eq} = G/Q \tag{56}$$

or

$$C_{eq} = G/kQ. \tag{57}$$

These equations require only two or three input variables and may, in fact, be the most practical (although not the most precise) models for estimating workplace concentration levels of PMN substances. Because the PMN substance will not have been manufactured or used during the PMN evaluation period, the many inputs found in the more complicated models cannot be sufficiently characterized to warrant the models' use.

A modified approach for solving equation (56) was proposed in a document written specifically for the purpose of describing how to predict exposures to new chemical substances (Becker et al. 1979). However, the model defines both G and Q as linear functions of production volume (or amount used). Therefore, airborne concentration is related solely to production rate according

to the model and ignores all other factors such as the different physical and chemical properties of substances. It is obvious that a plant that uses 500 pounds a day of a highly volatile solvent will have a higher airborne concentration of the solvent than a plant that uses 500 pounds of a less volatile solvent. As discussed in the Technical Appendix to this document, the generation rate will be related to both the physicochemical properties of the substance and engineering aspects of its use. Further, Figure V, a graphical representation of the model, shows that the airborne concentration of a gas should never exceed 0.9 mg/m^3. This has frequently been shown to be untrue.

At present, neither the Occupational Safety and Health Administration (OSHA) nor the National Institute of Occupational Safety and Health (NIOSH) have standard modeling methodologies for predicting workplace concentrations. One NIOSH official (Leidel 1981) explained that the agency is generally skeptical of such modeling procedures because so many relevant factors cannot be included in even the most complicated models. These factors include and are not limited to specific environmental determinant variables such as airflow patterns around specific workers, age and layout of plant, and degree of automation; temporal determinant variables such as time of day, day of year, and season; and behavioral determinant variables such as employee work practices, management attitudes, and presence of occupational health personnel. The errors associated with

each of these models in an actual industrial setting, although modified somewhat by the k factor, will still exist at an undetermined magnitude.

It should be noted, however, that OSHA and NIOSH have no specific need for mathematical models that predict airborne concentrations. They have the resources and capabilities to collect actual sampling data of existing chemicals. EPA, on the other hand, must predict the occupational exposure and subsequent risk of chemicals prior to their manufacture and use. It is therefore a question of policy to decide whether estimates of workplace exposure generated from existing modeling techniques, in spite of their limitations, are more beneficial in the PMN evaluation process than no exposure estimates.

TECHNICAL APPENDIX

ASSIGNMENT OF NUMERIC VALUES TO MODELS' INPUT VARIABLES

(2) Intrinsic properties of a chemical that determine its tendency to volatilize and, thus, enter the gas phase include:

- vapor pressure
- molecular weight
- molecular volume. ? repektwi

The manner in which these factors (especially the latter set) affect the extent of exposure will be described in the following sections with emphasis on procedures for estimating values of such factors to be used in exposure assessments.

A series of increasingly sophisticated models have been employed to calculate airborne contaminant concentrations. In such models, airborne concentrations are expressed as a function of the room volume, V; room ventilation rate, Q; and a generation rate, G. G is defined as the rate at which a contaminant enters the gas phase. Since room volume is easily determined, and methods for measuring or estimating ventilation rates have been developed (ACGIH 1978), the problems associated with performing an exposure assessment have been reduced to obtaining values for the generation rate, G. The remainder of this appendix is devoted to factors affecting G and the techniques for determining such generation rates from MPD elements and information found in the open literature.

METHODS FOR DETERMINING VAPOR GENERATION RATES

I. Introduction

The main section of this document discusses a series of models for calculating the concentration of airborne contaminants employed in exposure assessments. One of the key input parameters required in these models is the rate that a substance is transformed from a liquid or solid to a gas. These are termed generation rates, G. This section details methods for determining the parameter G using information available during the PMN period.

Frequently, the primary source of exposure associated with the manufacture or use of a particular chemical product is through local contamination of the ambient air space. The extent to which such contamination occurs is a function of two groups of factors:

(1) Engineering factors associated with the conditions under which a chemical is manufactured or used such as:

- ventilation rates
- room volume
- the extent to which a chemical is in direct contact with the air.

These factors have been discussed in the main body of this report.

suggests, G is a function of (1) the equilibrium vapor pressure, p^o, (2) the surface area of the liquid in contact with the air, A, and (3) the overall mass transport coefficient, K. A brief analysis of the evaporation process presented in the following section relates transport coefficients, K, to gas phase diffusion coefficients, D (which in turn are a function of molecular weights and volumes as outlined in Section IV-B).

III. The Evaporation Process

When a liquid is exposed to air, molecules in the vicinity of the surface with sufficient kinetic energy to overcome attractive forces present in the liquid, escape into the gas phase. Such migration is initially rapid and causes the air space immediately adjacent to the surface to become saturated. The net migration of material from the liquid into the gas phase decreases with time, however, because the number of molecules moving in the opposite direction increases with the concentration of molecules in the adjacent air space. (At equilibrium, the gas phase concentration of molecules reaches the intrinsic vapor pressure of the liquid and migration across the surface is equal in both directions. Thus, no net movement of material occurs.)

Movement of molecules away from the interface[1] into the bulk of the gas phase is governed by diffusion.

---

[1] An arbitrarily thin volume element centered on the surface of the liquid and extending equally into the gas and liquid phases.

II. Factors Affecting Generation Rates

The simplest equation describing the generation rate for a volatile liquid (Thibodeaux 1979) is:

assumptions?

$$G = \frac{M}{RT} KA(P^{o}-P) \qquad (1)$$

driving force

In equation 1, the generation rate, G, is in g/sec. A is the area of the surface from which the liquid is evaporating in cm^2. K is the overall mass transfer coefficient in cm/sec and represents a proportionality constant relating the driving force for evaporation to the generation rate. The driving force for evaporation, $(P^{o}-P)$, is the difference between the equilibrium vapor pressure, P^{o}, of the liquid at ambient temperature, and the actual partial pressure, P, of the vapor present in the gas phase. Both P^{o} and P are expressed in atmospheres. (M, the molecular weight of the liquid in g/mole; R, the universal gas constant in $cm^3 atm/mole^{o}k$; and T, the ambient temperature in ^{o}k all represent constants required solely for the units in equation 1 to be consistent.) For most important applications, $P^{o}>P$ so that G is effectively independent of the ambient gas phase concentration.

? basis

(depends on molecular interaction?)

$$G = \frac{M}{RT} KAP^{o} \qquad \text{for } P^{o} \gg P \qquad (2)$$

(A method for assessing exposure when P is significant is presented later in this appendix in Section IV-E.) As equation 2

In general, the rate of migration across the interface (intrinsic evaporation) is rapid relative to the rate of diffusion away from the vicinity of the interface. The rate at which a liquid appears to evaporate is therefore governed by diffusion. Since (P^o-P) is essentially a macroscopic pressure gradient, a comparison of equations 1 and 3 suggests that, to a first approximation, mass transfer coefficients are proportional to gas phase diffusion coefficients.

$$K = \text{const.}D \qquad (4)$$

Experiments demonstrate that turbulence (forced convection) contributes significantly to diffusion, however, so that K is more accurately a power function of D.[1]

$$K = \text{const.}(D)^{2/3} \qquad (5)$$

From this understanding, it should now be possible to estimate mass transfer coefficients and determine generation rates.

---

[1] Depending on the manner in which turbulence is modeled, the power of D in equation 5 can vary between 0.1 and 0.9. For most applications, 2/3 is expected to be the best estimate, though for thin films the value is probably closer to 1 (Thibodeaux 1979).

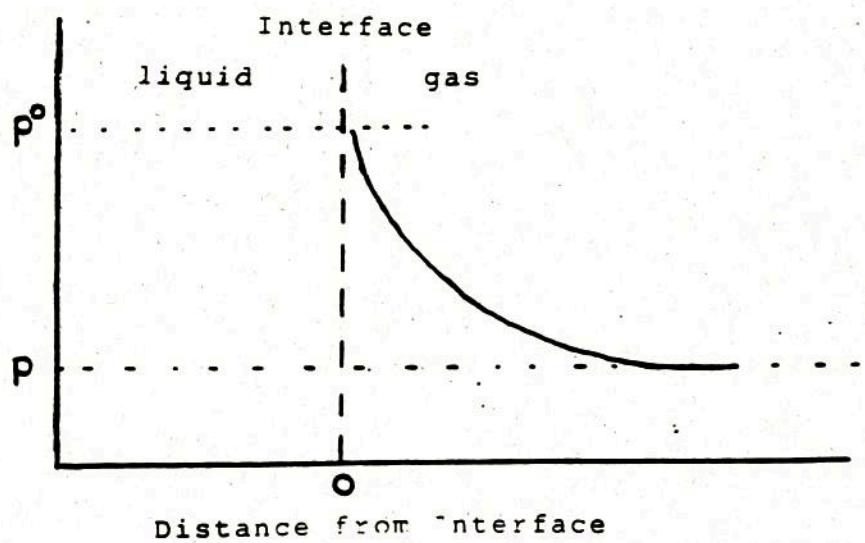
$N_A = x_A(N_A + N_B) - c\,\mathcal{D}_{AB}\,\nabla x_A$ stationary coord.

$$J = \frac{D}{RT}\,\frac{dP}{dX} \quad \text{moves relative to mixture} \tag{3}$$

Equation 3 is Fick's first law of diffusion (Moore 1972) where J is the flux of material in a direction normal to the interface and $\frac{1}{RT}\frac{dP}{dX}$ is the concentration gradient as a function of distance from the interface. The constant of proportionality, D, is known as a diffusion coefficient and is a function of intrinsic properties of both the vapor undergoing diffusion and the gaseous media (air in this case) through which it is diffusing. Diffusion coefficients also depend upon the temperature of the system.

Figure A-1 illustrates the concentration of material in the vicinity of an interface.

FIGURE A-1



A. Calculating Generation Rates from Mass Transfer Coefficients

The generation rate, G, for a pure liquid evaporating into still air[1] can be calculated using equation 2 in the following manner.

$$G = \frac{M}{RT} KAP^{o}$$

82.1

In equation 2, R is the universal gas constant equal to ~~8.21~~ 82. ~~x 10^-5~~ atm cm^3/mole^{o}k, and T is the ambient temperature and can be set equal to 298°K for most applications. Both the molecular weight, M, and equilibrium vapor pressure, P^o, are intrinsic properties of substances and are available in the literature for a large number of compounds. For new chemicals, both M and P^o are among the properties included in the MPD. This leaves only the mass transfer coefficient, K, to be determined.

Mass transfer coefficients, K, can either be measured experimentally or estimated. Methods for estimating K follow.

B. Determination of Coefficient Values

1. Mass Transfer Coefficients

Mass transfer coefficients, K, vary with the intrinsic properties of the liquid as well as properties of the medium

---

[1]Though empirical relationships accounting for the bulk movement of air are available (Mackay et al. 1973), manufacture and use of most chemicals being studied occur indoors where such movement is insignificant. For example, typical ventilation rates are 3,000 ft^3/min. Even in a small room 10 feet high and 10 feet deep, the average air velocity across the room will therefore average 30 ft/min (or 0.5 ft/sec). Due to the viscosity of air, velocities near surfaces will be even smaller. In contrast, typical gas phase diffusion rates are 0.5 cm/sec (15 ft/sec) larger than the average bulk flow rates by a factor of 30. Thus bulk air flow is insignificant. ?

IV. Determination of Generation Rates for Chemicals in Specific Environments

Equations presented previously in this document will be manipulated in this section to demonstrate their function. Part IV is divided into five sections.

- Section A details the relationship between generation rates, G, and mass transfer coefficients, K.
- Section B presents methods for estimating mass transfer coefficients. (Since mass transfer coefficients are closely associated with diffusion coefficients, methods for obtaining diffusion coefficients are also included in this section.)
- Section C extends the methods for estimating generation rates to include pure solids.
- Section D presents a method for estimating mass transfer coefficients (and, correspondingly, generation rates) for components of dilute solutions using Henry's law.
- Section E illustrates a method of modifying equations employed in exposure assessments when bulk gas phase partial pressures are significant so that generation rates are not independent of ambient pressure.

In all of these sections, required input parameters will be defined and either published sources will be referenced or methods for estimating such parameters will be included.

D_{H_2O} = 0.220 cm²/sec H_2O in air in perry

$$K_{H_2O} = \cancel{8.3}\ 0.83 \text{ cm/sec}$$

Substituting this value and the value for the diffusion coefficient of water in air (0.288 cm^2/sec) into equation 6 yields an equation for calculating mass transfer coefficients of other species.

$$K_1 = \cancel{8.3}\ 0.83 \left(\frac{D_1}{0.288}\right)^{2/3} \qquad (7)$$

The only required input for this equation is the diffusion coefficient in air for the new species of interest.

2. <u>Diffusion Coefficients</u>

Diffusion coefficients may be measured or estimated. A large number of experimental gaseous diffusion coefficients have been determined and are available in the literature (Reid et al. 1972).[1]

A number of methods are available for estimating diffusion coefficients that require different forms of data as inputs. These have been summarized (Reid et al. 1972). Based on the kinds of information likely to be available for exposure assessments (e.g., information contained in the MPD) the method of Fuller, Schettler, and Giddings (Reid et al. 1972) for estimating diffusion coefficients should be most useful, and is described below.

---

[1]Diffusion coefficients are generally defined with respect to two substances reflecting the fact that one species diffuses into another. For the gas phase diffusion coefficients referred to in these equations, one of the two substances will be air. For example, a useful diffusion coefficient for benzene would be the diffusion coefficient measured for a mixture of benzene and air.

into which the liquid evaporates. Because these coefficients also depend intimately on the shape of the pressure gradient depicted in Figure A-1, it is not generally possible to derive values for K from first principles. Although mass transfer coefficients have been shown to be proportional to a power of the gas phase diffusion coefficient (equation 5), the constant of proportionality in equation 5 cannot easily be theoretically derived. Thus, transfer coefficients are obtained from a combination of experimental observations and empirical relationships.

Manipulation of equation 5 leads to the conclusion that the ratio of two mass transfer coefficients depends only on the ratio of gas phase diffusion coeficients (there is no undetermined constant).

$$\frac{K_1}{K_2} = \left[\frac{D_1}{D_2}\right]^{2/3} \qquad (6)$$

Thus, knowledge of a mass transfer coefficient for one chemical can be employed to estimate the mass transfer coefficient for any other chemical, provided that the gas phase diffusion coefficients in air are known for both species. The subscripts in equation 6 denote reference to two different substances. Sources for values of diffusion coefficients are presented at the end of this section.

Since the evaporation rate for water into still air has been determined, a mass transfer coefficient can be calculated for this process (Mackay et al. 1980).

In equation 8, D_1 is the gas phase diffusion coefficient in cm^2/sec, P is the ambient pressure in atmospheres, T is the ambient temperature in ^oK, M_1 and M_M are the molecular weights of the diffusing vapor and background medium, respectively, and v is an atomic diffusion volume derived from Table A-I.

TABLE A-1

Atomic Diffusion Volumes for Use in Estimating ϑ_{AB} by the Method of Fuller, Schettler, and Giddings†

Atomic and Structural Diffusion-Volume Increments v			
C	16.5	(Cl)	19.5
H	1.98	(S)	17.0
O	5.48	Aromatic ring	−20.2
(N)	5.69	Heterocyclic ring	−20.2

Diffusion Volumes for Simple Molecules Σv			
H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2O	12.7
Air	20.1	(CCl_2F_2)	114.8
Ar	16.1	(SF_6)	69.7
Kr	22.8	(Cl_2)	37.7
(Xe)	37.9	(Br_2)	67.2
		(SO_2)	41.1

†Parentheses indicate that the value listed is based on only a few data points.

(This method has been compared with a large number of experimental values and is generally accurate to $\pm 20\%$.)

Diffusion coefficients are a function of temperature, molecular weight of the diffusing vapor, molecular weight of the medium into which the vapor is diffusing, and the molecular volumes of both species. Except for molecular volumes, all of the above factors should be readily available.

Molecular volumes may be estimated by summing contributions from atomic volumes, v, for each of the atoms present in the molecule. (The identity of these atoms may be obtained from the MPD element "structural formula".) Atomic volumes are tabulated in Table I which, in turn, is reproduced from Reid et al. (1972). The molecular volume of methane, CH_4, is determined to illustrate their use.

$$CH_4 = 1\ C + 4H$$

$$\Sigma v = (1)(16.5) + (4)(1.98) = 24.4$$

Molecular volumes so computed may be combined with the other factors above to derive diffusion coefficients.

gas in water $10^{-5}\ cm^2/s$

$$D_1 = \frac{10^{-3} T^{1.75} \left[\frac{M_1 + M_M}{M_1 M_M}\right]^{1/2}}{P\left[(\Sigma v)_1^{1/3} + (\Sigma v)_m^{1/3}\right]^2} \qquad (8)$$

$$G = \frac{M_1}{RT} K_{ref} \left[\left(\frac{D_1}{D_{ref}} \right) \right]^{2/3} AP^o \qquad (11)$$

In equation 11, G is the generation rate, M is the molecular weight of the liquid, R is the universal gas constant, T is the ambient temperature, A is the surface area in contact with the air, P^o is the equilibrium vapor pressure of the liquid, and K_{ref} is an experimental mass transfer coefficient determined for a reference compound (water can be used in most cases, see equation 7). Finally, D_1 and D_{ref} are gas phase diffusion coefficients for the liquid of interest and reference compound respectively. These can be estimated as suggested in Section B above.

Equation 11 should be applicable in all cases where a concentration gradient does not develop on the liquid side of the interface (see Section D). This would be true for all pure compounds including solids. Thus, generation rates for pure solids may also be calculated from equation 11 with two additional considerations. First, a potential problem associated with estimating generation rates for volatile solids is the surface area. The surface area of a solid need not be regular, unlike a liquid, so that considerably more effort may be required to estimate the extent of the surface area in direct contact with air. Second, since the mechanisms of evaporation for liquids and solids are not unrelated, water may be employed as a reference compound as in equation 7. An experimental mass transfer coefficient for any evaporating solid would be preferable to that for water, however.

mass transfer coefficient $K = \frac{3000\ cm/Hr}{3600} = 0.85\ cm/sec$

Since the background medium in these systems will be air, ambient pressure is 1 atmosphere, and ambient temperature is 298°K, equation 8 reduces to:

$$= \frac{3.99\left(1 + \frac{28.8}{M_1}\right)^{1/2}}{\left[(\Sigma v)^{1/3} + 2.72\right]^2}$$

$$D_1 = \frac{3.99\left(\frac{M_1 + 28.8}{M_1}\right)^{1/2}}{\left[(\Sigma v)^{1/3} + 2.72\right]^2} \qquad (9)$$

Thus, using the values supplied in Table A-I and the molecular weight for the species of interest, the diffusion coefficient for a substance in air can be derived.

Relative diffusion coefficients are even easier to derive since they are inversely proportional to the square root of molecular weight.

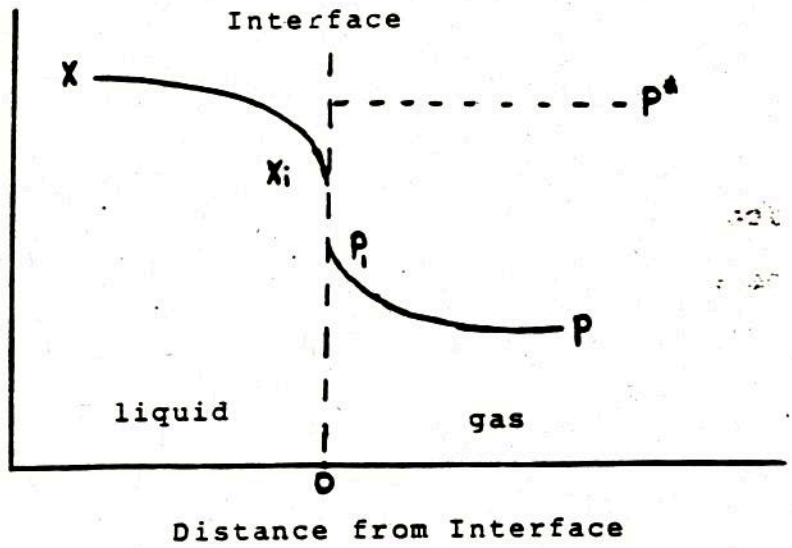
$$D_1 = D_{ref} \sqrt{\frac{M_{ref}}{M_1}} \qquad (10)$$

In equation 10, D_1 is the diffusion coefficient of interest, D_{ref} is a diffusion coefficient for a reference compound. M_1 and M_{ref} are the molecular weights of species 1 and the reference species, respectively. Presumably, D_{ref} can be derived from a table. NOTE: The more closely related a reference compound is to the compound of interest, the better the approximation derived in equation 10.

C. <u>Extending the Methods for Estimating Generation Rates: Pure Solids</u>

Combining equations 2 and 6, the most appropriate equation for estimating a generation rate for a pure liquid evaporating into still air is:

FIGURE A-2



2. Determination of Mass Transfer Coefficients

Mass transfer coefficients can be defined for each phase of the evaporation process.

$$J_g = k_g(P_i - P) \qquad (12)$$

$$J_l = k_l(X - X_i) \qquad (13)$$

J is the material flux across each phase. (Assuming a steady state is achieved, material leaving the liquid must equal material entering the gas phase at the interface which, in turn, must equal material dispersing into the bulk phase. Thus, all fluxes must be equal: $J_g = J_l = J_{Total} = G$.)

D. Modeling Evaporation of a Volatile Component from a Dilute Liquid Mixture

1. Processes Associated with Evaporation of a Volatile Component

Modifying equations developed for a pure liquid to include mixtures is conceptually simple. The major difference is that, in a mixture, a concentration gradient will develop on both sides of the interface. Thus, diffusion dominates movement of material on both sides of the interface. Figure A-2 represents the concentration of a contaminant present in solution which is escaping into the gas phase. As in Figure A-1, concentration gradients are large only in the vicinity of the interface.

In Figure A-2, X is the mole fraction of the contaminant in solution. As evaporation proceeds, the volatile component of the liquid in the vicinity of the interface becomes depleted so the mole fraction of contaminant at the interface is X_i. (The concentration of contaminant at the interface is maintained by diffusion from the bulk liquid.) Since resistance to evaporation at the interface is insignificant, the air space immediately adjacent to the interface will become saturated with contaminant yielding a vapor pressure, P_i, in equilibrium with X_i. Gas phase diffusion away from the interface governs the bulk concentration of contaminant, P, in the gas phase. (P* is the hypothetical vapor pressure that would be exhibited by the contaminant in equilibrium with the bulk concentration, X, in solution.)

In equation 16, P and X have been defined above and the constant of proportionality, H, is known as a Henry's law constant. Using equation 16, equation 15 may be revised.

$$(P^* - P) = \left(\frac{X}{H} - \frac{X_i}{H}\right) + (P_i - P) \qquad (17)$$

Using equation 17, the overall mass transfer coefficient, K_o, can now be related to the phase dependent mass transfer coefficients, k_l and k_g, by a simple algebraic substitution of equations 12, 13, and 14 into equation 17.

$$\frac{G}{K_o} = \frac{HJ_l}{k_l} + \frac{J_g}{k_g} \qquad (18)$$

Finally, since $J_l = J_g = G$ for a steady state system, equation 18 reduces to:

$$\frac{1}{K_o} = \frac{H}{k_l} + \frac{1}{k_g} \qquad (19)$$

Estimating generation rates for solutes of dilute solutions therefore reduces to the problem of obtaining k_l, k_g, and H. However, the gas phase mass transfer coefficient can be estimated as suggested in Section B. Henry's law constants can be obtained either from tabulations of such values (Thibodeaux 1979) or estimated, as depicted in the end of this section. Finally, liquid phase mass transfer coefficients, k_l, relate to liquid phase diffusion coefficients, D_l, in the same manner as gas

The subscripts "g" and "l" in equation 12 and 13 refer to the gas and liquid phases, respectively. Two problems are associated with such an approach, however. First, the overall generation rate and, correspondingly, the overall mass transfer coefficient are the quantities of interest. Second, the actual concentrations of contaminant at the interface, X_i and P_i, will not generally be known. Both of these problems can be overcome as follows.

An overall mass transfer coefficient can be defined for this process.

$$G = K_o(P^* - P) \tag{14}$$

In equation 14, the subscript "o" stands for the overall coefficient. In addition, the driving force (P*-P) now only contains terms relating to bulk phase concentrations, as in equation 1. This term can be expanded to relate to the gradient on each side of the interface.

$$(P^*-P) = (P^*-P_i) + (P_i-P) \tag{15}$$

At this point, the major component of a solution (solvent) and minor component (solute) must be treated separately. While major components approximate pure substances, for minor components of dilute solutions: gas phase and solution phase concentrations are related by Henry's law (Adamson 1973).

$$P = HX \tag{16}$$

into the exposure assessment equations and contaminant pressure, P, solved for directly. For example, the steady state solution to the equation:

$$\frac{dP}{dt} = G - QP \qquad (21)$$

is that contaminant concentration, P, is a function of G and Q.

$$P = G/Q \qquad (22)$$

When P is significant, however, the correct functional form of G (which is equation 1) must be substituted into the equation.

$$V\frac{dP}{dt} = \frac{M}{RT} KA(P^{o}-P) - QP \qquad (23)$$

The steady state solution to this equation is:

$$P = \frac{KAP^{o}}{(KA+Q)} \qquad (24)$$

Equation 24 is interesting in that:

(1) If KA>Q (ventilation is insignificant) then $P = P^{o}$ (the airborne concentration will reach the equilibrium concentration as expected).

phase coefficients relate to each other, equation 5, (see discussion in Section B). Similarly, liquid phase diffusion coefficients, D_1, may be acquired from tabulations (Reid et al. 1972) or extrapolated from related coefficients using equation 10.

3. Determination of Henry's Law Constants

Henry's law constants that have not been tabulated can be estimated by their dependence on vapor pressure and solubility. If the solubility, S, of a substance in the mixture being modeled is known, the Henry's law constant for such a substance can be easily derived (Adamson 1973).

$$P' = \frac{S}{S^{\bullet}} VP \qquad H = \frac{P^{o}}{S} \qquad (20)$$

solub.

sat sol.

In equation 20, P^{o} is the vapor pressure of pure solute, S is its solubility in the solvent under study, and H is the Henry's law constant.

E. Estimating Generation Rates When Airborne Contaminant Concentrations are Significant

For the vast majority of cases, airborne contaminant concentrations will be insignificant compared with equilibrium vapor pressures: $P \ll P^{o}$. In such circumstances, generation rates, G, are effectively independent of contaminant pressure; equation 2 is relevant; and G can be substituted into the equations to perform exposure assessments directly. As contaminant pressure, P, increases, however, generation rates become dependent upon P so that the functional form of G should then be substituted

- aerosols
- particulates
- rapidly moving fluids
- rapidly mixing fluids
- fugitive emissions
- and other cases.

It would be helpful, ultimately, to catalog and condense all of these models (along with sparse but available experimental generation rates) so that a complete manual for estimating generation rates could be prepared. These equations should yield reasonably quantitative estimates for the systems that they are specifically designed to model, in addition to providing a qualitative sense of the relative importance of factors affecting volatilization.

(2) If $KA < Q$ (the generation rate is small compared to the ventilation rate), then:

$$P = \frac{KAP^{o}}{Q}$$

Examination of equation 2 reveals that this solution is equivalent to equation 22.

(3) If $KA = Q$ (ventilation and generation rates are comparable) then equation 24 must be used to determine P accurately in an exposure assessment.

V. Discussion and Conclusions

Methods for obtaining values of parameters necessary to determine generation rates have been presented. The greatest strength of these methods rests with the ability to derive a generation rate for a new chemical, when the generation rate of another species has been determined for a comparable situation. Thus exposure assessments for new chemicals may be performed prior to commercial production. Because generation rates also depend on engineering factors, however, application of these methods is limited by the number of situations that have been analyzed in the past. Though the equations presented will likely cover a majority of important cases, other equations are available that would permit estimation of generation rates for:

WORKPLACE MIXING FACTOR--k

General dilution ventilation air does not always mix perfectly and instantaneously with contaminated room air. If room air is not well mixed, pockets of poorly mixed air may be found in the room. Further, the time for an air change to occur in actuality will be much greater than the theoretical time for an air change (V/Q). Mathematically, k is defined as the ratio of times of a theoretical air change to occur to the time observed experimentally (t_{exp}).

$$k = \frac{V/Q}{t_{exp}} \tag{25}$$

The mixing factor, k, can also be thought of as the ratio of effective ventilation to actual ventilation, or:

$$k = Q_{eff}/Q \tag{26}$$

Mixing factors are usually determined by tracer gas technique (Drivas et al. 1972). A k value of 1 means that the room has ideal, perfect mixing. Actual values of k range from 1/3 to 1/10, depending on the air supply system and room size. Table A-2 lists some recommended values of k for rooms of approximately 1,000 ft^3 (28 m^3). Larger rooms will have smaller k values.

TABLE A-2

RECOMMENDED VALUES OF THE MIXING FACTOR, k

Description of Supply Air System	k
Perforated ceiling	1/2
Trunk system with anemostats	1/3
Trunk system with diffusers	1/4
Natural draft with ceiling exhaust fans	1/6
Infiltration and natural draft	1/10

SOURCE: Brief 1960

REFERENCES

ADAMSON, A.W. 1973. A Textbook of Physical Chemistry. Academic Press, New York

AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (ACGIH) 1978. Industrial Ventilation--A Manual of Recommended Practice. Edwards Brothers, Lansing, Mich.

BAKER, J.C. 1977. Testing a Model for Predicting Solvent Vapor Concentrations in an Industrial Environment. Thesis submitted to the faculty of the University of North Carolina, Department of Environmental Sciences and Engineering, School of Public Health, Chapel Hill, N.C.

BECKER, D., FOCHTMAN, E., GRAY, A., and JACOBIUS, T. 1979. Methodology for Estimating Direct Exposure to New Chemical Substances. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C. July 1979. EPA 560/13-79-008

BENDER, E.A. 1978. An Introduction to Mathematical Modeling. John Wiley and Sons, New York. P. 2

BRIDBORD, J., BRUBAKER, P.E., GAY, G., and FRENCH, J.G. 1975. Exposure to halogenated hydrocarbons in the indoor environment. Environ. Health Perspect. 11:215-220

DAVIS, R.J. 1971. A simple model for the estimation of aerosol concentration in a closed vessel. Am. Ind. Hyg. Assoc. J. 32:603-609

DRAKE, R.L. 1979. Mathematical Models for Atmospheric Pollutants. Battelle Pacific Laboratories. Prepared for Electric Power Research Institute (EPRI). EA-1131. Research Project 805

ESMAN, N.A. 1978. Characterization of contaminant concentrations in enclosed spaces. Environ. Sci. Technol. 12:337-339

HARRIS, R.L., and ARP, E.W. 1979. The emission inventory. In Cralley, L.J., and Cralley, L.V., eds. Patty's Industrial Hygiene and Toxicology. John Wiley and Sons, New York. Vol. 3, pp. 11-41

ISHIZU, Y. 1980. General equation for the estimation of indoor pollution. Environ. Sci. Technol. 14:1254-1257

LEIDEL, N.A. 1981. Personal communication. National Institute of Occupational Safety and Health (NIOSH)

MACKAY, D. and MATSUGU, R.S. 1973. Evaporation rates of liquid hydrocarbons spills on land and water Can. J. Chem. Eng. Vol. 51

MACKAY, D., PATERSON, S., and NADEAU, S. 1980. Calculation of the Evaporation Rate of Volatile Liquids. Control Hazard Meter Spills, Prec. Natl. Conf.

MILLER, C. 1978. Exposure Assessment Modeling: A State-of-the-Art Review. U.S. Environmental Protection Agency, Washington, D.C. April 1978. EPA 600/3-78-065

MOORE, W.J. 1972. Physical Chemistry. 4th ed., Prentice-Hall, Englewood Cliffs, N.J.

REID, R.C., PRAUSNITZ, J.M., and SHERWOOD, T.K. 1977. The Properties of Gases and Liquids. 3rd ed. McGraw Hill Co., New York

ROACH, S.A. 1977. A most rational basis for air sampling programmes. Ann. Occup. Hyg. 20:65-84

SCHROY, J.M. 1979. Prediction of Workplace Contaminant Levels. Paper presented at NIOSH symposium, Control Technology Assessment of Plastics and Resins Industries, February 1979, Atlanta, Ga. (In press)

THIBODEAUX, L.J. 1979. Chemodynamics. John. Wiley and Sons, New York

TURK, A. 1963. Measurement of odorous vapors in hot chambers. ASHRAE J. 5:55-58

TURNER, B.D. 1969. Handbook of Atmospheric Dispersion Estimates. U.S. Department of Health, Education and Welfare, Washington, D.C. Pub. No. 999-AP-26