PREDICTION OF WORKPLACE CONTAMINANT LEVELS

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The prediction of concentration of specific chemicals in the workplace based on engineering design data is a major concern for the designer. A workplace procedure which utilizes emission rate data and gaussian dispersion models has been developed for the process design engineer.

The information presented provides vapor emission rate data for estimating losses from equipment, piping and open pools of pure components when actual data are unavailable.

Case studies related to vinyl chloride and acrylonitrile will be discussed in terms of present OSHA regulations for these materials.

Introduction

The papers presented during the past two days have principally addressed situations related to existing facilities. The questions of controlling personnel exposure have involved field testing actual exposure conditions, revising work practices and retrofitting engineering controls. While this approach is effective for existing facilities it does not meet the needs of revised or new technology. And with the increasing number of chemicals considered to be hazardous at low concentrations, field correction of design errors is becoming even more impractical. In fact, the drain on technical resources at the plant level is also limiting production innovation and product development activities.

It is important to note that the problem is in effect created by good engineering practices. The designer selects the most economical equipment which fits the process requirements. And present chemical processing technology involves use of equipment and/or operating and maintenance techniques with a wide range of loss or leakage characteristics. (1, 2, 3, 9).

While the design engineer can attempt to economically optimize a process, by maximizing conversion, yield and/or recovery; the process economics do not preclude loss of small quantities of raw materials, products and/or by-products to the workspace. Unfortunately, present research and development practices provide little or no data on the loss of leakage rates of specific chemicals from key process equipment. For these reasons, the problems of controlling emissions have been left unanswered during the design phase of project. While this practice has been satisfactory for materials with low volatility or high allowable exposure limits (i.e. 100 ppm(v)), this practice has proved to be costly for volatile materials such as vinyl chloride. The costs are not just capital they also involve overcommitment of human resources.

When exposure concerns arise in an operating unit the corrections must be handled by the plant hygienist and operating personnel as a retrofitting project. While most hygienist are capable of identifying exposure control concerns they frequently have little engineering background. Therefore, design changes which would have involved simple layout revisions during design, often become expensive local ventilation systems.

Until recently, stipulations to correct exposure concerns during design have led to installation of engineering controls which may unnecessarily increase the cost of the facilities.

To avoid committing our human technical resources to retrofitting work and/or overcommitment of capital resources to unnecessary controls, a design procedure is needed to predict the impact of design decisions prior to completion of project definition. One method which has been developed based on literature data, and which shows merit if properly applied, is described below.

Discussion

To meet the need described above a method was developed to define the impact of a chemical's physical properties on its behavior as a workplace contaminant. When the importance of physical property differences was described it became obvious the methodology was a valuable design tool.

The design procedure is based on a gaussian dispersion model.(1) At present gaussian models represented the most practical method of analyzing the downwind impact of an emission to the workplace. The dispersion correlation has been developed for use when the source and receiver are relatively close.(5) The relationship is designed to predict maximum downwind concentrations as a function of distance from the source, where the dispersed plume does not reflect from a solid surface (i.e. an unconfined plume, see Figure 1 in the appendix). Utilizing vapor emission rate data, the design engineer can calculate the expected workplace concentration from either one source of a number of sources which would impact the same point.

The air dispersion equation for maximum downwind concentration, assuming that there is some air movement, at a given downwind distance from the unconfined vapor leak is given by Equation 1:

$$C'_{max} = 1337.786 \cdot Q / [M \times \overline{U}'] \cdot [1/(2\pi\sigma_y\sigma_z)] \quad \text{(Eng. 1)}$$

Where

C'_{max} = is concentration of the chemical of concern in parts per million by volume (ppm (v)) at some distance, d, downwind from the leaking source.

Q = is the quantity of the chemical of concern being released from the source in grams per hours.

$\overline{U}'$ = is the velocity of the workplace ambient air passing the point of release in feet per minute.

σ_y & σ_z = are diffusion coefficients in meters which are functions of the distance, d, from the leak source which is being considered gives values of the function $1/(2\pi\sigma_y\sigma_z)$ as a function of distance, d. (See table 1 in Appendix, also a graphical representation is given in Figure 2.)

M = molecular weight of the chemical of concern.

Graphical presentations of Equation 1 are given in the Appendix for Acrylonitrile and Vinyl Chloride (i.e. Figures 3 and 4 respectively). The graphs allow rapid determination of the maximum workplace concentrations for a set of normal ambient conditions. For ambient conditions not covered by the graphs, Table 1 (Diffusion Functions) is given to allow calculation of the workplace concentrations.

The correlation can also be used to provide conservative results for large surface sources (eg. pools or open tanks). However, if the results of the emissions from an open surface are critical to the design, a more detailed correlation, which recognizes the importance of pool length and width, should be considered.96) Predictive methods are available for calculation of emission rates from quiescent pools(7) and surface aerated pools. (8)

Emission rate data is tabulated in the Appendix (Table 3) for quiescent pools of pure vinyl chloride (VCM) or pure acrylonitrile (AN) and water-VCM or Water-AN mixtures.

As can be seen from the relationship (Equation 1) or the graphical presentations (Figure 3 and 4) valid emission rate data is the key to determining the maximum workplace contaminant concentration. Whenever possible this data should be determined experimentally during the research and development phase of a project. When emission rate data are not available, from material balances or R&D results, estimates of emissions should be used. The data presented in Table 2 (Vapor Emission Rates) represents the best literature values for Acrylonitrile or vinyl chloride emissions from specific process loss points. It is critical to note that emission points are not unit operations but seal points, either dynamic or static seals.

Recommendation

Utilizing the correlations and data described above the designer should determine the impact of proposed design alternatives. The following methodology should be applied to quantify the workplace risks for alternate methods to control workplace contaminant levels.

1. Summarize all key emission points and tabulate either actual or estimated emission rate data, for each design case being considered.

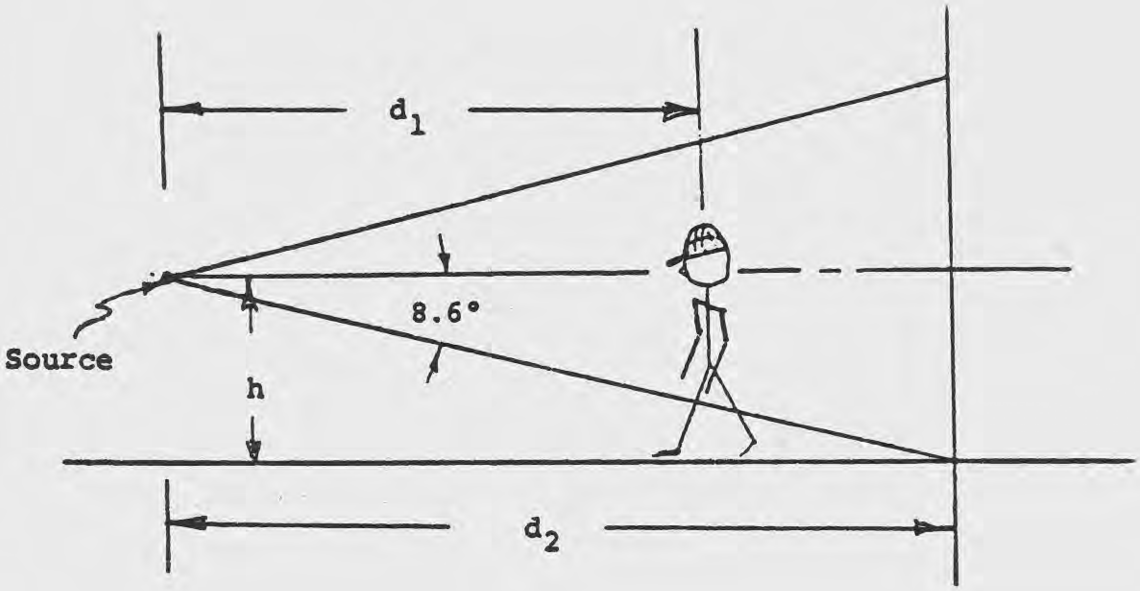
2. Define the ambient conditions, including prevailing wind directions, and identify key operations areas which will be impacted by know vapor emissions. For a process which is subject to frequent maintenance access, periodic emissions should also be defined.

3. Workplace concentrations should be calculated for each "hot spot" by summing the concentrations due to individual sources.

$$(C'_{max})_{total} \equiv \sum_{i=1}^{n} (C'_{max})_1 \qquad \text{(Egn. 2)}$$

4. The risk associated with each engineering control or operations change should be summarized and reviewed to identify the actions which provide the maximum benefit in terms of its cost.

APPENDIX



d_2 = limit of correlation validity

d_1 = distance from source of interest

h = source height above confining surface

$h_{max} = d_2 \times \tan 8.6^0$

Figure 1. Limit of correlation validity.

VALUES OF $(1/(2\pi\ \sigma_y\ \sigma_z))$ FOR EQUATION 1, m^{-2}

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			

Table 1. Diffusion function.

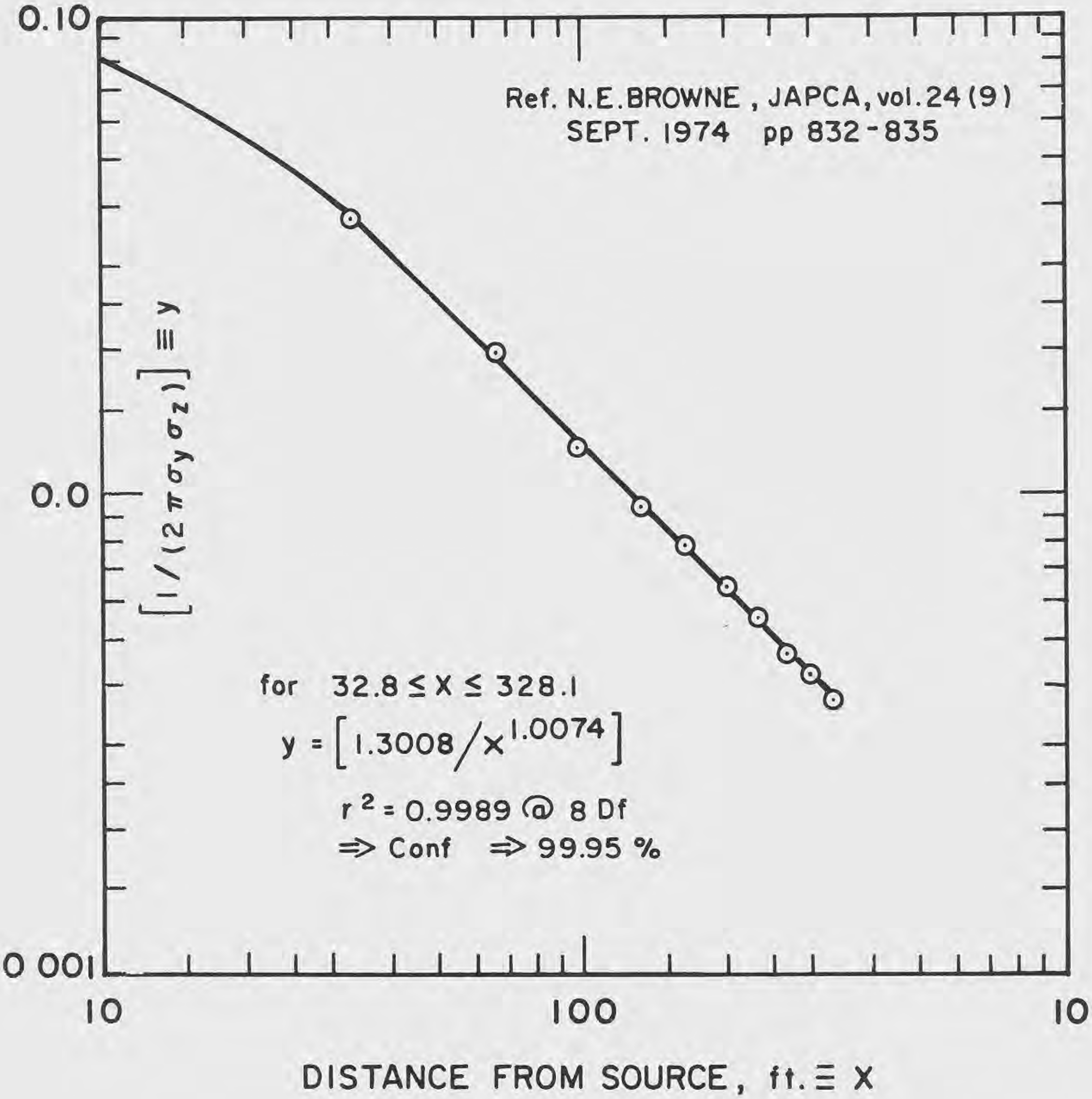
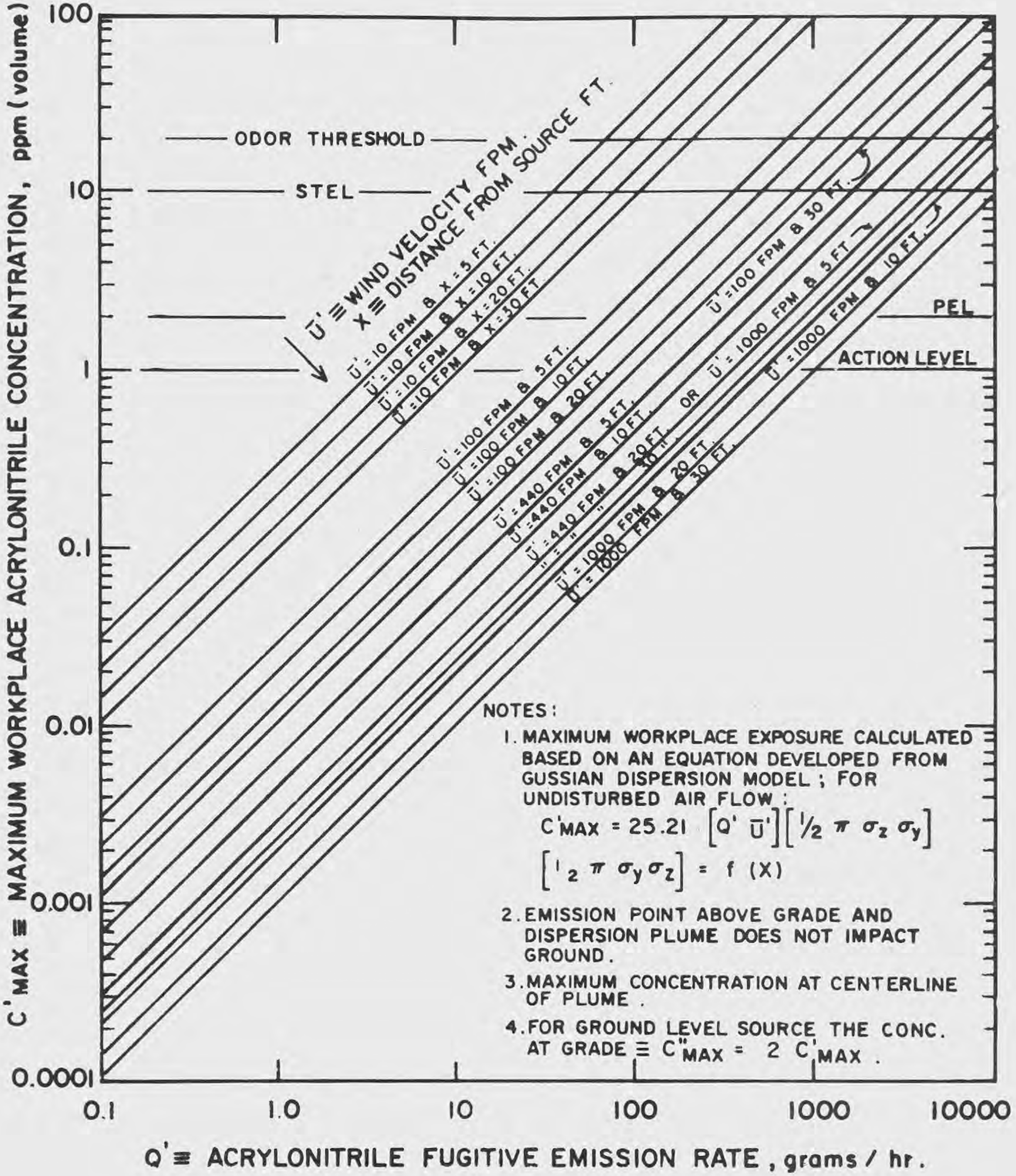


Figure 2. Diffusion function.



NOTES:

1. MAXIMUM WORKPLACE EXPOSURE CALCULATED BASED ON AN EQUATION DEVELOPED FROM GUSSIAN DISPERSION MODEL; FOR UNDISTURBED AIR FLOW:

$$C'_{MAX} = 25.21\ \left[Q'\ \bar{U}'\right]\left[{}^{1}\!/_{2}\ \pi\ \sigma_z\ \sigma_y\right]$$

$$\left[{}^{1}{}_{2}\ \pi\ \sigma_y \sigma_z\right] = f\ (X)$$

2. EMISSION POINT ABOVE GRADE AND DISPERSION PLUME DOES NOT IMPACT GROUND.
3. MAXIMUM CONCENTRATION AT CENTERLINE OF PLUME.
4. FOR GROUND LEVEL SOURCE THE CONC. AT GRADE ≡ $C''_{MAX} = 2\ C'_{MAX}$.

Figure 3. Dispersion of fugitive acrylonitrile emission.

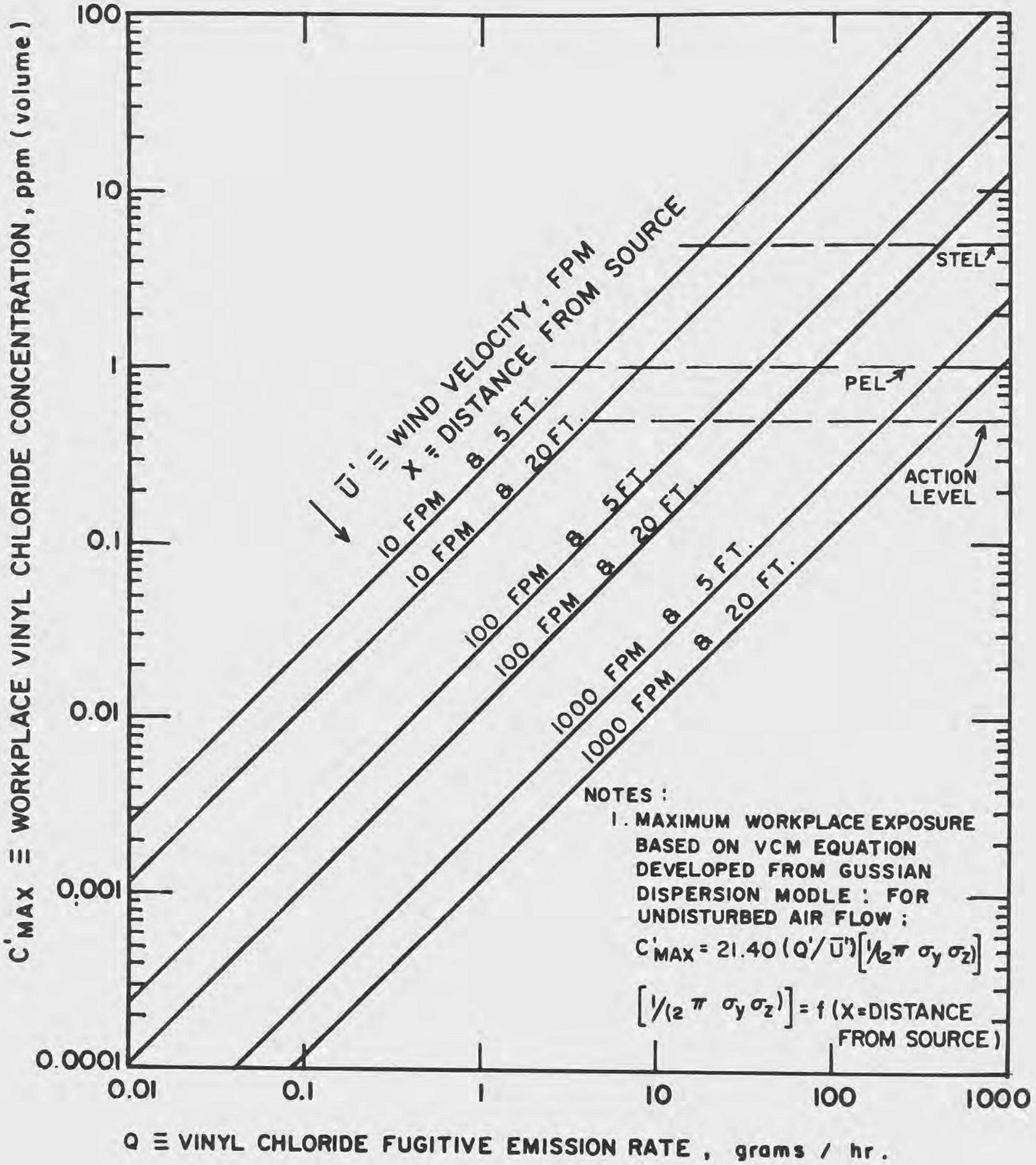


Figure 4. Dispersion of fugitive VCM emission.

TABLE 2

COMPILATION EMISSION RATES FROM PIPING SYSTEMS AND PROCESS EQUIPMENT

	LEAKAGE RATE, GRAMS PER HOUR (Except as Noted)		
ITEM	Good Preventive Maintenance	Average to Poor Prev. Maintenance	Remarks
1) FLANGES			
a) 150-300 lb:			
·Gas Service	0.0061 (1)	0.061 (1)	
·Liq.Service	0.0610 (1)	0.610 (1)	
b) 600-1200 lb:			
·Unspecified	0.0031 (1)	0.061 (1)	
2) VALVES (Stem Seals)			
a) Gate & Control:			
·150-300 lb	6	30	
·600-1200 lb	0.1	2.8	
b) Ball (1/4 Turn)	0.015	2.8	
c) Press Relief to ATM	2.8	55	
d) Press Relief w/ rupt. disk	NIL	55 (2)	Poor Maint. No Rupt.Disk Replacement
3) PUMPS ~~or~~ COMPRESSORS (3)			
a) Rotary Seals:			
·Packed	80	473	Estimate of Face Velocity on Seal is 375 fpm
·Single Mechanical			
-Proc. Fluid Flush	6	60	
-Water Flush (2)	0.02	60	Estimate Poor Maint. Seal Fluid Failure
·Double Mechanical	NIL	6+ (2)	+Flush Fluid Problem or Internal Seal Problem
4) COMPRESSORS			
a) Reciprocating Seals:			
Rod packing (2)			
• Single	16	509	
• Double	13	104	
5) AGITATORS	Estimate losses using data on Packed or Double Mechanical Rotary Seals for Pumps. Losses Agitator=Pump Seal Losses x (Face Velocity, fpm ÷ 375 fpm)		
6) TANKS (D)			
a) Floating Roof	Use 60% of API Bul. 2517 Calcs.		

Refs: (A) A. Bierd, A. Stoekel, R. Sinn & H. Kremer, Chem-Ing Tech, 49 (1977) 589 (2/77)

(B) F.D. Snell, Benzene Survey, Memo to MC (from J.A. Mullens with Shell Oil Proposal, September 20, 1977.

(C) D.D. Rosebrook "Fugitive Hydrocarbon Emissions" Chemical Engineering Deskbook, October 17, 1977, pp 147, McGraw Hill.

(D) __________, Compilation of Air Pollutant Emission Factors, 3rd Edition (with Supplements 1 to 7), U.S. Environmental Protection Agency, Apr 77, PB 270281, (AP42).

(1) Grams per Hour per Ft. of Outer Flange Circumference. Approximate flange circumferences given in Table 4.

(2) Estimated value also valid for use of a high molecular weight oil as a flush fluid

(3) Values for Pumps would be estimates for Compressors

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Table 3 - Emissions from Unconfined Surfaces
Chemical Emission Rate, grams/(hr x ft^2)

System	Solar* Radiation, BTU/hr/ft^2	Chemical Emission Rate, grams/hr/ft^2 — Wind Speed, fpm (mph) 10(0.114)	100(1.14)	440(5)
Pure Components (Pool depth 1/2")				
Acrylonitrile	0	24.2	111.6	255.9
	250	65.4	234.9	437.3
Vinyl Chloride	0	764.9	2392.6	5052
	250	1243.6	2280.4	6304
Water Mixtures (At concentrations at or above saturation, water depth $\leq$4 feet, for Solar Radiation of 0 or 250 BTU/(hr ft^2))				
Acrylonitrile $\geq$7.0 wt%		24.2	111.6	255.9
Vinyl Chloride $\geq$0.27 wt %		764.9	2392.6	5052
Water Mixtures (At concentrations below saturation, for Solar Radiation of 0 to 250 BTU/(hr ft^2), * pool depth = 1 ft, ** pool depth = 4 ft)				
	Concentration wt %			
Acrylonitrile	0.2 *	0.70	2.62	4.17
	0.2 **	0.55	1.29	1.58
	7.0 *	20.14	81.75	140.12
	7.0 **	16.54	43.46	55.83
Vinyl Chloride	0.135*	3.96	4.07	4.09
	0.135**	1.25	1.26	1.26
	0.27*	7.89	8.13	8.16
	0.27**	2.49	2.51	2.52

Notes: Solar radiation = 0 ≡ Dark or indoors, and 250 ≡ Daylight

The rate is highly dependent on liquid phase diffusion. Therefore maximum rates (i.e. initial) are given for each condition noted. To correct the data for pool depth divide the emission rate by pool depth (feet) to the 0.85 power. For correction of the rate for concentration multiply the value noted by the factor of the desired concentration divided by the reference concentration (note: do not exceed the solubility limit noted).

Example Calculations

The example presented below is intended to clarify use of the tables and graphs. The designer should note that the intent of the guideline is to define conditions which will protect people. For this reason assumptions should be made which will give conservative answers, or the assumptions should be clearly identified as operating criteria. A few examples are as follows:

1. When emission sources are at different elevations, such that the maximum plume concentration will not coincide, the designer should assume that the maximum concentrations will be additive.
2. When a large surface source, such as an open manhole, is evaluated the designer should consider the center of the surface as a point source.
3. When using estimated vapor emission rate data, values for good preventive maintenance practices may be used. However, operations must commit to this type of a maintenance program.

An acrylonitrile (AN) mix tank and transfer pump are to be installed in an existing unit. The objective is to install the tank the pump such that the AN concentration in the workplace will not exceed the action level (i.e. 1 ppm (v)) at a nearby work station.

The unit is an indoors installation with once through building ventilation. The average air velocity is 10 feet per minute. The tank is to be installed as shown in Figure 5. The AN is at ambient temperature, $75^{o}F$.

The design questions to be answered are as follows:

- What type of agitator seal should be used: Packed or double mechanical seal?
- What type of pump seal should be used? Packed, single or double mechanical seals? (An oil flush fluid would be compatible with use in either a single or double mechanical seal).
- Is a ventilation system needed to collect emissions during additive additions?

As indicated in the procedure outlined on Page 4, the process emission points are summarized in Table 4. Using Table 2 the emission rates are tabulated for various scenarios with Table 3 used to determine the emission rate from the open manhole.

The scenarios considered are as follows:

I. Packing glands are used on both the pump and agitator and no control is used to limit emissions from the hand hole.

II. A single mechanical seal with flush fluid is used for the pump and a double mechanical seal is used for the agitator. A fume control system is used to limit emissions from the hand hole.

III. Double mechanical seals are used for both the pump and agitator. A fume control system is used to limit emissions from the hand hole.

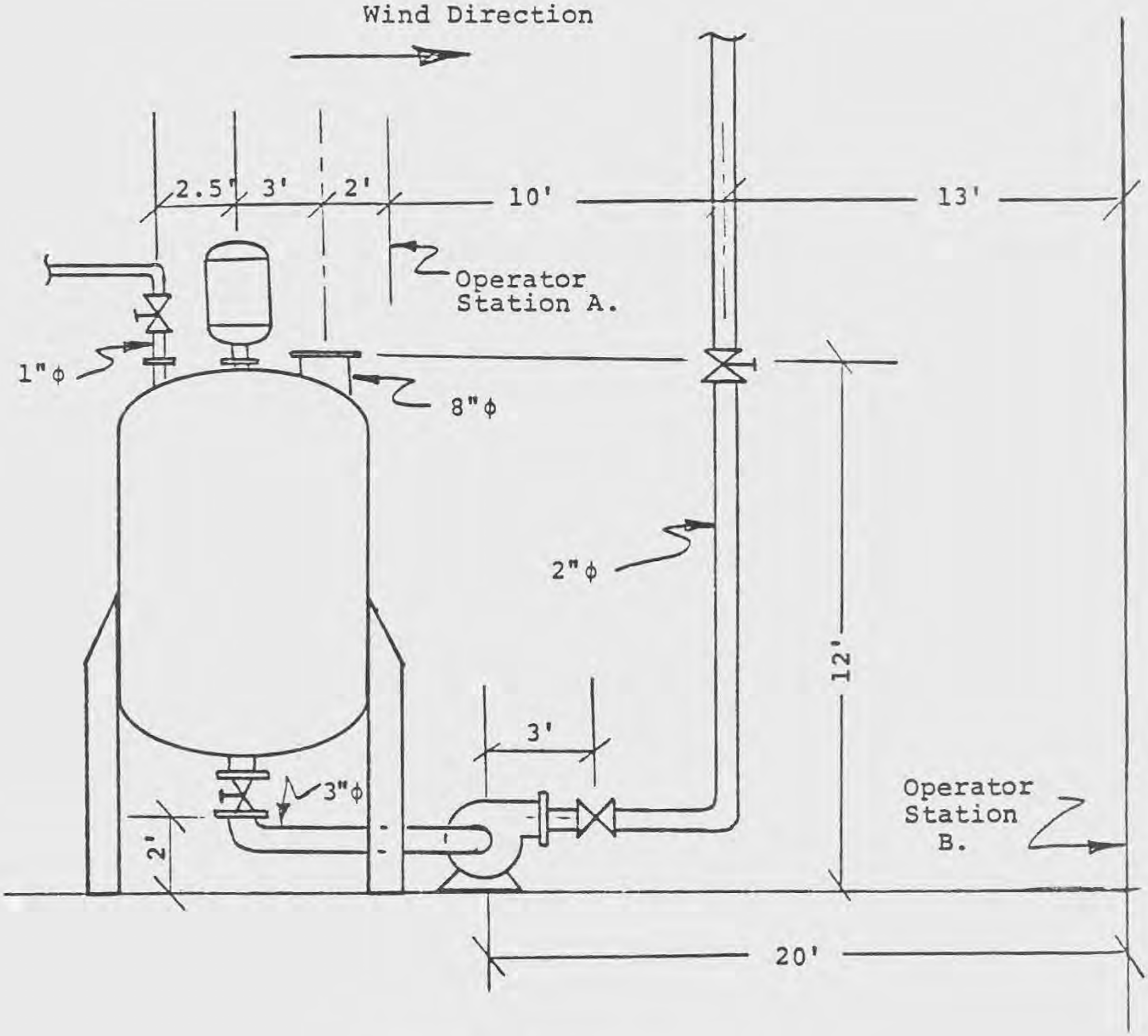

Figure 5. Example layout.

Table 4. Emission analysis.

	Distance from point of emission to receptor, ft		Emission Rate (grams/hour) for Scenarios #			Concentration at Work Station, (ppm (v))					
						A Once Thru Air, 10 fpm			B Once Thru Air, 10 fpm		
Emission Points/(Number)	A	B	I	II	III	I	II	III	I	II	III
1" φ Ball Valve Stem/(1)	7.5	30.5	0.015	0.015	0.015	≤ 0.01	≤0.01	≤ 0.01	≤ 0.003	≤ 0.003	≤ 0.003
Flanges on 1" valve/(2)	7.5	30.5	0.156	0.156	0.156	0.038	0.038	0.038	0.011	0.011	0.011
Agitator Seal											
Packed/(1)	5	28	80	-	-	23.5			8.8		
Double mechanical/(1)	5	-	-	0	0		0	0		0	0
8" φ Hand Hole/(1)	2	25	9	0	0	3.22	0	0	1.11		0
2" φ Ball Valve Stem/(1)	10	13	0.015	0.015	0.015	≤ 0.01	≤0.01	≤ 0.01	≤ 0.006	≤ 0.006	≤0.006
Flanges on 2" valve/(2)	10	13	0.208	0.208	0.208	0.042	0.042	0.042	0.037	0.037	0.037
Subtotal @ EL = 12'			89.394	0.394	0.394	≤26.8	≤0.10	≤0.10	≤10.0	≤0.06	≤0.06
3" φ Ball valve stem/(1)	5	28	0.015	0.015	0.015	≤0.004	≤0.004	≤0.004	≤0.002	≤0.002	≤0.002
Flanges on 3" valves/(2)	5	28	0.264	0.264	0.264	0.08	0.08	0.08	0.03	0.03	0.03
Pump Seal											
Packed/(1)	3	20	80			27.16			11.0		
Single Mechanical*/(1)	3	20		0.02			≤0.007			≤0.003	
Double Mechanical⁼/(1)	3	20			0			0			0
2" φ Ball Valve Stem/(1)	6	17	0.015	0.015	≤0.015	≤0.004	0.004	≤0.004	≤0.002	≤0.002	≤0.002
Flanges on 2" Valve/(2)	6	17	0.208	0.208	0.208	0.056	0.056	0.056	0.032	0.032	0.032
Flanges on Pump											
2" φ /(1)	4	19	0.104	0.104	0.104	0.033	0.033	0.033	0.015	0.015	0.015
3" φ /(1)	3	20	0.132	0.132	0.132	0.045	0.045	0.045	0.018	0.018	0.018
Subtotal @ EL = 2'			80.738	0.758	0.738	≤27.4	0.023	≤0.22	≤11.1	≤0.1	≤0.1
Total All sources			170.132	1.152	1.132	≤54.2	≤0.33	≤0.32	≤21.1	≤0.16	≤0.16

* with flush ⁼ with seal fluid

As can be seen from Table 4 Scenario II offers the desired emission control for a building with once through air flow.

The data compiled in Table 4 can also be used to determine the impact of a ventilation system which recirculates air. Considering the workspace volume shown in Figure 5 as representative of the building, the equilibrium concentration can be calculated using the chemical emission rate and air exhaust rate from the workspace. The workplace volume is 9000 cubic feet (15'x20'x30') and for a ventilation rate of 15 air changes per hour the exhaust air is 2250 CFM. The concentration in the exhaust air is assumed to be equal to the room air and can be claculated as follows.

$$\text{Conc., ppm} = \frac{\dfrac{(\text{Emission rate gm/hr} \; / \; (454 \text{ gm/lb} \times \text{mol wt.})}{[\text{Exhaust volume CFM} \times 60 \text{ min/hr.}]}}{\left[\;359 \text{ CF/lb mole} \times 10^6 \times \dfrac{(460+74)}{(460+32)}\right]}$$

$$= \left\{\frac{\text{Emission Rate gm/hr}}{\text{Exhaust Volume, CFM}}\right\} \left\{\frac{[390 \times 10^6]}{[454 \times 60 \times 53.1]}\right\}$$

$$\text{Conc., ppm} = \left\{\frac{\text{Emission Rate, gm/hr}}{\text{Exhaust Volume, CFM}}\right\} \left\{270.05\right\}$$

For the conditions cited for Scenario I, II and III a recirculation air system with 15 air changes per hour would have the following workplace contaminant levels.

Scenario	Workplace Acrylonitrile Concentration, ppm (v)
I	20.4
II	0.14
III	0.14

To achieve a level of 1 ppm (v) for conditions given in Scenario I, air recirculation would require 306.3 air changes per hour or a once through wind velocity of 153.2 fpm (1.74 mph).

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* * *

MR. JOHN T. TALTY: Thank you, Jerry. If there are any questions later you can bring them up.

The next speaker is Louis C. Knox. He's the Vice President and Chief Engineer of Catalytic Incorporated. He is a chemical engineer with 35 years experience in the refining and engineering/construction industry. The title of his presentation is Design of High-Containment Polymerization Process.

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