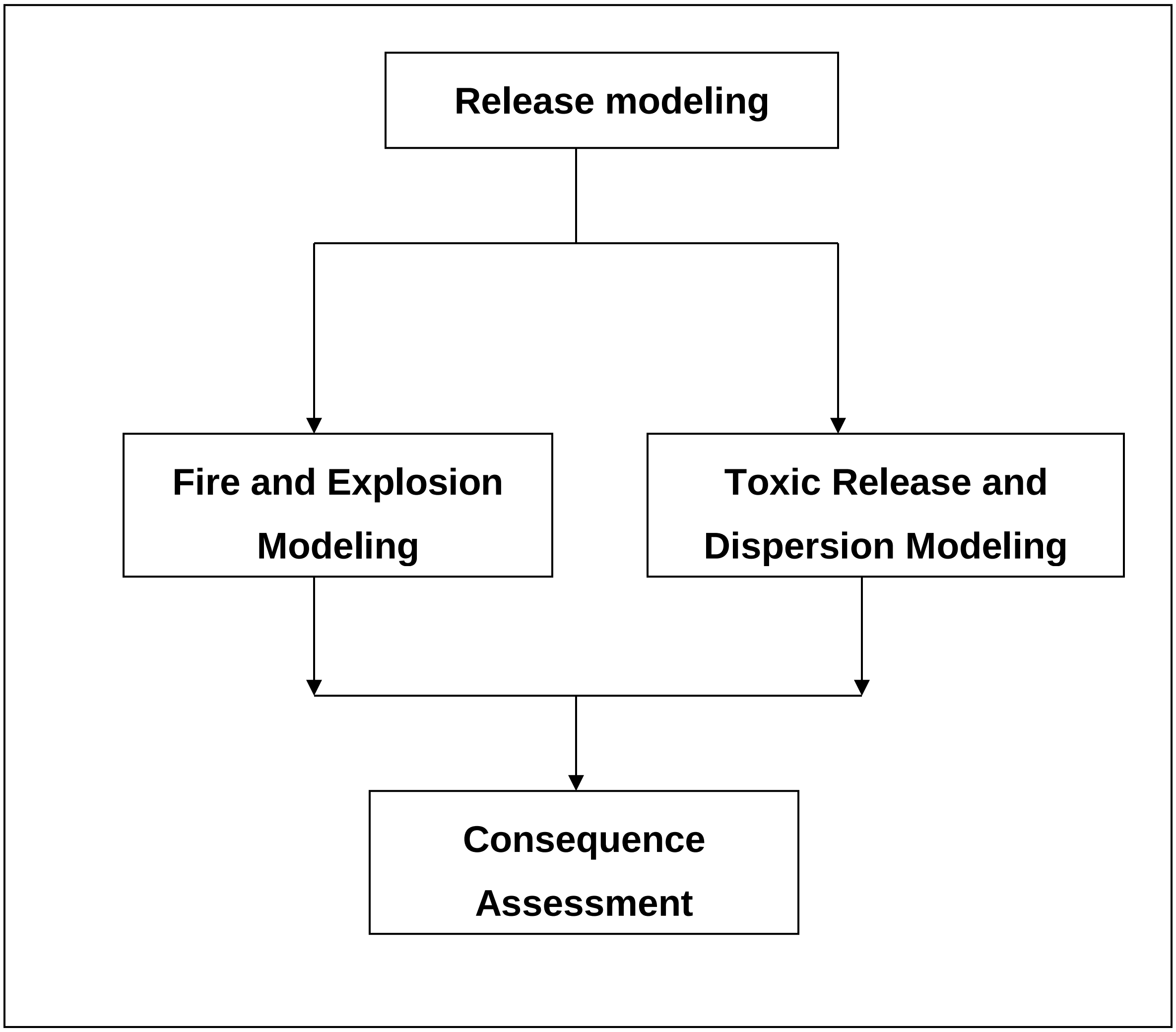
Accident model



Toxic Release and Dispersion

1. Release and dispersion modeling

- Identifying the release type
- Assessing how materials are released or release rate
- Estimating the downwind concentrations of the material

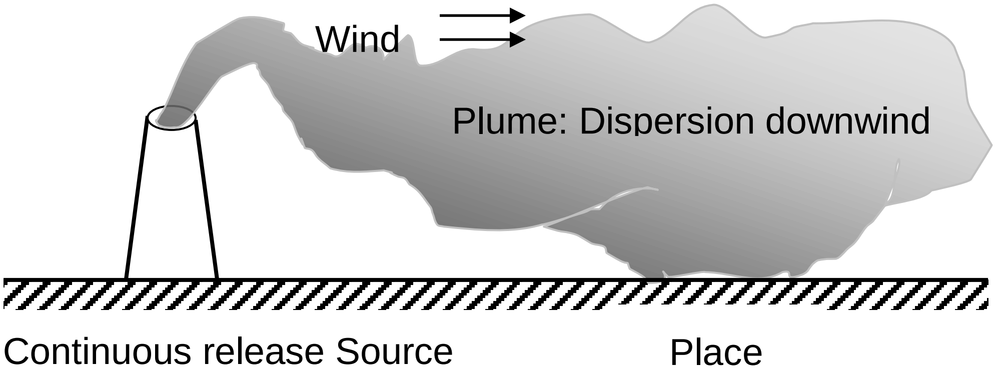
2. Dispersion Model

- Describe how vapors are transported downwind of a release.
- Three different kinds of vapor cloud behaviors and release-time modes are considered to model the released gas dispersion.

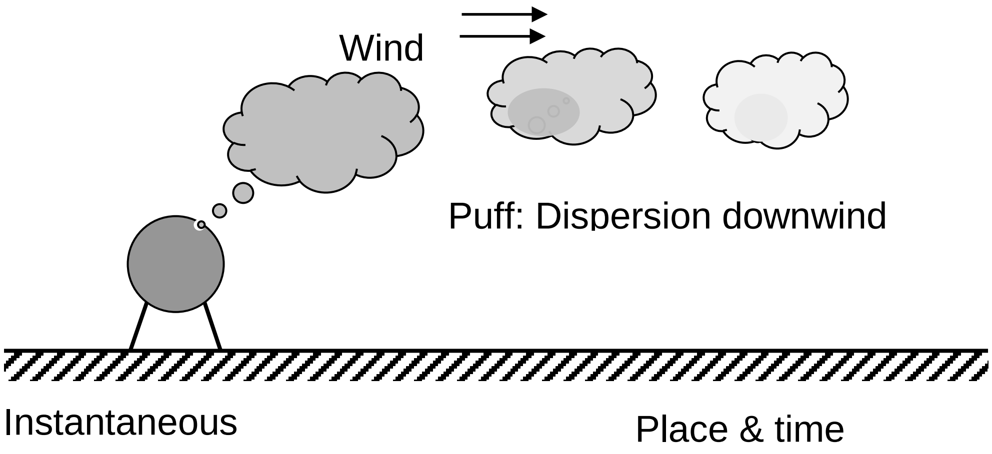
Vapor cloud behavior	Release-time mode
Neutrally buoyant gas	Instantaneous (Puff)
Positively buoyant gas	Continuous (Plumes)
Dense buoyant gas	Time varying continuous

3. Release modes

Continuous release (Plumes):



Instantaneous release (Puff):



4. Factors Affecting Dispersion

- Wind Speed
- Atmospheric Stability
- Ground Conditions
- Height of the Release above ground
- Initial momentum of the released material

Wind Speed

- Any emitted gas is initially diluted with the passing volumes of air.
- The emitted gas is carried downwind faster but is diluted faster by a larger quantity of air.
- Wind speed and direction are often presented by wind rose diagram.

- Near-neutral and stable air condition wind profile is given by:

$$U_z = U_{10}\left(\frac{Z}{10}\right)^p$$

Where, *p* is the power co-efficient. For Urban area *p* = 0.40; Sub urban area *p* =0.28; and Rural area *p* = 0.16.

Ground Conditions/Local Terrain effects:

- Ground conditions/Terrain Characteristics affect the mechanical mixing at the surface and the wind profile with height.
- Trees and buildings increase mixing, whereas lakes and open areas decrease it.
- Following Figure shows the change in wind speed versus height for a variety of surface conditions.

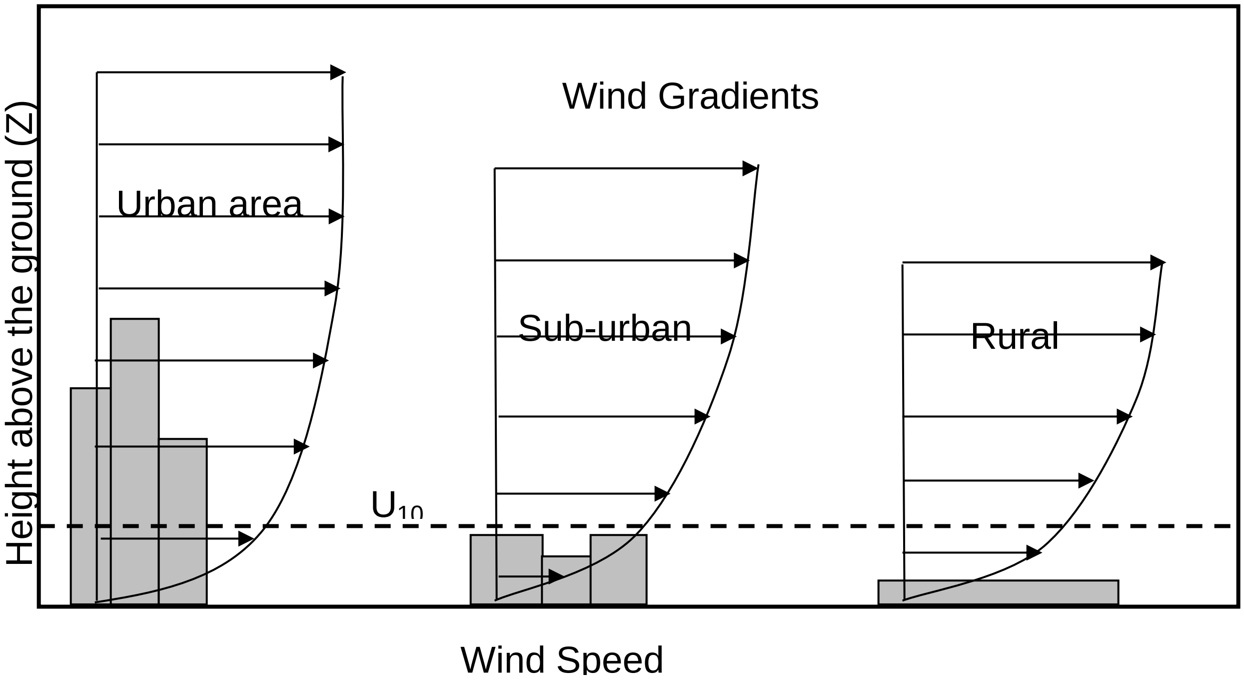


Figure: Effect of ground conditions on vertical wind gradient

Atmospheric Stability:

Stability is defined by atmospheric vertical temperature gradient. At day time, the air temperature decreases rapidly with height, encouraging vertical motions. In the night time, the temperature decrease is less, resulting in less vertical motion.

Laps rate: Negative of the temperature gradient in atmosphere

Dry adiabatic lap's rate:

$$\Gamma = -\left(\frac{dT}{dZ}\right) \cong 1^{o}C/100m$$

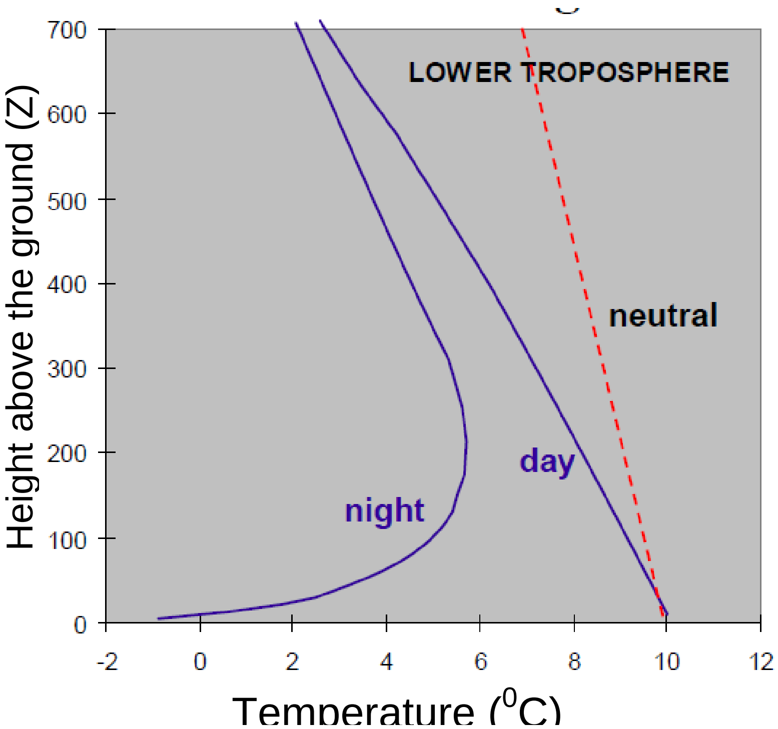


Figure: Air temperature as a function of altitude for day and night conditions. Adiabatic temperature gradient humid air: 0.5 ^{0}C / 100 m

Atmospheric stability is classified into:

Unstable: Sun heats ground faster than heat can be removed so that air temperature near the ground is higher tan the air temperature at higher elevations.

Neutral: The air above the ground warms and the wind speed increases, reducing the effect of solar input.

Stable: The sun cannot heat the ground as fast as the ground cools - temperature at ground is lower.

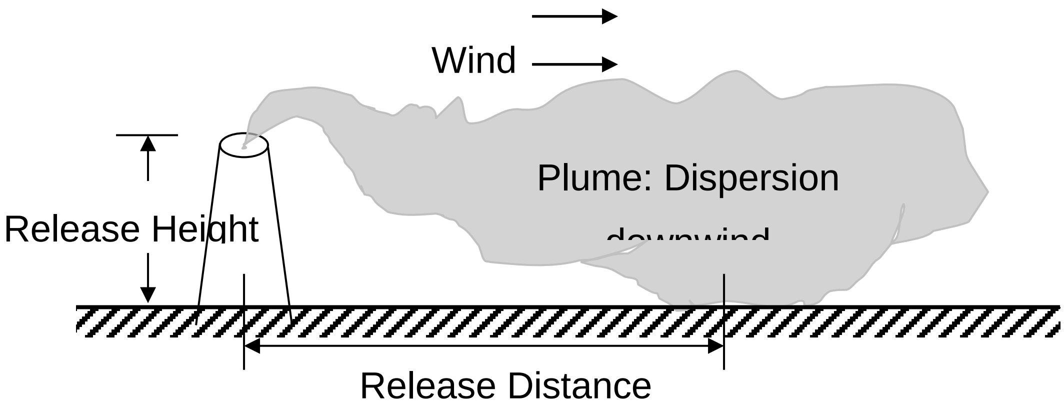
According to Pasqual stability classes (Denoted by A to F), the air conditions are normally classified into six sub-classes as shown in the following table:

Surface wind speed	**Day, incoming solar radiation**			**Night, Cloud cover thickly overcast**		**Anytime**
	Strong	Moderate	Slight	>1/2 Low clouds	<3/8 clouds	**Heavy overcast**
<2 m/s	*A	A-B	B	F	F	D
2-3 m/s	A-B	B	C	E	F	D
3-5 m/s	B	B-C	D	D	E	D
5-6 m/s	C	C-D	D	D	D	D
> 6 m/s	C	D	D	D	D	D

*A- Extremely unstable, B- Moderately unstable, C- slightly stable, D- Neutrally stable, E- Slightly stable and F- Moderately stable

Height of the Release above ground:

Ground level concentration of a dispersed plume is decreased with the increase of source of release height.



Momentum of the released material:

- Effective release height depends on initial buoyancy and momentum of the released material. The momentum of a high-velocity jet will carry the gas higher than the point of release.
- The gas heavier than air becomes neutral downwind as it mixes with air. It will initially be negatively buoyant and will slump toward the ground.
- The gas has a lower density than air, will initially be positively buoyant and will lift upward.

5. Neutral and Positively Buoyant Gas Dispersion Models:

- Neutrally and Positively Buoyant gas dispersion models estimates the average concentrations and predict the time profiles of flammable/toxic gases downwind of a release source.
- Plume and the puff models are commonly used to model the vapor cloud dispersion.

Plume Model:

It describes the continuous emissions of materials from steady state source at height H above the ground level and wind blowing in X direction.

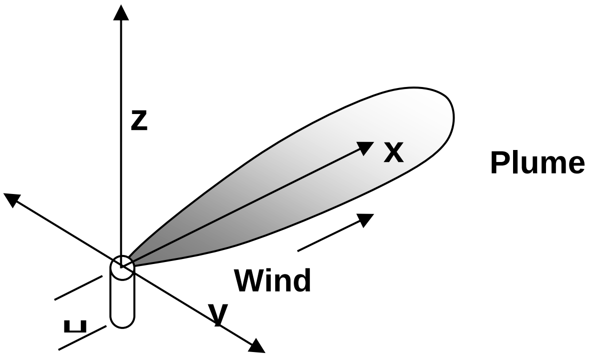


Figure: Coordinate systems of released gas dispersion

Average released materials/gas concentration:

$$C(x,y,z)=\frac{Q}{2\Pi\sigma_z\sigma_y U}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\times$$
$$\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Where

C (x,y,z) is the avg. concentration (kg/m^3),

H is height of the releasing source (m),

X, Y, and Z, are distances from the source in downwind, cross wind and vertical direction, respectively (m)

Q is release strength (kg/s)

U is wind velocity (m/s)

σ_y and σ_z are dispersion coefficients in y and z direction respectively (m). σ_y and σ_z = f (stability class, downwind distance).

Special cases of Plume modeling:

Case-1: Ground level Centerline concentration (y=z=0)

$$C(x,0,0) = \frac{Q}{\Pi \sigma_z \sigma_y U} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2 \right]$$

Case-2: Ground, centerline, release height H = 0,

$$\mathrm{C(x,0,0)} = \frac{\mathrm{Q}}{\Pi \sigma_{\mathrm{z}} \sigma_{\mathrm{y}} \mathrm{U}}$$

In both cases x is implicit in the dispersion coefficients.

Maximum Concentrations – Plume

- Always occurs at release point.
- For releases above ground, maximum concentration occurs downwind along the centerline (X-axis). Distance at which maximum ground level concentration would occur is given by:

$$\sigma_z = \frac{H}{\sqrt{2}}$$

- The max. concentration is estimated by:

$$C(\max) = \frac{2Q}{e \Pi U H^2} \left[\left(\frac{\sigma_z}{\sigma_y} \right) \right]$$

Puff model:

- It describes the instantaneous releases of material. Example: Sudden release of a fixed amount of material from a ruptured vessel. Large vapor cloud is dispersed from the rupture point.
- The puff model can be used to describe a plume. For instance (the effect on a plume of a change in wind direction), puff modeling is a kind of dynamic modeling of plumes.

The average concentration is estimated for puff release by:

$$C(x,y,z,t)=\frac{Q_{inst}}{(2\Pi)^{3/2}\sigma_x\sigma_y\sigma_z}\times\exp\left[-\frac{1}{2}\left(\frac{x-ut}{\sigma_x}\right)^2\right]$$
$$\times\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\times\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Where Q_{inst} is quantity released (kg). All other parameters definitions are same.

Special cases of puff modeling:

Case-1: Total integrated dose at ground level i.e. z=0 is given by:

$$Dose(x,y,0)=\frac{Q_{inst}}{\Pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right]$$

Case-2: Concentration on ground below puff center

$$C(x,0,0,t) = \frac{Q_{inst}}{\sqrt{2}\Pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right]$$

Case-3: Puff center on ground i.e., H = 0.

$$C(x,0,0,t) = \frac{Q_{inst}}{\sqrt{2}\Pi^{3/2}\sigma_x\sigma_y\sigma_z}$$

Maximum Concentration - Puff

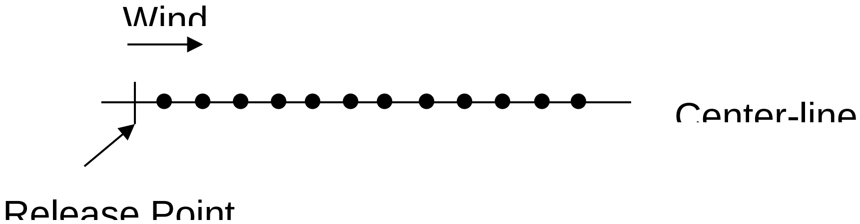
- Puff center always at release height.
- Center of puff located at: *x* = *u t*
- On ground, maximum concentration always occurs directly below puff center**.**

5.0 Isopleths

- It measures the cloud boundary at a fixed concentration.
- Represents the lines of constant concentration

Determining Isopleths: Plume and Puff

1. Determine concentrations along centerline at fixed points downwind.

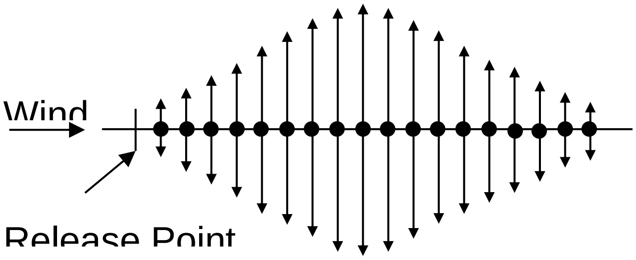


2. Use the following equation to find y at each fixed point.

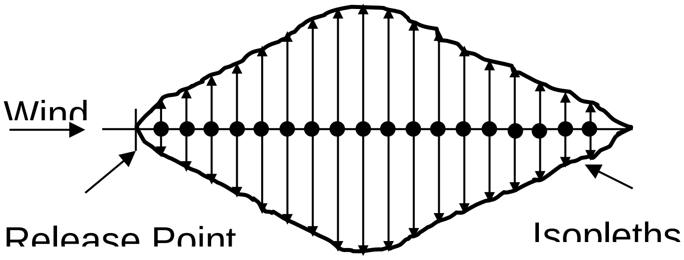
$$y = \sigma_y \sqrt{2 \ln \left(\frac{C(x,0,0,t)}{C(x,y,0,t)} \right)}$$

Here y = off-center distance to isopleth, $C(x,0,0,t)$ = Downwind, ground centerline conc. And $C(x,y,0,t)$ = Isopleths conc.

3. Plot y for both directions at each fixed point.



4. Connect the points.



5. Estimation of dispersion coefficients

1. Classify the stability class by using meteorological data such as wind speed, heat radiation, cloud cover etc.

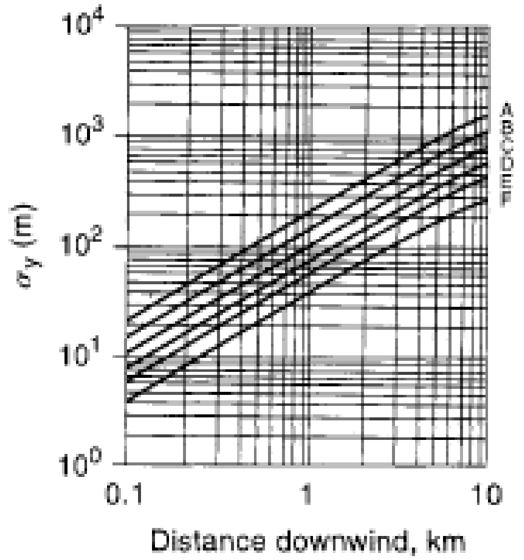
Stability classification based on meteorological data

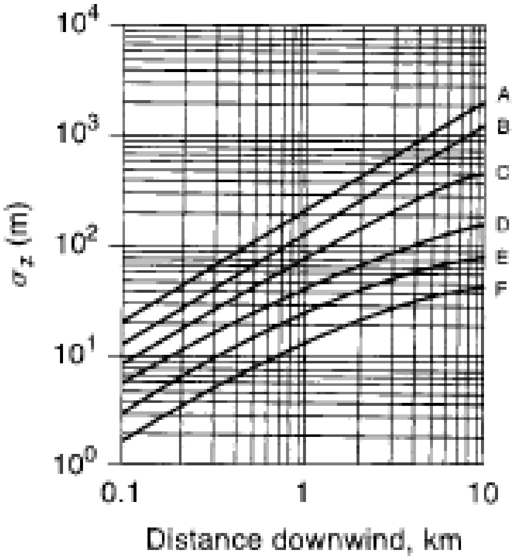
Surface wind speed	**Day, incoming solar radiation**			**Night, Cloud cover thickly overcast**		**Anytime**
	Strong	Moderate	Slight	>1/2 Low clouds	<3/8 clouds	**Heavy overcast**
<2 m/s	A	A-B	B	F	F	D
2-3 m/s	A-B	B	C	E	F	D
3-5 m/s	B	B-C	D	D	E	D
5-6 m/s	C	C-D	D	D	D	D
> 6 m/s	C	D	D	D	D	D

2. Classify the area, whether it is rural or urban, flat or hilly, etc.
3. So using either figures or fitted equations, depending upon the type of release and terrain, calculate dispersion coefficient at required downwind distance.

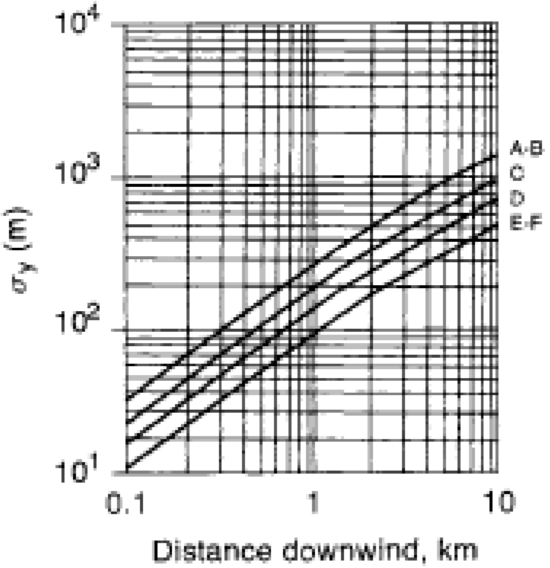
Figures for determining the dispersion coefficients (Source: Crowl & Louvar)

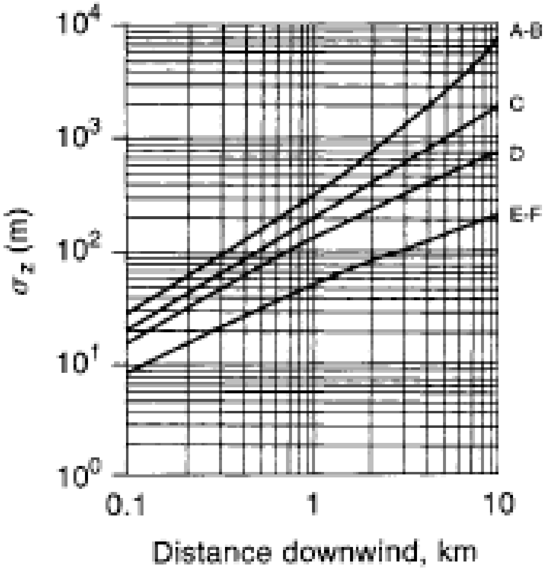
Plume model for fural Release:



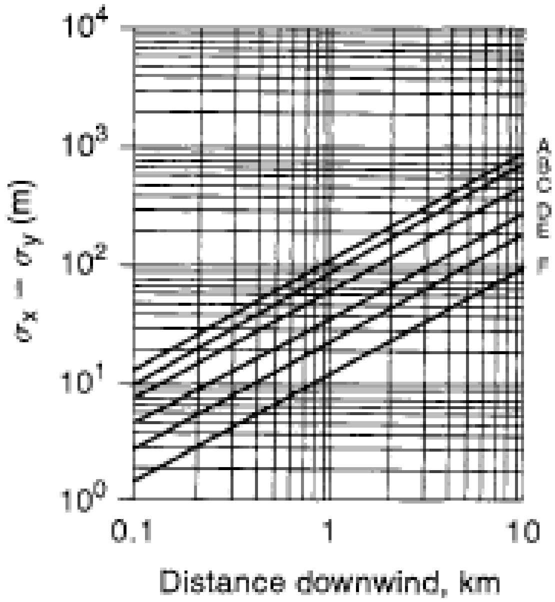


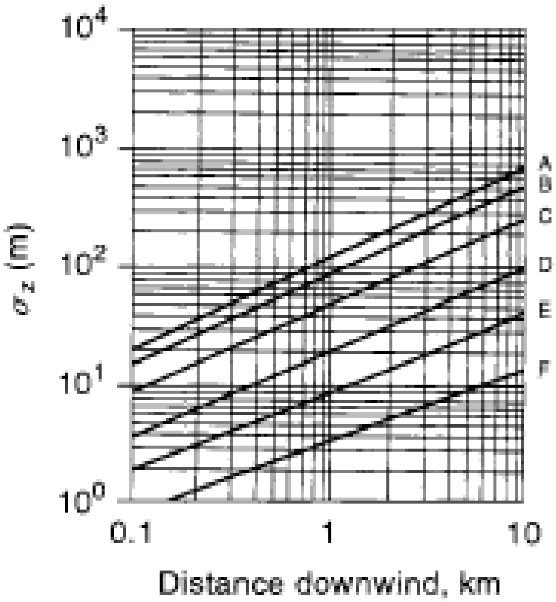
Plume model for urban Release:





Puff dispersion model:





Equations to determine the dispersion coefficients (Source: Crowl & Louvar)

Plume Dispersion (Continuous release):

Area	*Stability Class*	σ_y *(m)*	σ_z *(m)*
Rural conditions	**A**	$0.22X\,(1+0.0001X)^{-0.5}$	$0.20X$
	B	$0.16X\,(1+0.0001X)^{-0.5}$	$0.12X$
	C	$0.11X\,(1+0.0001X)^{-0.5}$	$0.08X\,(1+0.0002X)^{-0.5}$
	D	$0.08X\,(1+0.0001X)^{-0.5}$	$0.06X\,(1+0.0015X)^{-0.5}$
	E	$0.06X\,(1+0.0001X)^{-0.5}$	$0.03X\,(1+0.0003X)^{-1.0}$
	F	$0.04X\,(1+0.0001X)^{-0.5}$	$0.016X\,(1+0.0003X)^{-1.0}$
Urban conditions	**A-B**	$0.32X\,(1+0.0004X)^{-0.5}$	$0.24X\,(1+0.0001X)^{0.5}$
	C	$0.22X\,(1+0.0004X)^{-0.5}$	$0.20X$
	D	$0.16X\,(1+0.0004X)^{-0.5}$	$0.14X\,(1+0.0003X)^{-0.5}$
	E-F	$0.11X\,(1+0.0004X)^{-0.5}$	$0.08X\,(1+0.0015X)^{-0.5}$

Puff model (Instantaneous release)

Area	*Stability Class*	σ_x or σ_y (m)	σ_z (m)
Rural conditions	**A**	$0.18X^{0.92}$	$0.60X^{0.75}$
	B	$0.14X^{0.92}$	$0.53X^{0.73}$
	C	$0.10X^{0.92}$	$0.34X^{0.71}$
	D	$0.06X^{0.92}$	$0.15X^{0.70}$
	E	$0.04X^{0.92}$	$0.10X^{0.65}$
	F	$0.02X^{0.89}$	$0.05X^{0.61}$

X is downwind distance in meter from release source

Consideration of worst-Case Conditions

- For a plume the highest concentration is always found at the release point. If the release occurs above ground level, then the highest concentration on the ground is found at a point downwind from the release.
- For a puff the maximum concentration is always found at the puff center. For a release above ground level the puff center will move parallel to the ground and the maximum concentration on the ground will occur directly below the puff center.
- For a puff isopleth the isopleths is close to circular as it moves downwind. The diameter of the isopleth increases initially as the puff travels downwind, reaches a maximum, and then decreases in diameter.
- If weather conditions are not known or are not specified, then certain assumptions can be made to result in a

worst-case result; that is, the highest concentration is estimated.

- The maximum concentration is estimated by selecting the weather conditions and wind speed that result in the smallest values of the dispersion coefficients. The smallest dispersion coefficients occur with F stability. Clearly, the wind speed cannot be zero, so a finite value must be selected.
- The EPA suggests that F stability can exist with wind speeds as low as 1.5 m/s. Some risk analysts use a wind speed of 2 m/s.
- The assumptions used in the calculation must be clearly stated.

7.0 Dense Gas Dispersion

- Gases having density higher than air are called dense gases
- Released dense gases initially slump toward the ground and move both upwind and downwind.
- Mixing mechanisms with air are completely different from neutrally buoyant releases.
- Britter-McQuaid Dense Gas dispersion Model is commonly used

Following steps have to be followed:

1. Characterize the initial buoyancy

$$g_o = g\frac{(\rho_o - \rho_a)}{\rho_a},$$

Where, g is gravitational acceleration, ρ_o and ρ_a are density of released material and ambient air respectively

2. Decide whether release is instantaneous or continuous

$$F = \left(\frac{uR_d}{x} \right)$$

Where is u is wind velocity, x is distance from the release point and R_d is release duration

If F => 2.5, Continuous

If F<= 0.6, Instantaneous

For 0.6<F<2.5, use both approaches and take maximum one

3. Characterize source dimension
   - Continuous

$$D_c = \left(\frac{q_o}{u} \right)^{1/2}$$

Where, D_c is source dimension (m), qo is initial plume volume flux (volume/time), and u is wind speed (length/time)

- Instantaneous

$$D_i = V_0^{1/3}$$

Where, D_i is source dimension (m), V_o is initial volume ($Length^3$)

4. Checking criteria

- Continuous release:

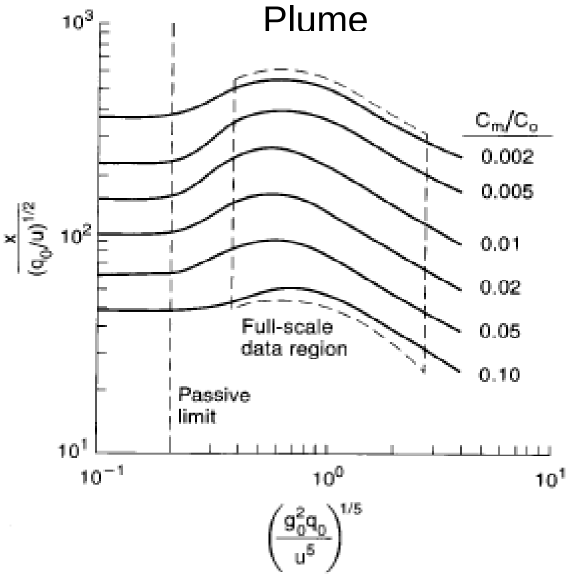
$$\left(\frac{g_o q_o}{u^3 D_c}\right)^{1/3} \geq 0.15$$

- Instantaneous release:

$$\frac{\sqrt{g_o V_o}}{u D_i} \geq 0.20$$

If the criterion satisfies concentration may either be read from the following figure or calculated using equations given in the table. These equations or graphs in the figure are valid of rural terrain.

Figure: Britter-McQuaid dimensional correlation for dispersion of dense gas (Source: Crowl & Louvar)



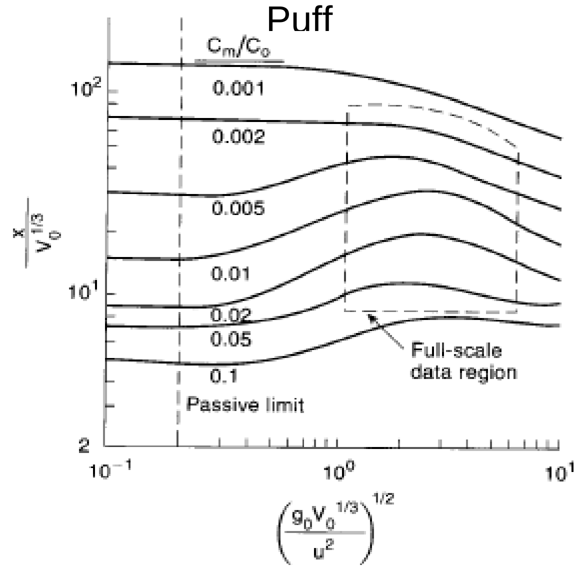
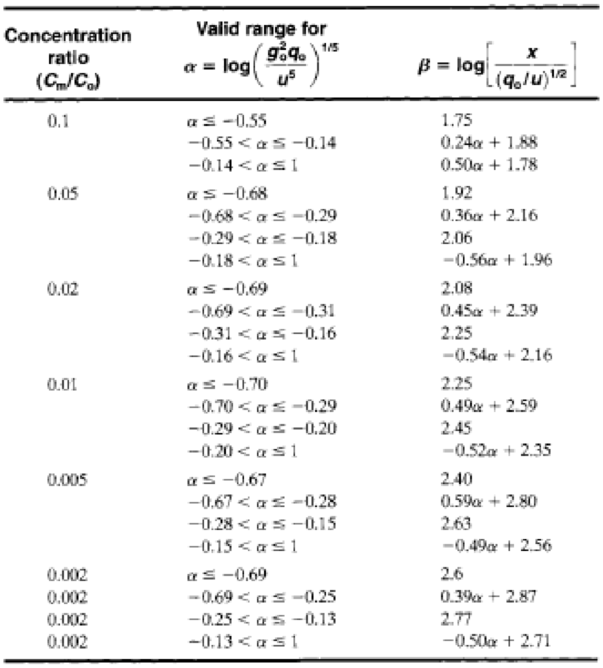


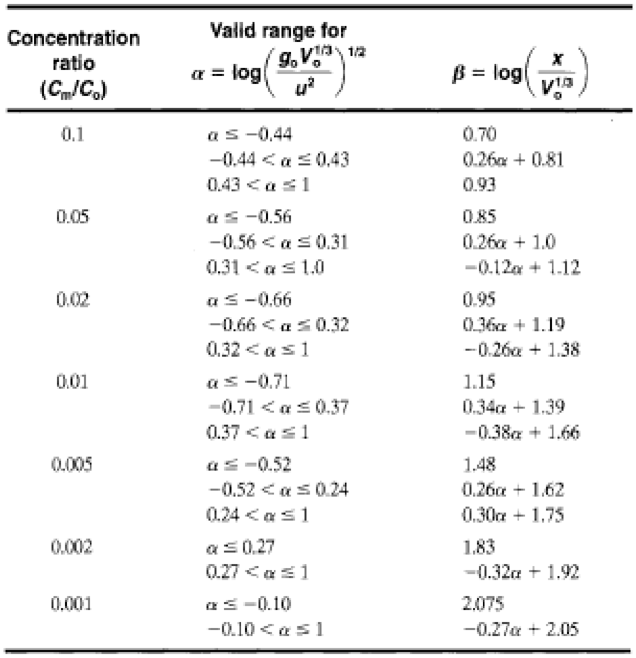
Table: Equation to approximate Britter-McQuaid dimensional correlation (Source: Crowl & Louvar)

Dispersion of dense gas plumes



Concentration ratio (C_m/C_o)	Valid range for $\alpha = \log\left(\frac{g_o^2 q_o}{u^5}\right)^{1/5}$	$\beta = \log\left[\frac{x}{(q_o/u)^{1/2}}\right]$
0.1	$\alpha \le -0.55$	1.75
	$-0.55 < \alpha \le -0.14$	$0.24\alpha + 1.88$
	$-0.14 < \alpha \le 1$	$0.50\alpha + 1.78$
0.05	$\alpha \le -0.68$	1.92
	$-0.68 < \alpha \le -0.29$	$0.36\alpha + 2.16$
	$-0.29 < \alpha \le -0.18$	2.06
	$-0.18 < \alpha \le 1$	$-0.56\alpha + 1.96$
0.02	$\alpha \le -0.69$	2.08
	$-0.69 < \alpha \le -0.31$	$0.45\alpha + 2.39$
	$-0.31 < \alpha \le -0.16$	2.25
	$-0.16 < \alpha \le 1$	$-0.54\alpha + 2.16$
0.01	$\alpha \le -0.70$	2.25
	$-0.70 < \alpha \le -0.29$	$0.49\alpha + 2.59$
	$-0.29 < \alpha \le -0.20$	2.45
	$-0.20 < \alpha \le 1$	$-0.52\alpha + 2.35$
0.005	$\alpha \le -0.67$	2.40
	$-0.67 < \alpha \le -0.28$	$0.59\alpha + 2.80$
	$-0.28 < \alpha \le -0.15$	2.63
	$-0.15 < \alpha \le 1$	$-0.49\alpha + 2.56$
0.002	$\alpha \le -0.69$	2.6
0.002	$-0.69 < \alpha \le -0.25$	$0.39\alpha + 2.87$
0.002	$-0.25 < \alpha \le -0.13$	2.77
0.002	$-0.13 < \alpha \le 1$	$-0.50\alpha + 2.71$

Dispersion of dense gas puffs



Concentration ratio (C_m/C_o)	Valid range for $\alpha = \log\left(\frac{g_o V_o^{1/3}}{u^2}\right)^{1/2}$	$\beta = \log\left(\frac{x}{V_o^{1/3}}\right)$
0.1	$\alpha \le -0.44$	0.70
	$-0.44 < \alpha \le 0.43$	$0.26\alpha + 0.81$
	$0.43 < \alpha \le 1$	0.93
0.05	$\alpha \le -0.56$	0.85
	$-0.56 < \alpha \le 0.31$	$0.26\alpha + 1.0$
	$0.31 < \alpha \le 1.0$	$-0.12\alpha + 1.12$
0.02	$\alpha \le -0.66$	0.95
	$-0.66 < \alpha \le 0.32$	$0.36\alpha + 1.19$
	$0.32 < \alpha \le 1$	$-0.26\alpha + 1.38$
0.01	$\alpha \le -0.71$	1.15
	$-0.71 < \alpha \le 0.37$	$0.34\alpha + 1.39$
	$0.37 < \alpha \le 1$	$-0.38\alpha + 1.66$
0.005	$\alpha \le -0.52$	1.48
	$-0.52 < \alpha \le 0.24$	$0.26\alpha + 1.62$
	$0.24 < \alpha \le 1$	$0.30\alpha + 1.75$
0.002	$\alpha \le 0.27$	1.83
	$0.27 < \alpha \le 1$	$-0.32\alpha + 1.92$
0.001	$\alpha \le -0.10$	2.075
	$-0.10 < \alpha \le 1$	$-0.27\alpha + 2.05$

Toxic Effect Evaluation Criteria

- The concentration that is considered as a dangerous release.
- PELs or TLV-TWAs are too much conservative and estimated for the work exposures.

Methods of evaluating Toxic effect criteria:

1. American Industrial Hygiene Association's *Emergency Response Planning Guidelines (ERPG)*
    - ERPG-1is the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing effects other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.
    - ERPG-2 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.
    - ERPG-3 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing life-threatening health effects (similar to EEGLs).
2. NIOSH's Immediately Dangerous to Life and Health (IDLH)
3. NRC's Emergency exposure Guidance Levels (EEGLs)
    - 1hr EEGLs

  - 24 hr EEGLs

4. ACGIH’s Threshold Limit Values (TLVs)
    - Time weighted TLVs (TLV-TWA)
    - Short Term TLVs (TLV- STEL)
    - Ceiling point TLVs (TLV-C)
5. OSHA’s Permissible Exposure Limits (PELs)
6. EPA’s toxic end point

8.0 Effect of Release Momentum and Buoyancy

- The release characteristics of a puff or plume depend on the initial release momentum and buoyancy.
- The initial momentum and buoyancy change the effective height of release.
- A release that occurs at ground level but in an upward spouting jet of vaporizing liquid has a greater effective height than a release without a jet. Similarly, a release of vapor at a temperature higher than the ambient air temperature will rise because of buoyancy effects, increasing the effective height of the release.
- The following Holland formula is suggested to compute the additional height resulting from the buoyancy and momentum of the release for smokestack releases.

$$\Delta H_r = \frac{\bar{u}_s d}{\bar{u}}\left[1.5 + 2.68 \times 10^{-3} P d\left(\frac{T_s - T_a}{T_s}\right)\right]$$

Here,

ΔH, is the correction to the release height H,

$\bar{u}_s$is the stack gas exit velocity (in mls), d is the inside stack diameter (in m),

$\bar{u}$ is the wind speed (in mls),

P is the atmospheric pressure (in mb),

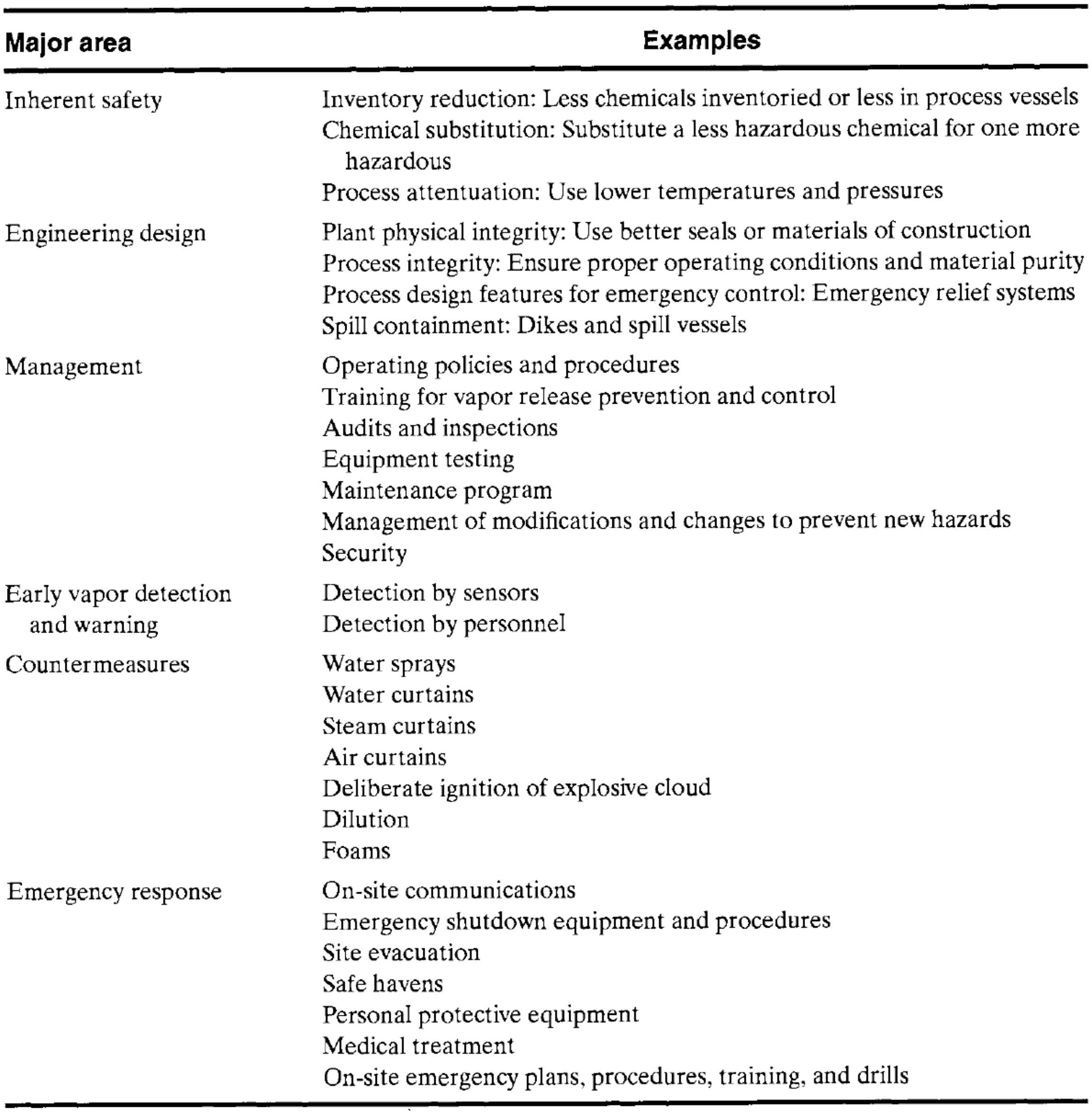
T, is the stack gas temperature (in K), and

Ta is the air temperature (in K).

9.0 Release Mitigation

- The purpose of the toxic release model is to provide a tool for performing release mitigation.
- Release mitigation is defined as "lessening the risk of a release incident by acting on the source (at the point of release) either (1) in a preventive way by reducing the likelihood of an event that could generate a hazardous vapor cloud or (2) in a protective way by reducing the magnitude of the release andlor the exposure of local persons or property
- Risk is composed of both consequence and probability. Thus an estimate of the consequences of a release provides only half the total risk assessment. It is possible that a particular release incident might have high consequences, leading to extensive plant mitigation efforts to reduce the consequence. However, if the probability is low, the effort might not be required.
- Both the consequence and the probability must be included to assess risk.
- The following table contains a number of measures to mitigate a release.

Table Release Mitigation Approaches



Major area	Examples
Inherent safety	Inventory reduction: Less chemicals inventoried or less in process vessels Chemical substitution: Substitute a less hazardous chemical for one more hazardous Process attentuation: Use lower temperatures and pressures
Engineering design	Plant physical integrity: Use better seals or materials of construction Process integrity: Ensure proper operating conditions and material purity Process design features for emergency control: Emergency relief systems Spill containment: Dikes and spill vessels
Management	Operating policies and procedures Training for vapor release prevention and control Audits and inspections Equipment testing Maintenance program Management of modifications and changes to prevent new hazards Security
Early vapor detection and warning	Detection by sensors Detection by personnel
Countermeasures	Water sprays Water curtains Steam curtains Air curtains Deliberate ignition of explosive cloud Dilution Foams
Emergency response	On-site communications Emergency shutdown equipment and procedures Site evacuation Safe havens Personal protective equipment Medical treatment On-site emergency plans, procedures, training, and drills

References used in the lecture note:

American Institute of Chemical Engineers (AIChE), (2000). *Guidelines for chemical process quantitative risk analysis.* Second Edition, New York: AIChE.

Crowl D.A., Louvar J.F. (2002). ”*Chemical Process Safety, Fundamentals with Applications – 2nd edition*”, Upper Saddle River, N.J.: Prentice Hall PTR.

http://www.chem.mtu.edu/~crowl/cm4310/

Table: Emergency Response Planning Guidelines (ERPGs) for selected chemicals

Chemical	**ERPG-1**	**ERPG-2**	**ERPG-3**
Acetaldehyde	10	200	1000
Acrolein	0.1	0.5	3
Acrylic acid	2	50	750
Acrylonitrile	NA	35	75
Allyl chloride	3	40	300
Ammonia	25	200	1000
Benzene	50	150	1000
Benzyl chloride	1	10	25
Bromine	0.2	1	5
1,3-Butadiene	10	50	5000
n-Butyl acrylate	0.05	25	250
n-Butyl isocyanate	0.01	0.05	1
Carbon disulfide	1	50	500
Carbon tetrachloride	20	100	750
Chlorine	1	3	20
Chlorine trifluoride	0.1	1	10
Chloroacetyl chloride	0.1	1	10
Chloropicrin	NA	0.2	3
Chlorosulfonic acid	2 mg/m^3	10 mg/m^3	30 mg/m^3
Chlorotrifluoroethylene	20	100	300
Crotonaldehyde	2	10	50
Diborane	NA	1	3
Diketene	1	5	50
Dimethylamine	1	100	500
Dimethylchlorosilane	0.8	5	25
Dimethyl disulfide	0.01	50	250
Epichlorohydrin	2	20	100
Ethylene oxide	NA	50	500
Formaldehyde	1	10	25
Hexachlorobutadiene	3	10	30
Hexafluoroacetone	NA	1	50
Hexafluoropropylene	10	50	500
Hydrogen chloride	3	20	100
Hydrogen cyanide	NA	10	25
Hydrogen fluoride	54	20	50
Hydrogen sulfide	0.1	30	100
Isobutyronitrile	10	50	200
2-Isocyanatoethyl methacrylate	NA	0.1	1
Lithium hydride	25 μg/m^3	100 μg/m^3	500 μg/m^3
Methanol	200	1,000	5,000
Methyl chloride	NA	400	1000
Methylene chloride	200	750	4000
Methyl iodide	25	50	125