Toxic Release and Dispersion Models

- During an accident, process equipment can release toxic materials quickly and in significant enough quantities to spread in dangerous clouds throughout a plant site and the local community.
- A few examples are explosive rupture of a process vessel as a result of excessive pressure caused by a runaway reaction, rupture of a pipeline containing toxic materials at high pressure, rupture of a tank containing toxic material stored above its atmospheric boiling point, and rupture of a train or truck transportation tank following an accident.
- Serious accidents (such as Bhopal) emphasize the importance of planning for emergencies and of designing plants to minimize the occurrence and consequences of a toxic release.
- Toxic release models are routinely used to estimate the effects of a release on the plant and community environments.

- An excellent safety program strives to identify problems before they occur.
- Chemical engineers must understand all aspects of toxic release to prevent the existence of release situations and to reduce the impact of a release if one occurs.
- This requires a toxic release model.
- Toxic release and dispersion models are an important part of the consequence modelling procedure.
- The toxic release model represents the first three steps in the consequence modeling procedure.
- These steps are

    1. Identifying the release incident (what process situations can lead to a release?

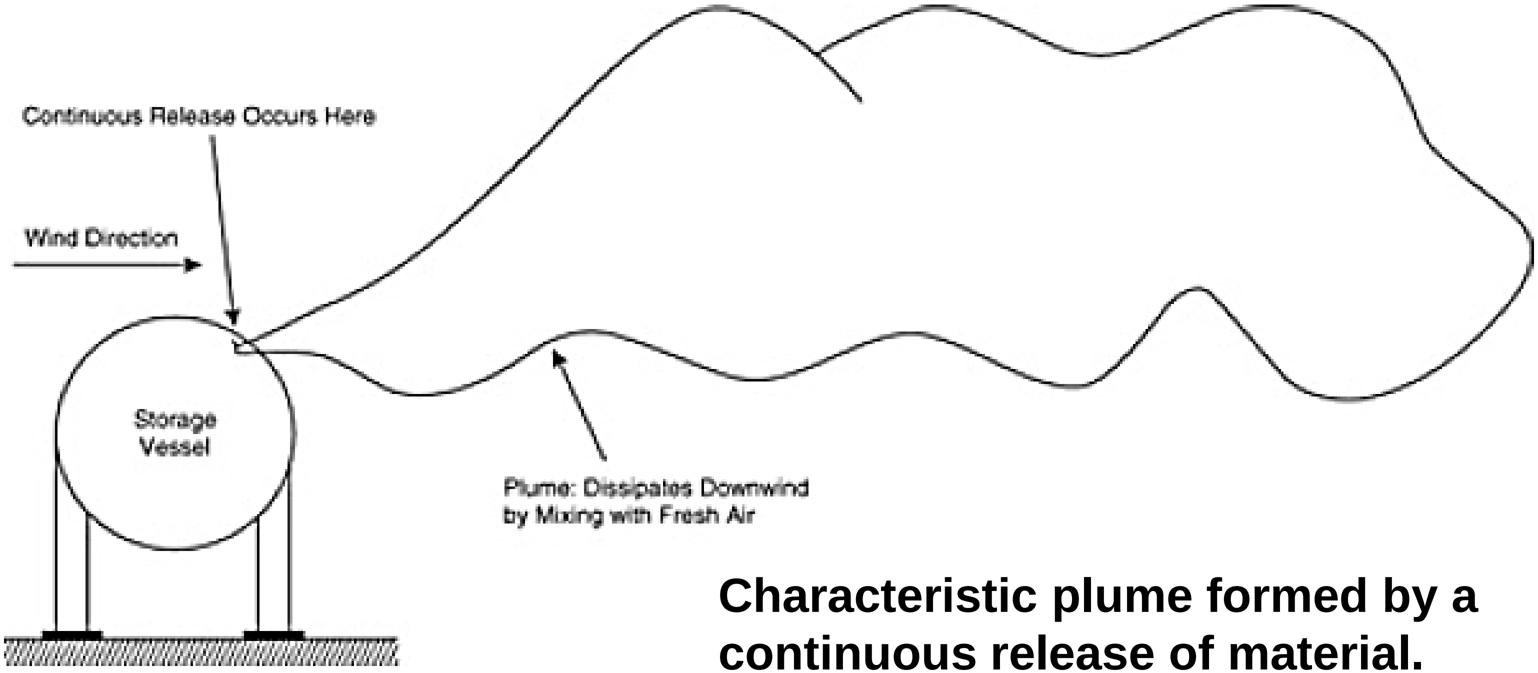
    2. Developing a source model to describe how materials are released and the rate of release

    3. Estimating the downwind concentrations of the toxic material using a dispersion model (once the downwind concentrations are known, several criteria are available to estimate the impact or effect)

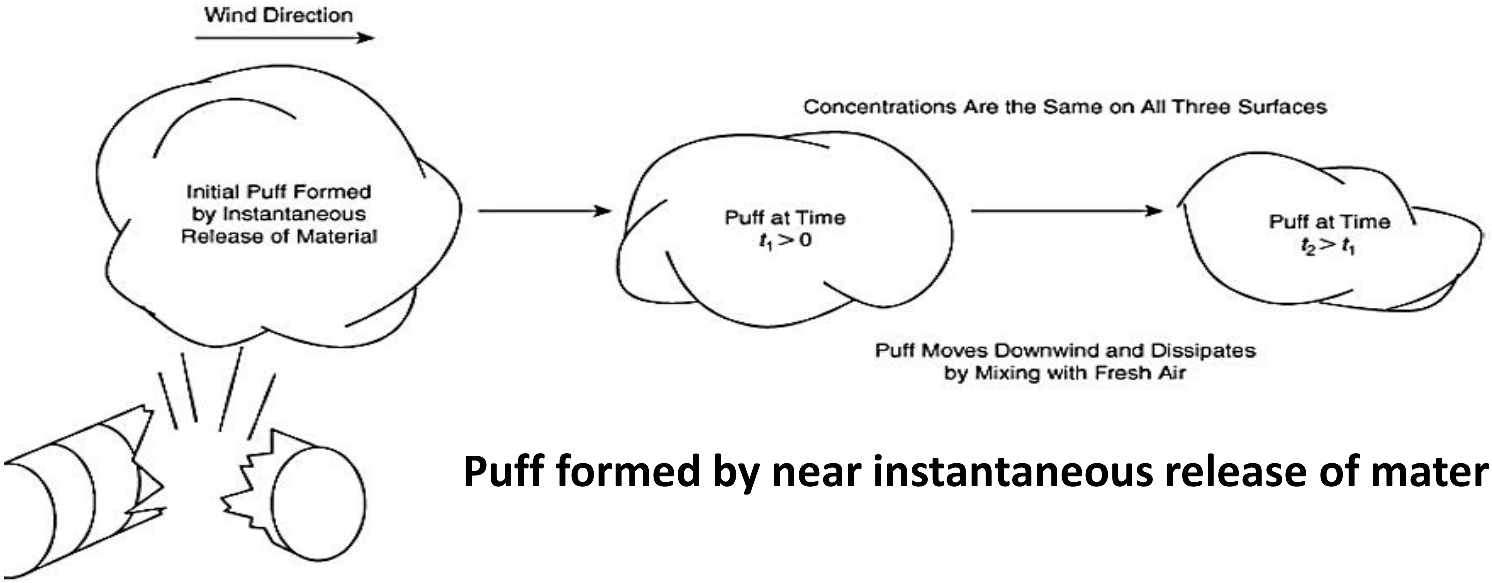
- Various options are available, based on the predictions of the toxic release model,
- For example,
  - (1) developing an emergency response plan with the surrounding community,
  - (2) developing engineering modifications to eliminate the source of the release,
  - (3) enclosing the potential release and adding appropriate vent scrubbers or other vapor removal equipment,
  - (4) reducing inventories of hazardous materials to reduce the quantity released,
  - (5) adding area monitors to detect incipient leaks and providing block valves and
- Engineering controls to eliminate hazardous levels of spills and leaks. These options are discussed in more detail on release mitigation.

Parameters Affecting Dispersion

- Dispersion models describe the airborne transport of toxic materials away from the accident site and into the plant and community.
- After a release the airborne toxic material is carried away by the wind in a characteristic plume, or a puff, as shown in Figures.
- The maximum concentration of toxic material occurs at the release point (which may not be at ground level).
- Concentrations downwind are less, because of turbulent mixing and dispersion of the toxic substance with air.



Characteristic plume formed by a continuous release of material.



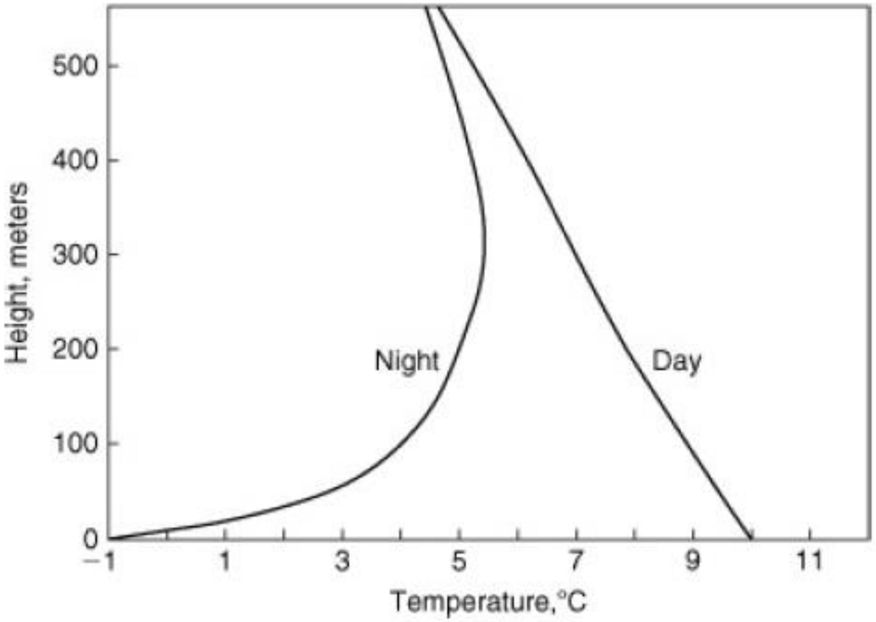
Puff formed by near instantaneous release of material.

A wide variety of parameters affect atmospheric dispersion of toxic materials:

- Wind speed
- Atmospheric stability
- Ground conditions (buildings, water, trees)
- Height of the release above ground level
- Momentum and buoyancy of the initial material released

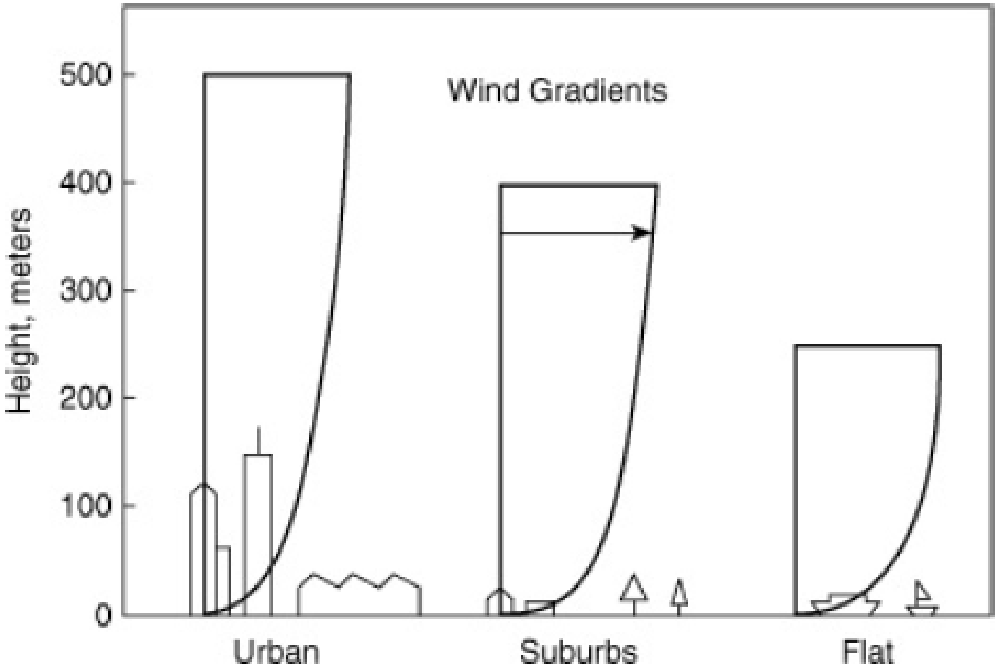
As the wind speed increases, the plume in becomes longer and narrower. The substance is carried downwind faster but is diluted faster by a larger quantity of air.

- Atmospheric stability relates to vertical mixing of the air.
- During the day, the air temperature decreases rapidly with height, encouraging vertical motions.
- At night the temperature decrease is less, resulting in less vertical motion.
- Temperature profiles for day and night situations are shown in Figure.
- Sometimes an inversion occurs. During an inversion, the temperature increases with height, resulting in minimal vertical motion.
- This most often occurs at night because the ground cools rapidly as a result of thermal radiation.

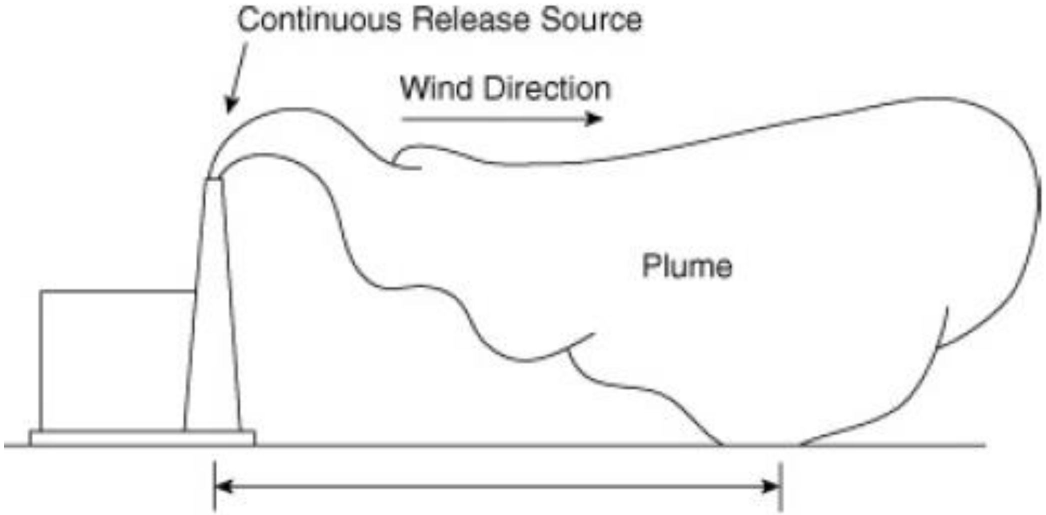


- Atmospheric stability is classified according to three stability classes: unstable, neutral, and stable.
- For unstable atmospheric conditions the sun heats the ground faster than the heat can be removed so that the air temperature near the ground is higher than the air temperature at higher elevations, as might be observed in the early morning hours.
- This results in instable stability because air of lower density is below air of greater density.
- This influence of buoyancy enhances atmospheric mechanical turbulence.
- For neutral stability the air above the ground warms and the wind speed increases, reducing the effect of solar energy input, or insolation.
- The air temperature difference does not influence atmospheric mechanical turbulence.
- For stable atmospheric conditions the sun cannot heat the ground as fast as the ground cools; therefore the temperature near the ground is lower than the air temperature at higher elevations.
- This condition is stable because the air of higher density is below air of lower density.
- The influence of buoyancy suppresses mechanical turbulence.

- Ground conditions 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.
- Figure shows the change in wind speed versus height for a variety of surface conditions.

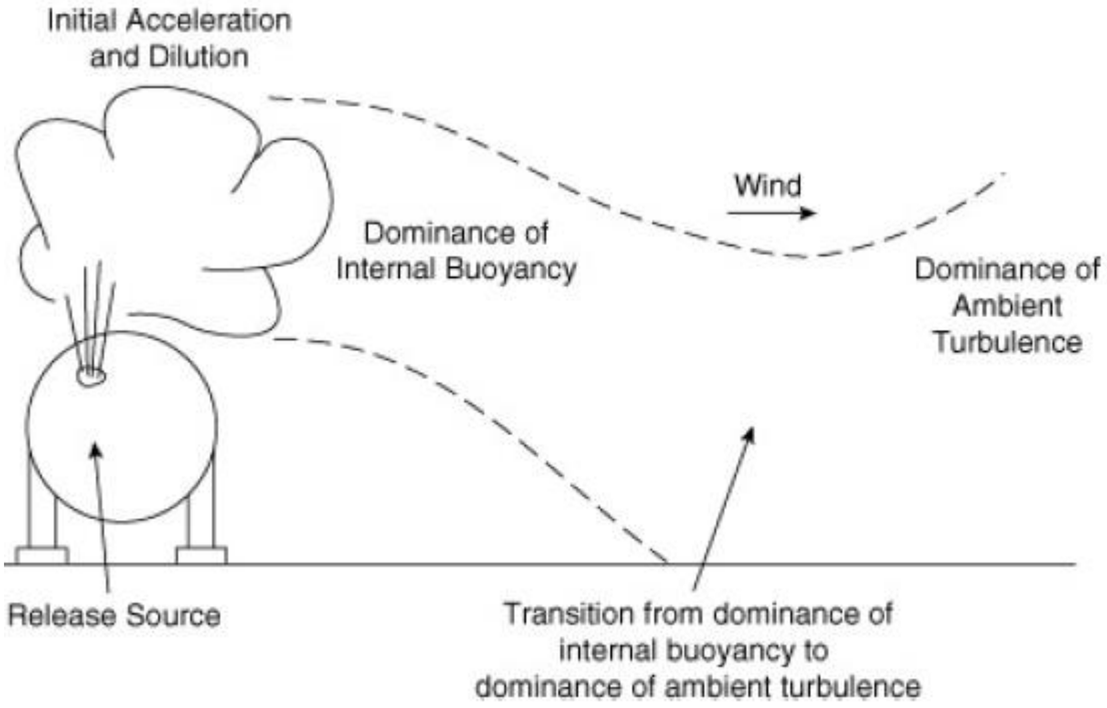


- The release height significantly affects ground-level concentrations.
- As the release height increases, ground-level concentrations are reduced because the plume must disperse a greater distance vertically.



As release height increases, this distance increases. The increased distance leads to greater dispersion and a lower concentration at ground level.

The buoyancy and momentum of the material released change the effective height of the release demonstrates these effects



- The momentum of a high-velocity jet will carry the gas higher than the point of release, resulting in a much higher effective release height.
- If the gas has a density less than air, the released gas will initially be positively buoyant and will lift upward.
- If the gas has a density greater than air, then the released gas will initially be negatively buoyant and will slump toward the ground.

Neutrally Buoyant Dispersion Models

- Neutrally buoyant dispersion models are used to estimate the concentrations downwind of a release in which the gas is mixed with fresh air to the point that the resulting mixture is neutrally buoyant.
- Thus these models apply to gases at low concentrations, typically in the parts per million range.
- Two types of neutrally buoyant vapor cloud dispersion models are commonly used: the plume and the puff models.
- The plume model describes the steady-state concentration of material released from a continuous source.
- The puff model describes the temporal concentration of material from a single release of a fixed amount of material.
- For the plume model a typical example is the continuous release of gases from a smokestack.
- A steady-state plume is formed downwind from the smokestack.
- For the puff model a typical example is the sudden release of a fixed amount of material because of the rupture of a storage vessel. A large vapor cloud is formed that moves away from the rupture point.

- The puff model can be used to describe a plume; a plume is simply the release of continuous puffs.
- However, if steady-state plume information is all that is required,
- The plume model is recommended because it is easier to use.
- For studies involving dynamic plumes (for instance, the effect on a plume of a change in wind direction), the puff model must be used.
- Consider the instantaneous release of a fixed mass of material, Qm, into an infinite expanse of air (a ground surface will be added later). The coordinate system is fixed at the source.
- Assuming no reaction or molecular diffusion, the concentration ‘C’ of material resulting from this release is given by the advection equation

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_j}(u_j C) = 0,$$

- where u_j is the velocity of the air and the subscript j represents the summation over all coordinate directions x, y, and z.
- If the velocity u_j in Equation is set equal to the average wind velocity and the equation is solved, we would find that the material disperses much faster than predicted.
- This is due to turbulence in the velocity field.

- If we could specify the wind velocity exactly with time and position, including the effects resulting from turbulence, Equation 5-1 would predict the correct concentration.
- Unfortunately, no models are currently available to adequately describe turbulence.
- As a result, an approximation is used.
- Let the velocity be represented by an average (or mean) and stochastic quantity

$$u_j = \langle u_j \rangle + u_j',$$

- Where

$\langle u_j \rangle$ is the average velocity and

u_j' is the stochastic fluctuation resulting from turbulence.

- It follows that the concentration *C* will also fluctuate as a result of the velocity field;

$$C = \langle C \rangle + C',$$

$\langle C \rangle$ is the mean concentration and

C' is the stochastic fluctuation.

- Because the fluctuations in both *C* and *uj* are around the average or mean values, it follows that

$$\langle u_j' \rangle = 0,$$

$$\langle C' \rangle = 0.$$

- Substituting Equations in to main Equation and averaging the result over time yields

$$\frac{\partial \langle C \rangle}{\partial t} + \frac{\partial}{\partial x_j}(\langle u_j \rangle \langle C \rangle) + \frac{\partial}{\partial x_j}\langle u_j' C' \rangle = 0.$$

The terms $\langle u_j \rangle C'$ and $u_j' \langle C \rangle$ are zero when averaged ($\langle \langle u_j \rangle C' \rangle = \langle u_j \rangle \langle C' \rangle = 0$), but the turbulent flux term $\langle u_j' C' \rangle$ is not necessarily zero and remains in the equation.

- An additional equation is required to describe the turbulent flux. The usual approach is to define an eddy diffusivity K_j (with units of area/time) such that

$$\langle u_j' C' \rangle = -K_j \frac{\partial \langle C \rangle}{\partial x_j}$$

Substituting Equation

$$\frac{\partial \langle C \rangle}{\partial t} + \frac{\partial}{\partial x_j}(\langle u_j \rangle \langle C \rangle) = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial \langle C \rangle}{\partial x_j} \right).$$

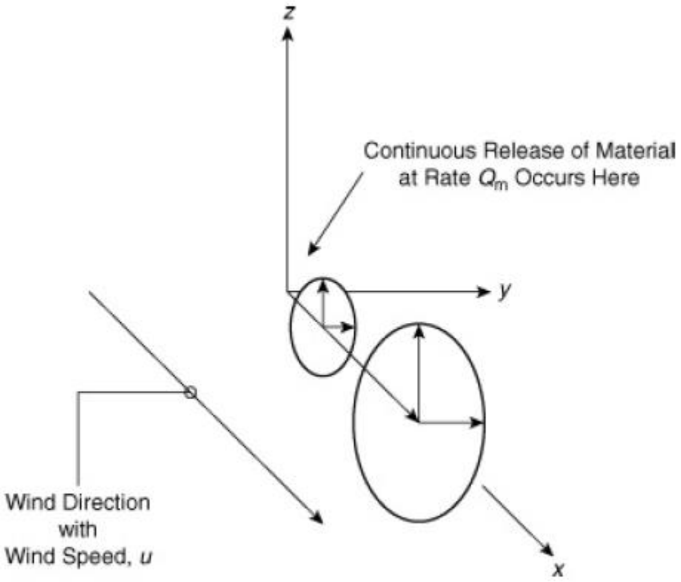
- If the atmosphere is assumed to be incompressible, then

$$\frac{\partial \langle u_j \rangle}{\partial x_j} = 0,$$

$$\frac{\partial\langle C\rangle}{\partial t} + \langle u_j\rangle \frac{\partial \langle C\rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial\langle C\rangle}{\partial x_j}\right)$$

with appropriate boundary and initial conditions forms the fundamental basis for dispersion modeling.

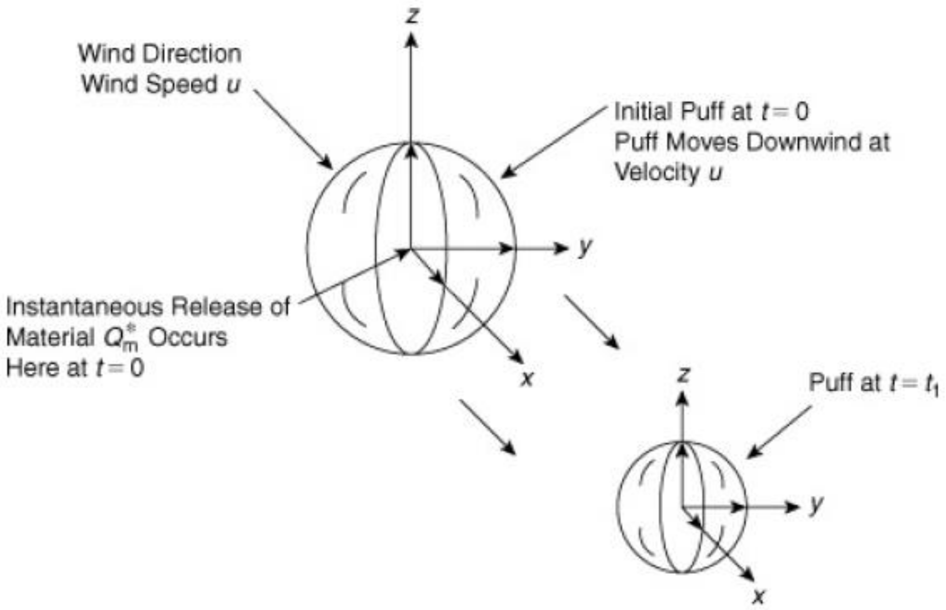
This equation will be solved for a variety of cases.



The coordinate system used for the dispersion models is shown in Figures

- The *x* axis is the center line directly downwind from the release point and is rotated for different wind directions.
- *y* axis is the distance off the center line,
- *z* axis is the elevation above the release point.
- The point (*x*, *y*, *z*) = (0, 0, 0) is at the release point.
- coordinates (*x*, *y*, 0) are level with the release point, and the coordinates (*x*, 0, 0) are along the centerline,or *x* axis.

Puff with wind



Case 1: Steady-State Continuous Point Release with No Wind

The applicable conditions are

- Constant mass release rate (Q_m = constant)
- No wind ($\langle u_j \rangle = 0$)
- Steady state ($\partial\langle C\rangle/\partial t = 0$)
- Constant eddy diffusivity ($K_j = K^*$ in all directions)

$$\frac{\partial^2\langle C\rangle}{\partial x^2}+\frac{\partial^2\langle C\rangle}{\partial y^2}+\frac{\partial^2\langle C\rangle}{\partial z^2}=0.$$

more tractable by defining a radius as $r^2 = x^2 + y^2 + z^2$.

Transforming Equation in terms of *r* yields

$$\frac{d}{dr}\left(r^2\frac{d\langle C\rangle}{dr}\right) = 0.$$

For a continuous steady-state release the concentration flux at any point *r* from the origin must equal the release rate Q_m (with units of mass/time). This is represented mathematically by the following flux boundary condition:

$$-4\pi r^2 K^* \frac{d\langle C\rangle}{dr} = Q_{\mathrm{m}}.$$

The remaining boundary condition is

$$\text{As } r \to \infty, \qquad \langle C\rangle \to 0.$$

separated and integrated between any point *r* and *r* = ∞:

$$\int_{\langle C\rangle}^{0} d\langle C\rangle = -\frac{Q_{\mathrm{m}}}{4\pi K^*}\int_{r}^{\infty} \frac{dr}{r^2}.$$

$$\langle C\rangle(r) = \frac{Q_{\mathrm{m}}}{4\pi K^* r}.$$

It is easy to verify by substitution that Equation is also a solution to Equation and thus a solution to this case.
Equation is transformed to rectangular coordinates to yield

$$\langle C\rangle(x, y, z) = \frac{Q_{\mathrm{m}}}{4\pi K^* \sqrt{x^2 + y^2 + z^2}}.$$

Case 2: Puff with No Wind

- The applicable conditions are Puff release, that is, instantaneous release of a fixed mass of material (with units of mass)
  - No wind ($\langle u_j \rangle = 0$)
  - Constant eddy diffusivity ($K_j = K^*$ in all directions)

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle C \rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial \langle C \rangle}{\partial x_j} \right)$$

Reduces for this case to

$$\frac{1}{K^*}\frac{\partial \langle C \rangle}{\partial t} = \frac{\partial^2 \langle C \rangle}{\partial x^2} + \frac{\partial^2 \langle C \rangle}{\partial y^2} + \frac{\partial^2 \langle C \rangle}{\partial z^2}.$$

The initial condition required to solve

$$\langle C \rangle (x, y, z, t) = 0 \quad \text{at } t = 0.$$

Rectangular coordinates it is

$$\langle C \rangle (x, y, z, t) = \frac{Q_{\mathrm{m}}^*}{8(\pi K^* t)^{3/2}} \exp\left[-\frac{(x^2 + y^2 + z^2)}{4K^* t} \right].$$

The solution to Equation in spherical coordinates

$$\langle C \rangle (r, t) = \frac{Q_{\mathrm{m}}^*}{8(\pi K^* t)^{3/2}} \exp\left(-\frac{r^2}{4K^* t} \right)$$

Case 3: Non-Steady-State Continuous Point Release with No Wind

- The applicable conditions are
  - constant mass release rate (Q_m = constant),
  - no wind ($\langle u_j \rangle = 0$), and
  - constant eddy diffusivity ($K_j = K^*$ in all directions).

Original equation

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle C \rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial \langle C \rangle}{\partial x_j} \right).$$

$$\frac{1}{K^*}\frac{\partial \langle C \rangle}{\partial t} = \frac{\partial^2 \langle C \rangle}{\partial x^2} + \frac{\partial^2 \langle C \rangle}{\partial y^2} + \frac{\partial^2 \langle C \rangle}{\partial z^2}.$$

$$\langle C \rangle (x, y, z, t) = 0 \quad \text{at } t = 0. \qquad \text{As } r \to \infty, \quad \langle C \rangle \to 0.$$

The solution is found by integrating the instantaneous solution with respect to time. The result in spherical coordinates

$$\langle C \rangle (r, t) = \frac{Q_m}{4\pi K^* r}\,\mathrm{erfc}\left(\frac{r}{2\sqrt{K^* t}} \right)$$

Rectangular coordinates it is

$$\langle C \rangle (x, y, z, t) = \frac{Q_m}{4\pi K^* \sqrt{x^2 + y^2 + z^2}}\,\mathrm{erfc}\left(\frac{\sqrt{x^2 + y^2 + z^2}}{2\sqrt{K^* t}} \right)$$

As $t \to \infty$, reduce to the corresponding steady-state solutions

Case 4: Steady-State Continuous Point Source Release with Wind

- continuous release (Q_m = constant),
- wind blowing in x direction only ($\langle u_j \rangle = \langle u_x \rangle = u$ = constant), and
- constant eddy diffusivity ($K_j = K^*$ in all directions).

$$\frac{u}{K^*}\frac{\partial \langle C \rangle}{\partial x} = \frac{\partial^2 \langle C \rangle}{\partial x^2} + \frac{\partial^2 \langle C \rangle}{\partial y^2} + \frac{\partial^2 \langle C \rangle}{\partial z^2}$$

Solved together with boundary conditions expressed by Equations. The solution for the average concentration at any point is

$$\langle C \rangle (x, y, z) = \frac{Q_m}{4\pi K^* \sqrt{x^2 + y^2 + z^2}} \exp\left[-\frac{u}{2K^*}\left(\sqrt{x^2 + y^2 + z^2} - x\right)\right].$$

If a slender (thin)plume is assumed (the plume is long and slender and is not far removed from the *x* axis), that is

then by using $\sqrt{1 + a} \approx 1 + a/2$,

$$\langle C \rangle (x, y, z) = \frac{Q_m}{4\pi K^* x} \exp\left[-\frac{u}{4K^* x}(y^2 + z^2)\right]$$

Along the centerline of this plume, $y = z = 0$, and $\langle C \rangle (x) = \frac{Q_m}{4\pi K^* x}$.

Case 5: Puff with No Wind and Eddy Diffusivity Is a Function of Direction

- This case is the same as case 2 but with eddy diffusivity a function of direction. The applicable conditions are
  - puff release ($Q_m^* =$ constant),
  - no wind ($\langle u_j \rangle = 0$), and
  - each coordinate direction has a different but constant eddy diffusivity (K_x, K_y, and K_z).

$$\frac{\partial \langle C \rangle}{\partial t} = K_x \frac{\partial^2 \langle C \rangle}{\partial x^2} + K_y \frac{\partial^2 \langle C \rangle}{\partial y^2} + K_z \frac{\partial^2 \langle C \rangle}{\partial z^2}.$$

$$\langle C \rangle(x, y, z, t) = \frac{Q_m^*}{8(\pi t)^{3/2}\sqrt{K_x K_y K_z}} \exp\left[-\frac{1}{4t}\left(\frac{x^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z}\right)\right]$$

Case 6: Steady-State Continuous Point Source Release with Wind and Eddy Diffusivity Is a Function of Direction

- This case is the same as case 4 but with eddy diffusivity a function of direction. The applicable conditions are
  - continuous release (Q_m = constant),
  - steady state ($\partial\langle C\rangle/\partial t = 0$),
  - wind blowing in x direction only ($\langle u_j\rangle = \langle u_x\rangle = u$ = constant),
  - each coordinate direction has a different but constant eddy diffusivity (K_x, K_y, and K_z),

  Slender plume approximation

$$u\frac{\partial\langle C\rangle}{\partial x} = K_x\frac{\partial^2\langle C\rangle}{\partial x^2} + K_y\frac{\partial^2\langle C\rangle}{\partial y^2} + K_z\frac{\partial^2\langle C\rangle}{\partial z^2}.$$

$$\langle C\rangle(x, y, z) = \frac{Q_m}{4\pi x\sqrt{K_x K_y}}\exp\left[-\frac{u}{4x}\left(\frac{y^2}{K_y} + \frac{z^2}{K_z}\right)\right].$$

Along the centerline of this plume, $y = z = 0$, and the average concentration is given by

$$\langle C\rangle(x) = \frac{Q_m}{4\pi x\sqrt{K_y K_z}}.$$

Case 7: Puff with Wind

This case is the same as case 5 but with wind. Figure shows the geometry.

The applicable conditions are puff release ,

- wind blowing in *x* direction only ($\langle u_j \rangle = \langle u_x \rangle = u =$ constant),

  and each coordinate direction has a different but constant eddy diffusivity (K_x, K_y, and K_z).
- The solution to this problem is found by a simple transformation of coordinates.
- The solution to case 5 represents a puff fixed around the release point.
- If the puff moves with the wind along the *x* axis, the solution to this case is found by replacing the existing coordinate *x* by a new coordinate system, $(x - ut)$, that moves with the wind velocity.
- The variable *t* is the time since the release of the puff, and *u* is the wind velocity.
- The solution is simply Equation 5-29, transformed into this new coordinate system:

$$\langle C \rangle (x, y, z, t) = \frac{Q_m^*}{8(\pi t)^{3/2}\sqrt{K_x K_y K_z}} \exp\left\{ -\frac{1}{4t}\left[\frac{(x - ut)^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z} \right] \right\}.$$

Case 8: Puff with No Wind and with Source on Ground

- This case is the same as case 5 but with the source on the ground. The ground represents an impervious boundary.
- As a result, the concentration is twice the concentration in case 5.
- The solution is 2 times Equation :

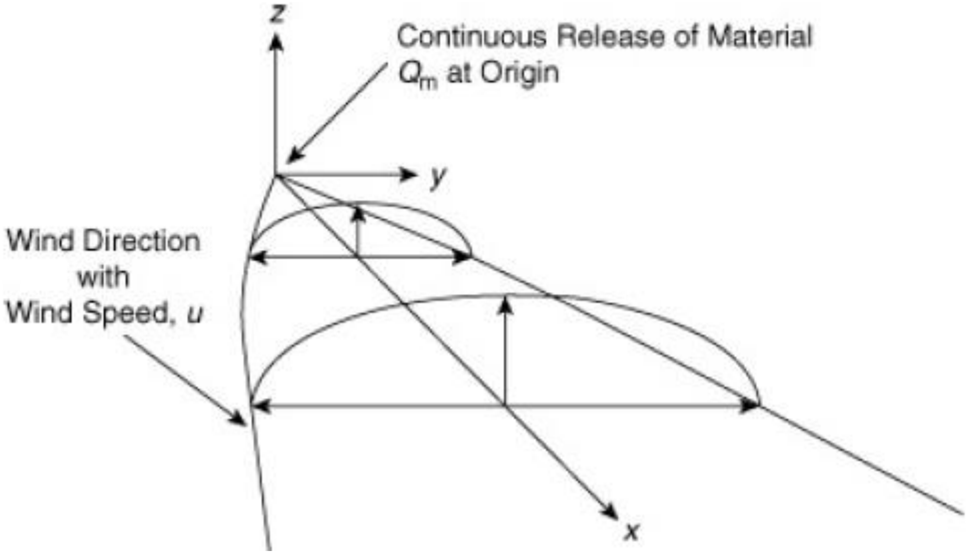
$$\langle C\rangle(x, y, z, t) = \frac{Q_{\mathrm{m}}^*}{4(\pi t)^{3/2}\sqrt{K_x K_y K_z}} \exp\left[-\frac{1}{4t}\left(\frac{x^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z}\right)\right]$$

Case 9: Steady-State Plume with Source on Ground

This case is the same as case 6 but with the release source on the ground, as shown in Figure.
The ground represents an impervious boundary.
As a result, the concentration is twice the concentration in case 6.
The solution is 2 times

$$\langle C\rangle(x, y, z) = \frac{Q_{\mathrm{m}}}{2\pi x\sqrt{K_x K_y}} \exp\left[-\frac{u}{4x}\left(\frac{y^2}{K_y} + \frac{z^2}{K_z}\right)\right]$$

Steady-state plume with source at ground level. The concentration is twice the concentration of a plume without the ground.



Case 10: Continuous Steady-State Source with Source at Height *H*r above the Ground

For this case the ground acts as an impervious boundary at a distance *H* from the source. The solution is

$$\langle C\rangle(x, y, z) = \frac{Q_\mathrm{m}}{4\pi x\sqrt{K_y K_z}}\exp\left(-\frac{uy^2}{4K_y x}\right) \times \left\{\exp\left[-\frac{u}{4K_z x}(z - H_\mathrm{r})^2\right] + \exp\left[-\frac{u}{4K_z x}(z + H_\mathrm{r})^2\right]\right\}.$$

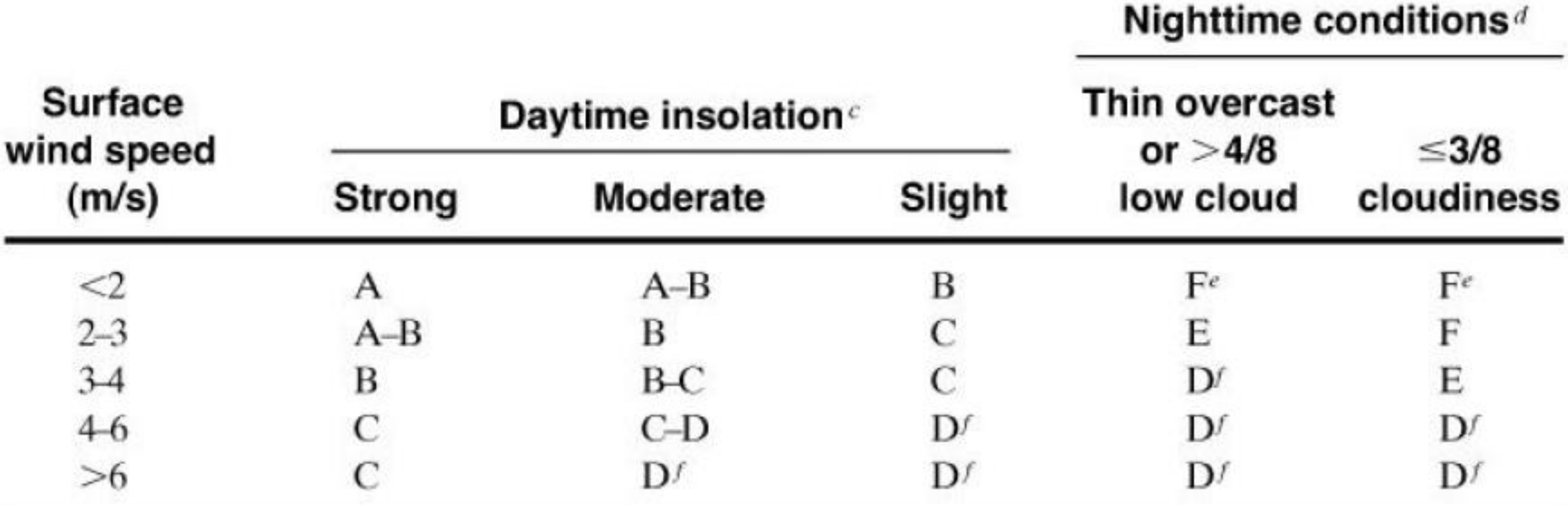
If $H_r = 0$, Equation reduces to Equation for a source on the ground

Pasquill-Gifford Model

- Cases 1 through 10 all depend on the specification of a value for the eddy diffusivity K_j.
- In general, K_j changes with position, time, wind velocity, and prevailing weather conditions.
- Although the eddy diffusivity approach is useful theoretically, it is not convenient experimentally and does not provide a useful framework for correlation.
- Sutton solved this difficulty by proposing the following definition for a *dispersion coefficient.* $\sigma_x^2 = \frac{1}{2}(C)^2(ut)^{2-n}$
- *W*ith similiar expressions given for σ*y* and σ*z*. The dispersion coefficients σ*x*, σ*y*, and σ*z* represent the standard deviations of the concentration in the downwind, crosswind, and vertical (*x*, *y*, *z*) directions, respectively.
- Values for the dispersion coefficients are much easier to obtain experimentally than eddy diffusivities.
- The dispersion coefficients are a function of atmospheric conditions and the distance downwind from the release.

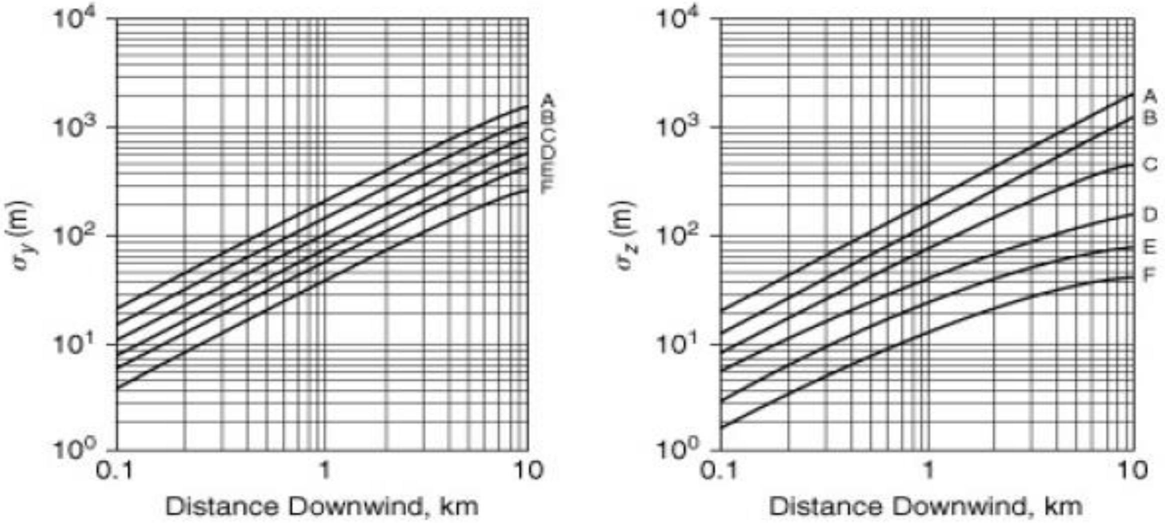
- The atmospheric conditions are classified according to six different stability classes, shown in Table. The stability classes depend on wind speed and quantity of sunlight.
- During the day, increased wind speed results in greater atmospheric stability, whereas at night the reverse is true.
- This is due to a change in vertical temperature profiles from day to night.

Atmospheric Stability Classes for Use with the Pasquill-Gifford Dispersion Model

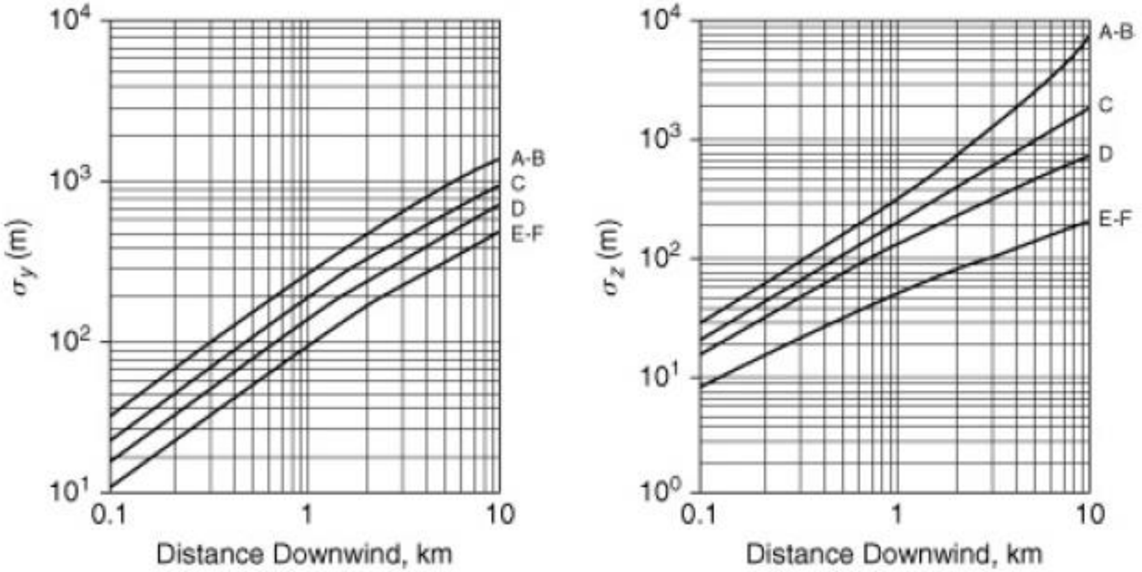


Surface wind speed (m/s)	Daytime insolation[c]			Nighttime conditions[d]	
	Strong	Moderate	Slight	Thin overcast or >4/8 low cloud	≤3/8 cloudiness
<2	A	A–B	B	F[e]	F[e]
2–3	A–B	B	C	E	F
3–4	B	B–C	C	D[f]	E
4–6	C	C–D	D[f]	D[f]	D[f]
>6	C	D[f]	D[f]	D[f]	D[f]

Stability classes:
- A, extremely unstable
- B, moderately unstable
- C, slightly unstable
- D, neutrally stable
- E, slightly stable
- F, moderately stable

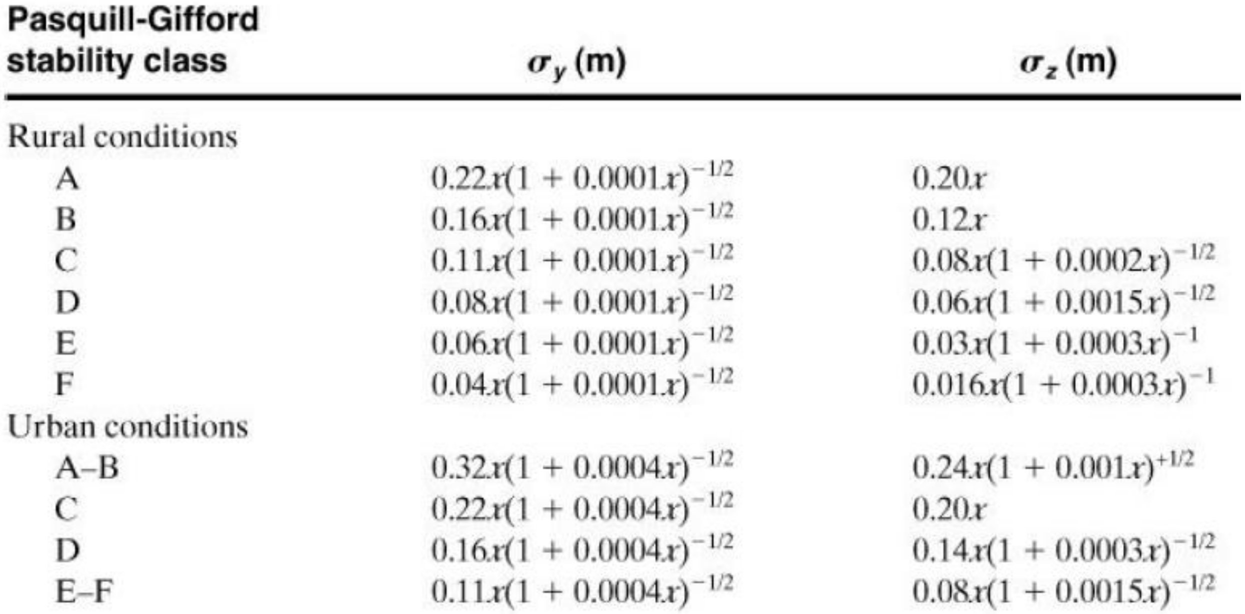


Dispersion coefficients for Pasquill-Gifford plume model for rural releases.



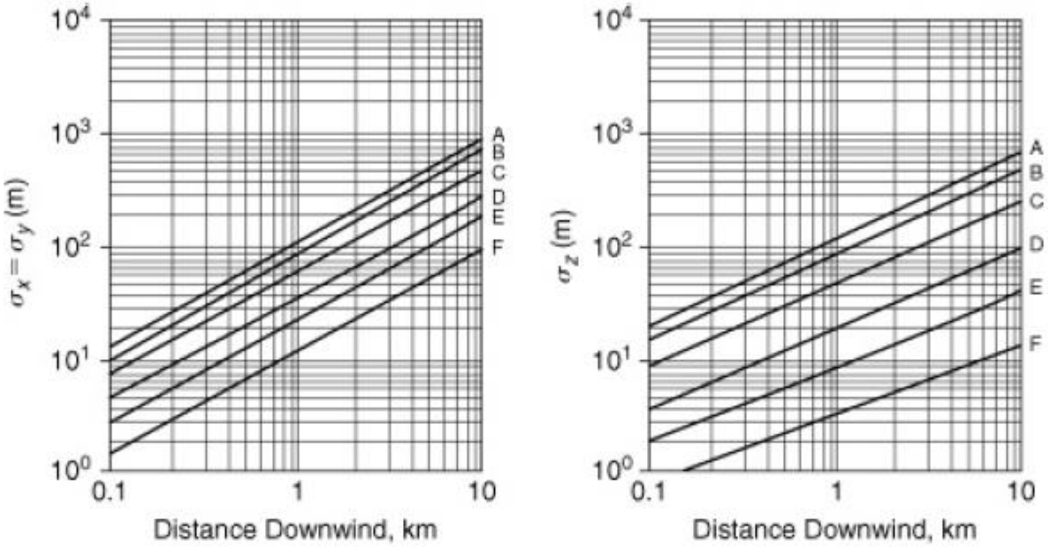
Dispersion coefficients for Pasquill-Gifford plume model for urban releases.

- Recommended Equations for Pasquill-Gifford Dispersion Coefficients for Plume Dispersion (the downwind distance *x* has units of meters)



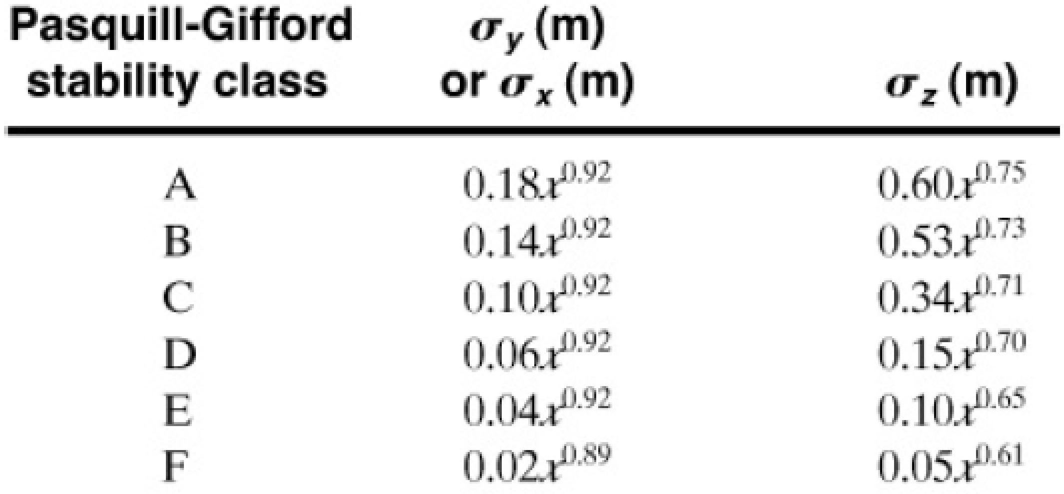
Pasquill-Gifford stability class	**σ_y (m)**	**σ_z (m)**
Rural conditions		
A	$0.22x(1 + 0.0001x)^{-1/2}$	$0.20x$
B	$0.16x(1 + 0.0001x)^{-1/2}$	$0.12x$
C	$0.11x(1 + 0.0001x)^{-1/2}$	$0.08x(1 + 0.0002x)^{-1/2}$
D	$0.08x(1 + 0.0001x)^{-1/2}$	$0.06x(1 + 0.0015x)^{-1/2}$
E	$0.06x(1 + 0.0001x)^{-1/2}$	$0.03x(1 + 0.0003x)^{-1}$
F	$0.04x(1 + 0.0001x)^{-1/2}$	$0.016x(1 + 0.0003x)^{-1}$
Urban conditions		
A–B	$0.32x(1 + 0.0004x)^{-1/2}$	$0.24x(1 + 0.001x)^{+1/2}$
C	$0.22x(1 + 0.0004x)^{-1/2}$	$0.20x$
D	$0.16x(1 + 0.0004x)^{-1/2}$	$0.14x(1 + 0.0003x)^{-1/2}$
E–F	$0.11x(1 + 0.0004x)^{-1/2}$	$0.08x(1 + 0.0015x)^{-1/2}$

- The dispersion coefficients σ*y* and σ*z* for a puff release are given in Figure the equations are provided in Table 5-3.
- The puff dispersion coefficients are based on limited data (shown in above Table 5-2) and should not be considered precise.



Dispersion coefficients for Pasquill-Gifford puff model

Pasquill-Gifford Dispersion Coefficients for Puff Dispersion



Pasquill-Gifford stability class	σ_y (m) or σ_x (m)	σ_z (m)
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	$0.02x^{0.89}$	$0.05x^{0.61}$

The equations for cases 1 through 10 were rederived by Pasquill using expressions of the form of Equation. These equations along with the correlations for the dispersion coefficients are known as the *Pasquill-Gifford model.*

Case 11: Puff with Instantaneous Point Source at Ground Level, Coordinates Fixed at Release Point, Constant Wind Only in *x* Direction with Constant Velocity *u*

- The solution has a form similar to

$$\langle C\rangle(x,y,z,t)=\frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)^2+\frac{y^2}{\sigma_y^2}+\frac{z^2}{\sigma_z^2}\right]\right\}.$$

The ground-level concentration is given at *z* = 0:

$$\langle C\rangle(x,y,0,t)=\frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)^2+\frac{y^2}{\sigma_y^2}\right]\right\}.$$

The ground-level concentration along the *x* axis is given at *y* = *z* = 0:

$$\langle C\rangle(x,0,0,t)=\frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{x-ut}{\sigma_x}\right)^2\right]$$

The center of the cloud is found at coordinates (*ut*, 0, 0).
The concentration at the center of this moving cloud is given by

$$\langle C\rangle(ut,0,0,t)=\frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}$$

- The total integrated dose D_{tid} received by an individual standing at fixed coordinates (x, y, z) is the time integral of the concentration:

$$D_{\mathrm{tid}}(x, y, z) = \int_0^\infty \langle C \rangle (x, y, z, t)\, dt.$$

- The total integrated dose at ground level is found by integrating Equation. The result is

$$D_{\mathrm{tid}}(x, y, 0) = \frac{Q_{\mathrm{m}}^*}{\pi \sigma_y \sigma_z u} \exp\left(-\frac{1}{2} \frac{y^2}{\sigma_y^2} \right)$$

- The total integrated dose alc he ground is

$$D_{\mathrm{tid}}(x, 0, 0) = \frac{Q_{\mathrm{m}}^*}{\pi \sigma_y \sigma_z u}$$

- Frequently the cloud boundary defined by a fixed concentration is required.
- The line connecting points of equal concentration around the cloud boundary is called an isopleth.
- For a specified concentration ⟨*C*⟩* the isopleths at ground level are determined by dividing the equation for the centerline concentration (Equation 5-40) by the equation for the general ground-level concentration (Equation 5-39). This equation is solved directly for *y*:

$$\frac{\langle C \rangle (x, 0, 0, t) = \dfrac{Q_{\mathrm{m}}^*}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left[-\dfrac{1}{2}\left(\dfrac{x - ut}{\sigma_x} \right)^2 \right]}{\langle C \rangle (x, y, 0, t) = \dfrac{Q_{\mathrm{m}}^*}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left\{ -\dfrac{1}{2}\left[\left(\dfrac{x - ut}{\sigma_x} \right)^2 + \dfrac{y^2}{\sigma_y^2} \right] \right\}}$$

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

- **Case 12: Plume with Continuous Steady-State Source at Ground Level and Wind Moving in *x* Direction at Constant Velocity *u***
- This case is identical to case 9. The solution has a form

$$\langle C\rangle(x, y, z) = \frac{Q_m}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right].$$

The ground-level concentration is given at $z = 0$:

$$\langle C\rangle(x, y, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right].$$

The concentration along the centerline of the plume directly downwind is given at $y = z = 0$:

$$\langle C\rangle(x, 0, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u}.$$

The isopleths are found using a procedure identical to the isopleth procedure used for case 11.

For continuous ground-level releases the maximum concentration occurs at the release point.

Case 13: Plume with Continuous Steady-State Source at Height *H*r above Ground Level and Wind Moving in *x* Direction at Constant Velocity *u*

- This case is identical to case 10. The solution has a form

$$\langle C\rangle(x,y,z)=\frac{Q_{\mathrm{m}}}{2\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\times\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H_{\mathrm{r}}}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H_{\mathrm{r}}}{\sigma_z}\right)^2\right]\right\}.$$

The ground-level concentration is found by setting $z = 0$:

$$\langle C\rangle(x,y,0)=\frac{Q_{\mathrm{m}}}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2-\frac{1}{2}\left(\frac{H_{\mathrm{r}}}{\sigma_z}\right)^2\right]$$

The ground-level centerline concentrations are found by setting $y = z = 0$:

$$\langle C\rangle(x,0,0)=\frac{Q_{\mathrm{m}}}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{H_{\mathrm{r}}}{\sigma_z}\right)^2\right].$$

The maximum ground-level concentration along the *x* axis ⟨*C*⟩max is found using

$$\langle C\rangle_{\max}=\frac{2Q_{\mathrm{m}}}{e\pi u H_{\mathrm{r}}^2}\left(\frac{\sigma_z}{\sigma_y}\right).$$

- The distance downwind at which the maximum ground-level concentration occurs is found from

$$\sigma_z = \frac{H_r}{\sqrt{2}}.$$

- The procedure for finding the maximum concentration and the downwind distance is to use above Equation

- **Case 14: Puff with Instantaneous Point Source at Height *H*r above Ground Level and a Coordinate System on the Ground That Moves with the Puff**

For this case the center of the puff is found at *x* = *ut*. The average concentration is given by

$$\langle C\rangle(x, y, z, t) = \frac{Q_m^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{\exp\left[-\frac{1}{2}\left(\frac{z - H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z + H_r}{\sigma_z}\right)^2\right]\right\}$$

- The time dependence is achieved through the dispersion coefficients, because their values change as the puff moves downwind from the release point.
- If wind is absent (*u* = 0),Equation does not predict the correct result
- At ground level, *z* = 0, and the concentration is computed using

$$\langle C\rangle(x, y, 0, t) = \frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2 - \frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right].$$

The concentration along the ground at the centerline is given at *y* = *z* = 0:

$$\langle C\rangle(x, 0, 0, t) = \frac{Q_{\mathrm{m}}^{*}}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right].$$

The total integrated dose at ground level is found by applying

$$D_{\mathrm{tid}}(x, y, z) = \int_0^\infty \langle C\rangle(x, y, z, t)\, dt.$$

$$D_{\mathrm{tid}}(x, y, 0) = \frac{Q_{\mathrm{m}}^{*}}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2 - \frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right]$$

Case 15: Puff with Instantaneous Point Source at Height *H*r above Ground Level and a Coordinate System Fixed on the Ground at the Release Point

- For this case the result is obtained using a transformation of coordinates similar to the transformation used for case 7.
- The result is

$$\langle C\rangle(x, y, z, t) = \begin{array}{l}\text{[Puff equations with moving coordinate} \\ \text{system (Equations 5-54 through 5-56)]} \\ \times \exp\left[-\frac{1}{2}\left(\frac{x - ut}{\sigma_x}\right)^2\right],\end{array}$$

where *t* is the time since the release of the puff.

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 isopleth 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 weather conditions in the Pasquill-Gifford dispersion equations are included by means of the dispersion coefficients and the wind speed.

- By examining the Pasquill-Gifford dispersion equations for estimating the concentrations, it is readily evident that the dispersion coefficients and wind speed are in the denominator.
- Thus the maximum concentration is estimated by selecting the weather conditions and wind speed that result in the smallest values of the dispersion coefficients and the wind speed.
- By inspecting Figures, we can see that 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.

Limitations to Pasquill-Gifford Dispersion Modeling

- Pasquill-Gifford or Gaussian dispersion applies only to neutrally buoyant dispersion of gases in which the turbulent mixing is the dominant feature of the dispersion.
- It is typically valid only for a distance of 0.1–10 km from the release point.
- The concentrations predicted by the Gaussian models are time averages.
- Thus it is possible for instantaneous local concentrations to exceed the average values predicted—this might be important for emergency response.
- The models presented here assume a 10-minute time average.
- Actual instantaneous concentrations may vary by as much as a factor of 2 from the concentrations computed using Gaussian models.

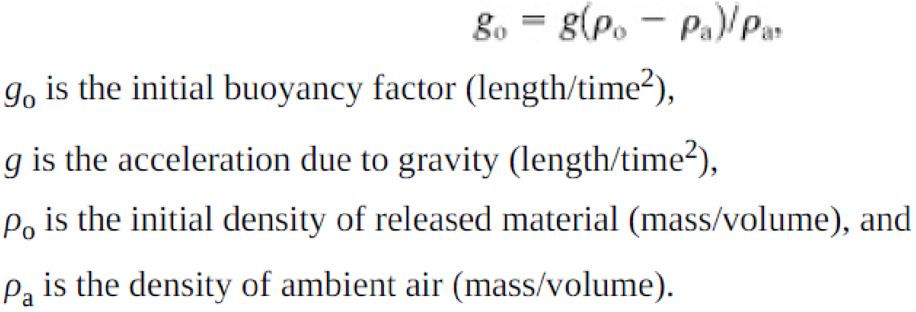
Dense Gas Dispersion

- A dense gas is defined as any gas whose density is greater than the density of the ambient air through which it is being dispersed.
- This result can be due to a gas with a molecular weight greater than that of air or a gas with a low temperature resulting from auto refrigeration during release or other processes.
- Following a typical puff release, a cloud having similar vertical and horizontal dimensions (near the source) may form.
- The dense cloud slumps toward the ground under the influence of gravity, increasing its diameter and reducing its height.
- Considerable initial dilution occurs because of the gravity-driven intrusion of the cloud into the ambient air.
- Subsequently the cloud height increases because of further entrainment of air across both the vertical and the horizontal interfaces.
- After sufficient dilution occurs, normal atmospheric turbulence predominates over gravitational forces and typical Gaussian dispersion characteristics are exhibited.

- The Britter and McQuaid model was developed by performing a dimensional analysis and correlating existing data on dense cloud dispersion.
- The model is best suited for instantaneous or continuous ground-level releases of dense gases.
- The release is assumed to occur at ambient temperature and without aerosol or liquid droplet formation.
- Atmospheric stability was found to have little effect on the results and is not a part of the model.
- Most of the data came from dispersion tests in remote rural areas on mostly flat terrain.
- Thus the results are not applicable to areas where terrain effects are significant.
- The model requires a specification of the initial cloud volume, the initial plume volume flux, the duration of release, and the initial gas density.
- Also required are the wind speed at a height of 10 m, the distance downwind, and the ambient gas density.

The first step is to determine whether the dense gas model is applicable.

The initial cloud buoyancy is defined as



$$g_o = g(\rho_o - \rho_a)/\rho_a,$$

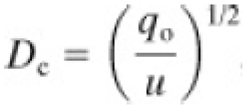
g_o is the initial buoyancy factor (length/time^2),

g is the acceleration due to gravity (length/time^2),

ρ_o is the initial density of released material (mass/volume), and

ρ_a is the density of ambient air (mass/volume).

A characteristic source dimension, dependent on the type of release, can also be defined. For continuous releases



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

D_c is the characteristic source dimension for continuous releases of dense gases (length),

q_o is the initial plume volume flux for dense gas dispersion (volume/time), and u is the wind speed at 10 m elevation (length/time).

- For instantaneous releases the characteristic source dimension is defined as

$$D_i = V_o^{1/3},$$

D_i is the characteristic source dimension for instantaneous releases of dense gases (length) and

V_o is the initial volume of released dense gas material (length^3).

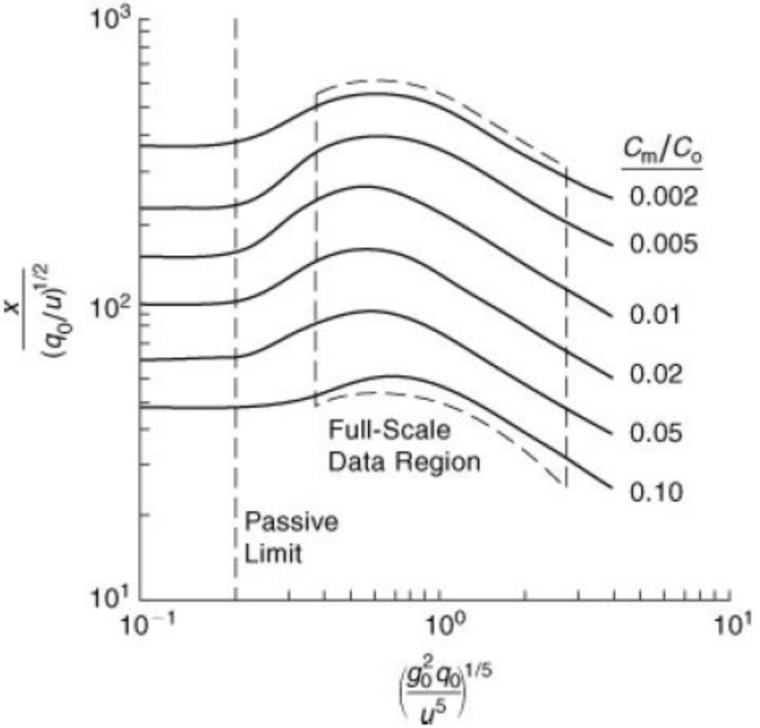
The criteria for a sufficiently dense cloud to require a dense cloud representation are, for continuous releases,

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

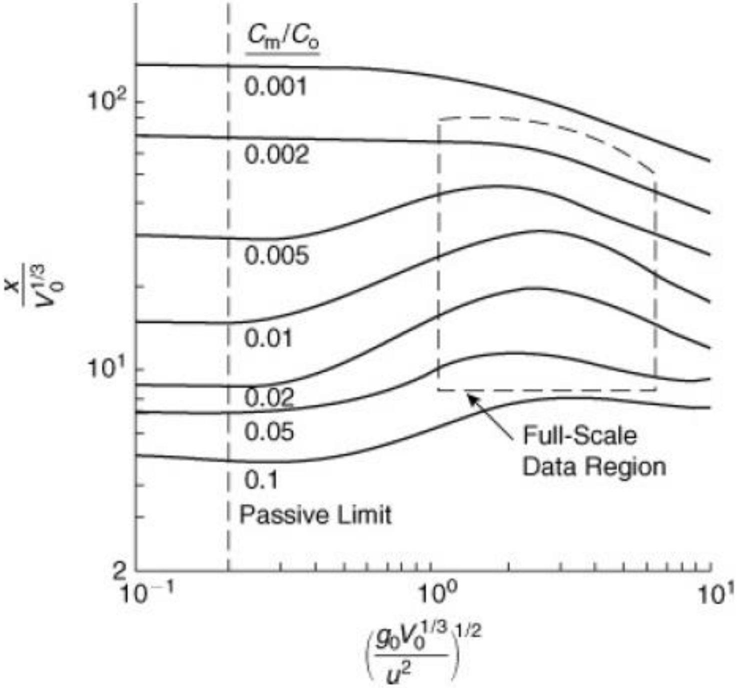
and, for instantaneous releases,

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

If these criteria are satisfied, then Figures are used to estimate the downwind concentrations.
Tables provide equations for the correlations in these figures.

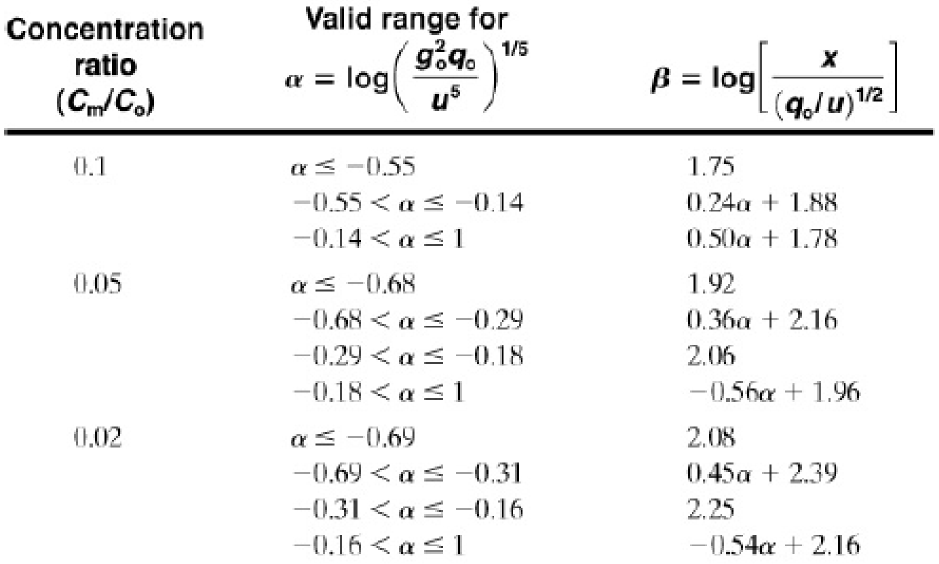


Britter-McQuaid dimensional correlation for dispersion of dense gas plumes.



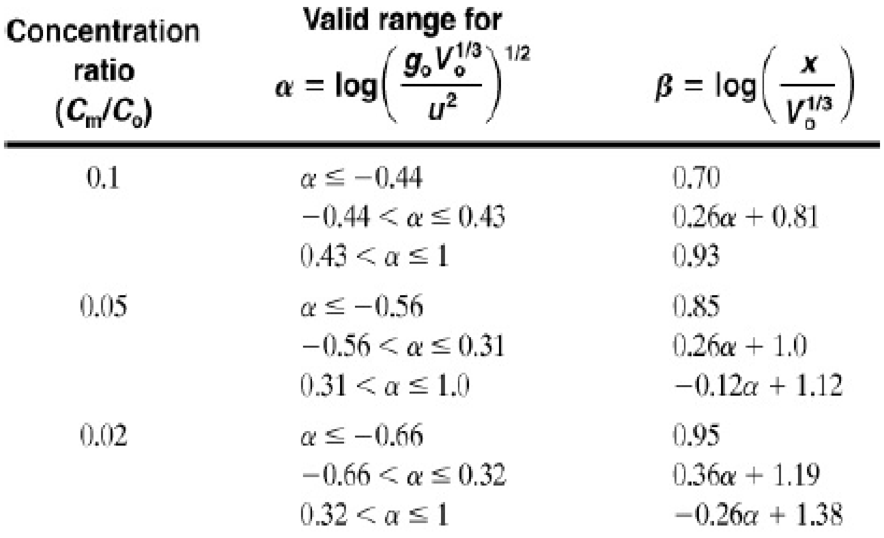
Britter-McQuaid dimensional correlation for dispersion of dense gas puffs.

Equations Used to Approximate the Curves in the Britter-McQuaid Correlations Provided in Figure for Plumes



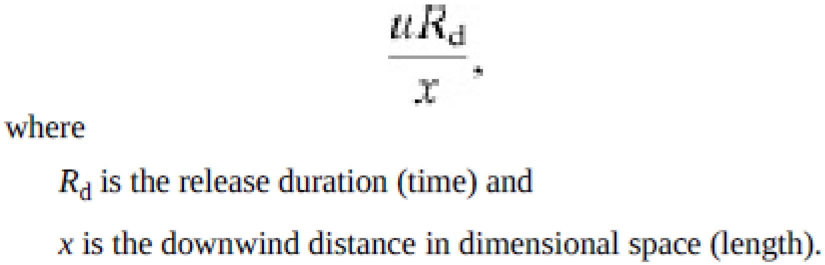
Concentration ratio (C_m/C_o)	Valid range for $\alpha = \log\left(\frac{g_o^2 q_o}{u^5}\right)^{1/5}$	$\beta = \log\left[\frac{x}{(q_o/u)^{1/2}}\right]$
0.1	$\alpha \leq -0.55$	1.75
	$-0.55 < \alpha \leq -0.14$	$0.24\alpha + 1.88$
	$-0.14 < \alpha \leq 1$	$0.50\alpha + 1.78$
0.05	$\alpha \leq -0.68$	1.92
	$-0.68 < \alpha \leq -0.29$	$0.36\alpha + 2.16$
	$-0.29 < \alpha \leq -0.18$	2.06
	$-0.18 < \alpha \leq 1$	$-0.56\alpha + 1.96$
0.02	$\alpha \leq -0.69$	2.08
	$-0.69 < \alpha \leq -0.31$	$0.45\alpha + 2.39$
	$-0.31 < \alpha \leq -0.16$	2.25
	$-0.16 < \alpha \leq 1$	$-0.54\alpha + 2.16$

Equations Used to Approximate the Curves in the Britter-McQuaid Correlations Provided in Figure 5-14 for 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	$\alpha \leq -0.44$	0.70
	$-0.44 < \alpha \leq 0.43$	$0.26\alpha + 0.81$
	$0.43 < \alpha \leq 1$	0.93
0.05	$\alpha \leq -0.56$	0.85
	$-0.56 < \alpha \leq 0.31$	$0.26\alpha + 1.0$
	$0.31 < \alpha \leq 1.0$	$-0.12\alpha + 1.12$
0.02	$\alpha \leq -0.66$	0.95
	$-0.66 < \alpha \leq 0.32$	$0.36\alpha + 1.19$
	$0.32 < \alpha \leq 1$	$-0.26\alpha + 1.38$

The criterion for determining whether the release is continuous or instantaneous is calculated using the following group



$$\frac{uR_d}{x},$$

where

R_d is the release duration (time) and

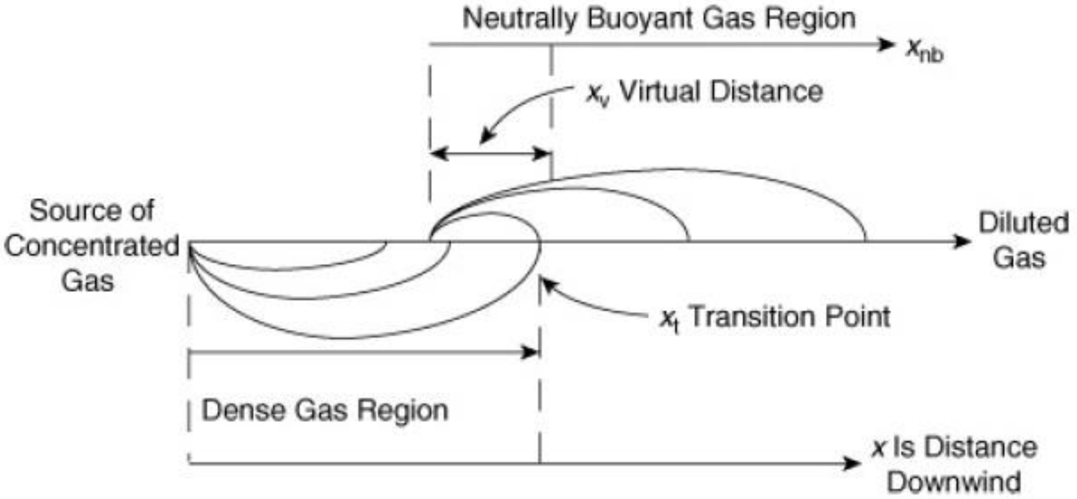
x is the downwind distance in dimensional space (length).

- If this group has a value greater than or equal to 2.5, then the dense gas release is considered continuous.
- If the group value is less than or equal to 0.6, then the release is considered instantaneous.
- If the value lies in-between, then the concentrations are calculated using both continuous and instantaneous models and the maximum concentration result is selected.
- For nonisothermal releases the Britter-McQuaid model recommends two slightly different calculations.
- For the first calculation a correction term is applied to the initial concentration.
- For the second calculation heat addition is assumed at the source to bring the source material to ambient temperature, which provides a limit to the effect of heat transfer.
- For gases lighter than air (such as methane or liquefied natural gas) the second calculation might be meaningless.
- If the difference between the two calculations is small, then the nonisothermal effects are assumed negligible.

- If the two calculations are within a factor of 2, then the calculation providing the maximum, or most pessimistic, concentration is used.
- If the difference is very large (greater than a factor of 2), then the maximum, or most pessimistic, concentration is selected, but further investigation using more detailed methods (such as a computer code) may be worthwhile.
- The Britter-McQuaid model is a dimensional analysis technique, based on a correlation developed from experimental data.
- However, the model is based only on data from flat rural terrain and is applicable only to these types of releases.
- The model is also unable to account for the effects of parameters such as release height, ground roughness, and wind speed profiles.

Dense Gas Transition to Neutrally Buoyant Gas

- As shown in Figure as a dense gas moves downstream the concentration decreases.
- At the transition *xt* it becomes a neutrally buoyant gas.



- In the dense gas region the downstream concentration is computed using the methods in above Section.
- After the transition, the compositions are computed using the neutrally buoyant equations for ground-level releases; see cases 11 and 12 on neutrally buoyant dispersion models.

- As shown in Figure, these neutrally buoyant gas compositions are computed
- from a point that is upwind of the transition.
- The methods for determining the virtual distance *xv* and the downwind compositions are described in this section

Continuous Release Transition

- To locate the transition point *xt* for a continuous release, Equation is modified to include the local properties.
- The local properties are shown below:

$$\rho_x = \rho_0\left(\frac{C_x}{C_0}\right) + \rho_a\left(1 - \frac{C_x}{C_0}\right),$$

$$g_x = g\left(\frac{\rho_x - \rho_a}{\rho_a}\right) = g\left(\frac{C_x}{C_0}\right)\left(\frac{\rho_0 - \rho_a}{\rho_a}\right),$$

C_x is the concentration at x downwind from the source (mass/volume),

C_0 is the concentration at the source (mass/volume),

ρ_x is the density at x downwind from the source (mass/volume), and

g_x is the buoyancy factor at x (length/time^2).

- Since the dense gas dispersions are based on the original volumes being diluted with entrained air, there is a simple material balance relationship between the concentrations and flows as shown in Equation :

$$q_x C_x = q_0 C_0,$$

- Where q_x is the plume volume flux at x (volume/time).
- To determine the transition point, the criterion shown in Equation is converted to local conditions as shown in Equation :

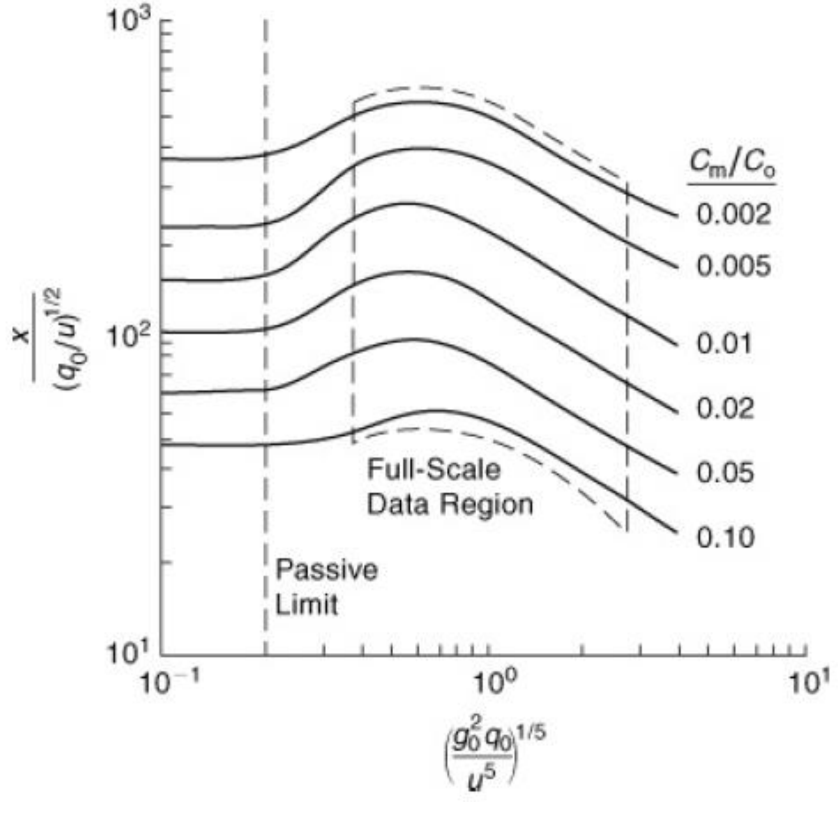
$$\left(\frac{g_x q_x}{u^3 D_{cx}}\right)^{1/3} \geq 0.15,$$

$$D_{cx} = \left(\frac{q_x}{u}\right)^{1/2}$$

- D_{cx} is the characteristic dimension for a continuous release of the dense gas at x (length).
- After replacing the gx, qx, and Dx in Equation with properties shown in Equations the criterion shown in Equation, is converted to

$$\left(\frac{C_x}{C_0}\right)^{1/6}\left(\frac{g_0 q_0}{u^3 D_c}\right)^{1/3} \geq 0.15.$$

- The concentration ratio C_x/C_0 at the transition (dense to neutrally buoyant gas) is determined at the transition by converting the inequality in Equation to an equality sign.
- The transition *xt* is then determined using Figure; that is, it is determined at the value of the ordinate corresponding to the intersection of the known abscissa and C_x/C_0.



Continuous Release Downwind Concentration

- If the concentration is desired in the dense gas region (see Figure), then the dense gas calculations are made using the methods shown in Section.
- If the concentration is desired in the neutrally buoyant region (at a distance downwind of the transition), the neutrally buoyant models are used for a ground-level release.
- The ground-level release is used because all heavy gas releases, even from stacks, slump to the ground.
- As shown in Figure, the neutrally buoyant calculations are made from a position upwind from the transition,
- at a distance x_v (virtual distance) that gives the neutrally buoyant concentration the same as the dense gas concentration at the transition.
- The virtual distance x_v is determined using Equation, where the concentration at the transition is C_x.

$$\sigma_y \sigma_z = \frac{q_0}{C_x \pi u}$$

- In this equation, the only unknown is x_v which is in both dispersion coefficients taken from Table.

- The composition at any distance *x* from the source is subsequently computed using the neutrally buoyant equations for continuous ground-level releases as shown in case 12.
- But the downwind distance for the dispersion coefficients is x_{nb} as shown in Figure. Equation shows the relationship between the various distances:

$$x_{nb} = x - x_t + x_v,$$

x is the distance from the source (length),

x_t is the distance from the source to the transition (length),

x_v is the virtual distance (length), and

x_{nb} is the distance used in the neutrally buoyant model to compute the concentration downwind of the transition.

Instantaneous Release Transition

- The equation for the dense gas criterion for a puff model is derived using Equations and the material balance equation

$$V_x C_x = V_0 C_0,$$

where V_x is the volume of gas at x (length^3)

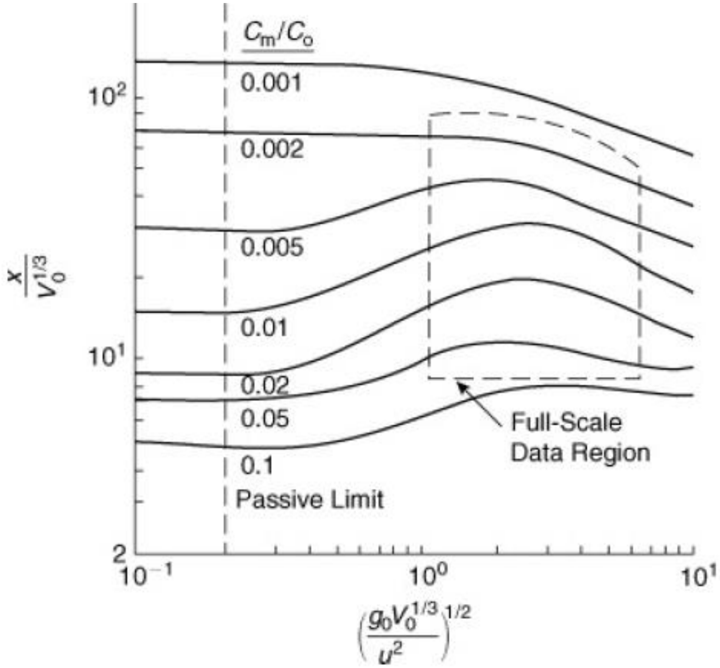
The criterion for any location is

$$\frac{\sqrt{g_x V_x}}{u D_{xi}} \geq 0.20, \qquad D_{xi} = (V_x)^{1/3}$$

- and D_{xi} is the characteristic dimension for an instantaneous release of dense gas at *x* (length).
- After replacing the *gx*, *qx*, and D_{xi} in Equation 5-74 with properties shown in Equations, the criterion is converted to

$$\left(\frac{C_x}{C_0}\right)^{1/3}\left(\frac{\sqrt{g_0 V_0}}{u V_0^{1/3}}\right) \geq 0.20.$$

- The concentration ratio C_x/C_0 at the transition (dense to neutrally buoyant gas) is determined by converting the inequality in Equation to an equality sign.
- The transition xt is then determined with Figure.



Instantaneous Release Downwind Composition

- The virtual distance x_v is determined using Equation where the concentration at the transition is C_x.
- In this equation the only unknown is *xv*, which is determined with *x* that gives the left-hand side equal to the right-hand side.
- The appropriate dispersion coefficients are taken from Table. The virtual distance x_v can then computed:

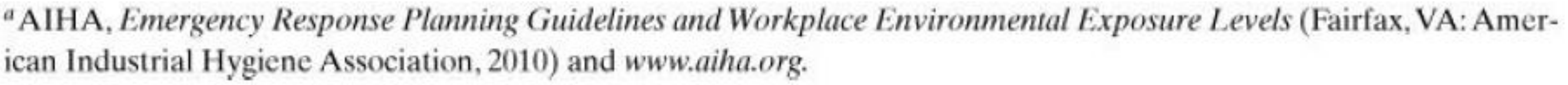
$$\sigma_x \sigma_y \sigma_z = \frac{V_0}{C_x \sqrt{2} \pi^{3/2}}.$$

- The composition at any distance x from the source is computed with the neutrally buoyant equations for ground-level puff releases as shown in case 11.
- But the downwind distance in the dispersion coefficients is x_{nb} as shown in Figure.
- Equation shows the relationship between the various distances.

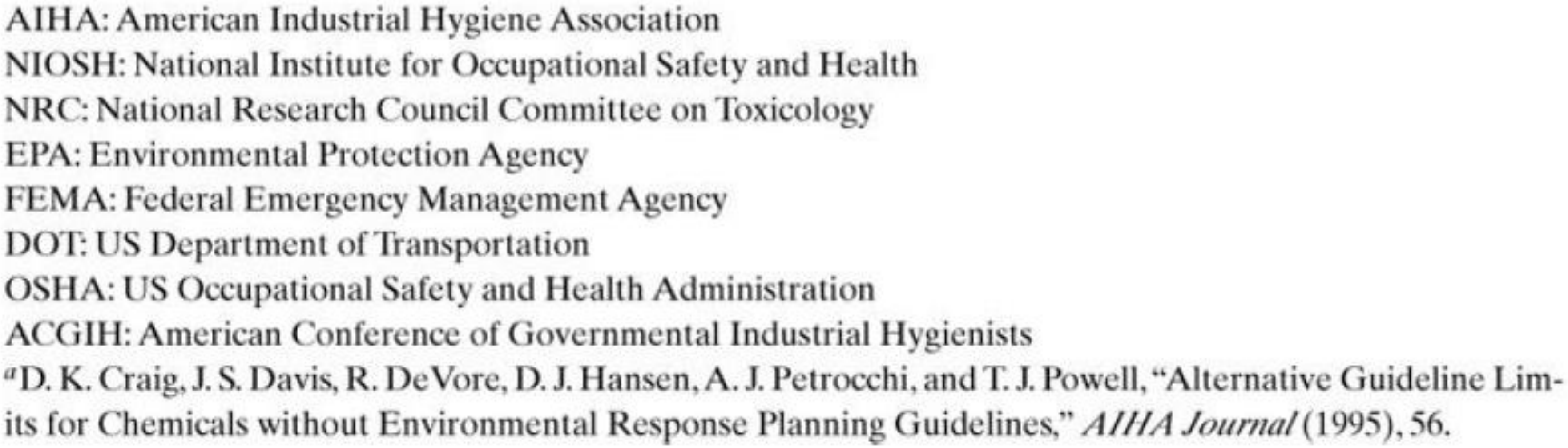
$$x_{nb} = x - x_t + x_v,$$

Toxic Effect Criteria

- Once the dispersion calculations are completed, the question arises: What concentration isconsidered dangerous?
- Concentrations based on TLV-TWA values, are overly conservative and are designed for worker exposures, not short-term exposures under emergency conditions.
- One approach is to use the probit models. These models are also capable of including the effects resulting from transient changes in toxic concentrations.
- Unfortunately, published correlations are available for only a few chemicals, and the data show wide variations from the correlations.
- One simplified approach is to specify a toxic concentration criterion above which it is assumed that individuals exposed to this value will be in danger.
- This approach has led to many criteria promulgated by several government agencies and private associations.



[a] AIHA, *Emergency Response Planning Guidelines and Workplace Environmental Exposure Levels* (Fairfax, VA: American Industrial Hygiene Association, 2010) and *www.aiha.org*.



AIHA: American Industrial Hygiene Association
NIOSH: National Institute for Occupational Safety and Health
NRC: National Research Council Committee on Toxicology
EPA: Environmental Protection Agency
FEMA: Federal Emergency Management Agency
DOT: US Department of Transportation
OSHA: US Occupational Safety and Health Administration
ACGIH: American Conference of Governmental Industrial Hygienists

[a] D. K. Craig, J. S. Davis, R. DeVore, D. J. Hansen, A. J. Petrocchi, and T. J. Powell, "Alternative Guideline Limits for Chemicals without Environmental Response Planning Guidelines," *AIHA Journal* (1995), 56.

Center for Chemical Process Safety (CCPS),

- Some of these criteria and methods include
  - Emergency response planning guidelines (ERPGs) for air contaminants issued by the American Industrial Hygiene Association (AIHA)
  - IDLH levels established by NIOSH
- Emergency exposure guidance levels (EEGLs) and short-term public emergency guidance levels (SPEGLs) issued by the National Academy of Sciences/National Research Council

• TLVs established by the ACGIH, including short-term exposure limits (TLV-STELs) and ceiling concentrations (TLV-Cs)

- PELs promulgated by OSHA
- Toxicity dispersion (TXDS) methods used by the New Jersey Department of Environmental Protection
- Toxic endpoints promulgated by the EPA as part of the RMP

These criteria and methods are based on a combination of results from animal experiments, observations of long- and short-term human exposures, and expert judgment.

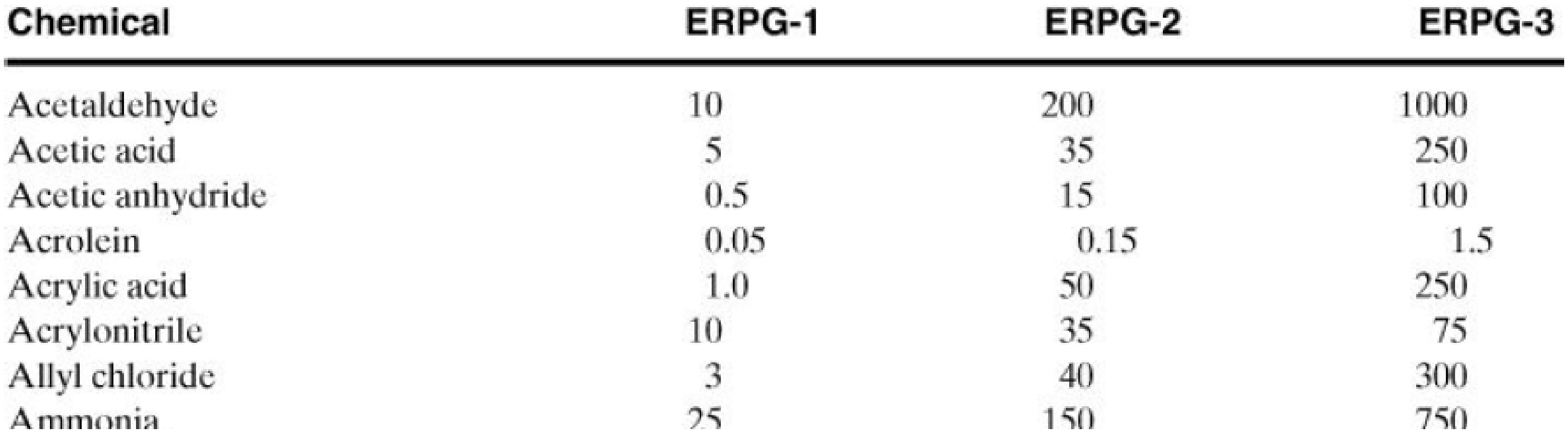
- The following paragraphs define these criteria and describe some of their features.
- ERPGs are prepared by an industry task force and are published by the AIHA.
- Three concentration ranges are provided as a consequence of exposure to a specific substance:

1. ERPG-1 is 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.

2. 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.

3. 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).

Emergency Response Planning Guidelines (ERPGs)a (all values are in ppm unless otherwise noted)



Chemical	ERPG-1	ERPG-2	ERPG-3
Acetaldehyde	10	200	1000
Acetic acid	5	35	250
Acetic anhydride	0.5	15	100
Acrolein	0.05	0.15	1.5
Acrylic acid	1.0	50	250
Acrylonitrile	10	35	75
Allyl chloride	3	40	300
Ammonia	25	150	750

- ERPG data are shown in Table. To date, 47 ERPGs have been developed and are being reviewed, updated, and expanded by an AIHA peer review task force.
- Because of the comprehensive effort to develop acute toxicity values, ERPGs are becoming an acceptable industry/government norm.

- NIOSH publishes IDLH concentrations to be used as acute toxicity measures for common industrial gases.
- An IDLH exposure condition is defined as a condition “that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment.
- IDLH values also take into consideration acute toxic reactions, such as severe eye irritation, that could prevent escape.
- The IDLH level is considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection is permitted.
- If IDLH values are exceeded, all unprotected workers must leave the area immediately.
- IDLH data are currently available for 380 materials.
- Because IDLH values were developed to protect healthy worker populations, they must be adjusted for sensitive populations, such as older, disabled, or ill populations.
- For flammable vapors the IDLH concentration is defined as one-tenth of the lower flammability limit (LFL) concentration.

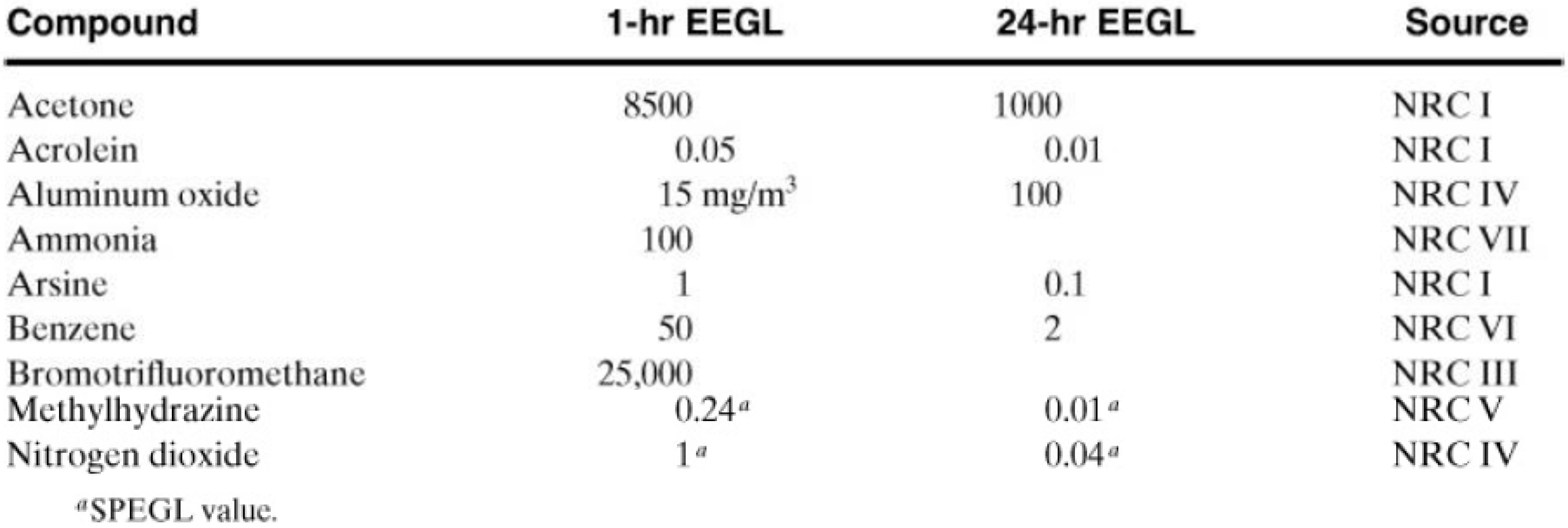
- Also note that IDLH levels have not been peer-reviewed and that no substantive documentation for the values exists.

Emergency Exposure Guidance Levels (EEGLs) from the National Research Council (NRC)

- Since the 1940s, the National Research Council's Committee on Toxicology has submitted EEGLs for 44 chemicals of special concern to the Department of Defense.
- An EEGL is defined as a concentration of a gas, vapor, or aerosol that is judged acceptable and that allows exposed individuals to perform specific tasks during emergency conditions lasting from 1 to 24 hr.
- Exposure to concentrations at the EEGL may produce transient irritation or central nervous system effects but should not produce effects that are lasting or that would impair performance of a task.
- In addition to EEGLs, the National Research Council has developed SPEGLs, defined as acceptable concentrations for exposures of members of the general public.
- SPEGLs are generally set at 10–50% of the EEGL and are calculated to take account of the effects of exposure on sensitive heterogeneous populations.

- The advantages of using EEGLs and SPEGLs rather than IDLH values are
  - (1) SPEGL considers effects on sensitive populations,
  - (2) EEGLs and SPEGLs are developed for several different exposure durations, and
  - (3) Methods by which EEGLs and SPEGLs were developed are well documented in National Research Council publications.

All values are in ppm unless otherwise noted



Compound	1-hr EEGL	24-hr EEGL	Source
Acetone	8500	1000	NRC I
Acrolein	0.05	0.01	NRC I
Aluminum oxide	15 mg/m^3	100	NRC IV
Ammonia	100		NRC VII
Arsine	1	0.1	NRC I
Benzene	50	2	NRC VI
Bromotrifluoromethane	25,000		NRC III
Methylhydrazine	0.24[a]	0.01[a]	NRC V
Nitrogen dioxide	1[a]	0.04[a]	NRC IV

[a] SPEGL value.

- Certain (ACGIH) criteria may be appropriate for use as benchmarks.
- The ACGIH threshold limit values—TLV-STELs and TLV-Cs—are designed to protect workers from acute effects resulting from exposure to chemicals; such effects include irritation and narcosis.
- These criteria can be used for toxic gas dispersion but typically produce a conservative result because they are designed for worker exposures.
- The PELs are promulgated by OSHA and have force of law.
- These levels are similar to the ACGIH criteria for TLV-TWAs because they are also based on 8-hr time-weighted average exposures.
- OSHA-cited “acceptable ceiling concentrations,” “excursion limits,” or “action levels” may be appropriate for use as benchmarks.
- The New Jersey Department of Environmental Protection uses the TXDS method of consequence analysis to estimate potentially catastrophic quantities of toxic substances, as required by the New Jersey Toxic Catastrophe Prevention Act (TCPA).

- An acute toxic concentration (ATC) is defined as the concentration of a gas or vapor of a toxic substance that will result in acute health effects in the affected population and 1 fatality out of 20 or less (5% or more) during a 1-hr exposure.
- ATC values, as proposed by the New Jersey Department of Environmental Protection, are estimated for 103 “extraordinarily hazardous substances” and are based on the lowest value of one of the following:

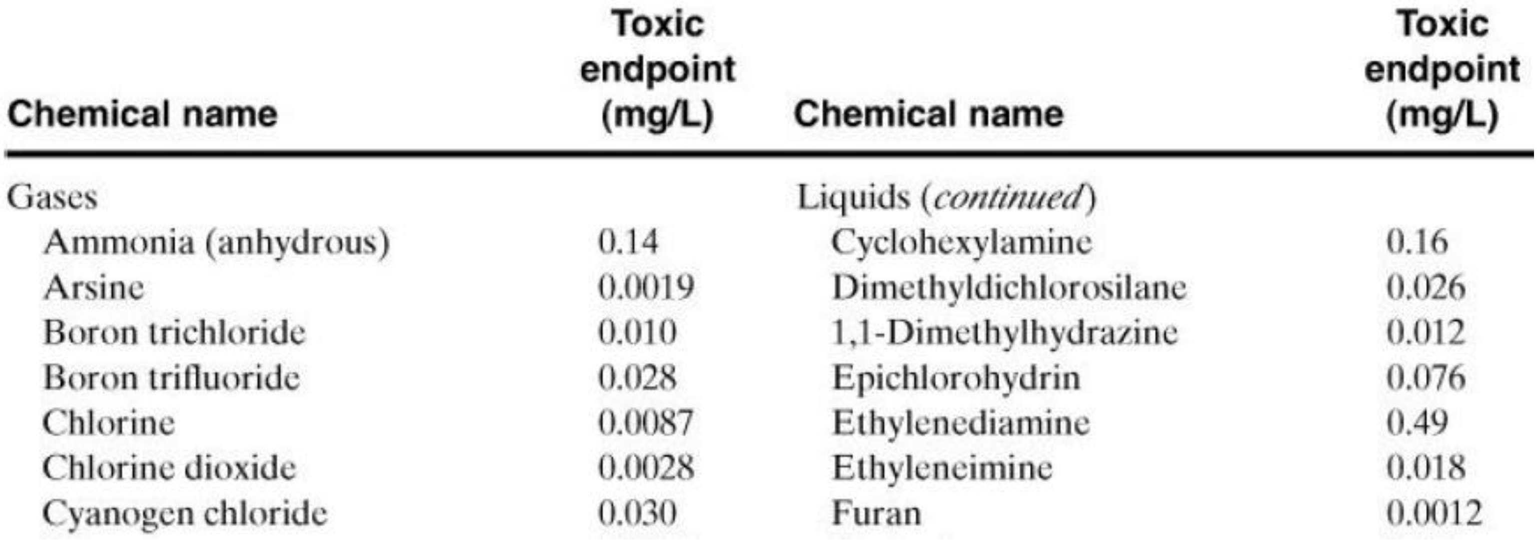
  (1) the lowest reported lethal concentration (LCLO) value for animal test data,

  (2) the median lethal concentration (LC50) value from animal test data multiplied by 0.1, or

  (3) the IDLH value.
- The EPA has promulgated a set of toxic endpoints to be used for air dispersion modeling for toxic gas releases as part of the EPA RMP.
- The toxic endpoint is, in order of preference, (1) the ERPG-2 or (2) the level of concern (LOC) promulgated by the Emergency Planning and Community Right-to-Know Act.

- The LOC is considered “the maximum concentration of an extremely hazardous substance in air that will not cause serious irreversible health effects in the general population when exposed to the substance for relatively short duration.”
- Toxic endpoints are provided for 74 chemicals under the RMP rule and are shown in Table

Toxic Endpoints Specified by the EPA Risk Management Plan



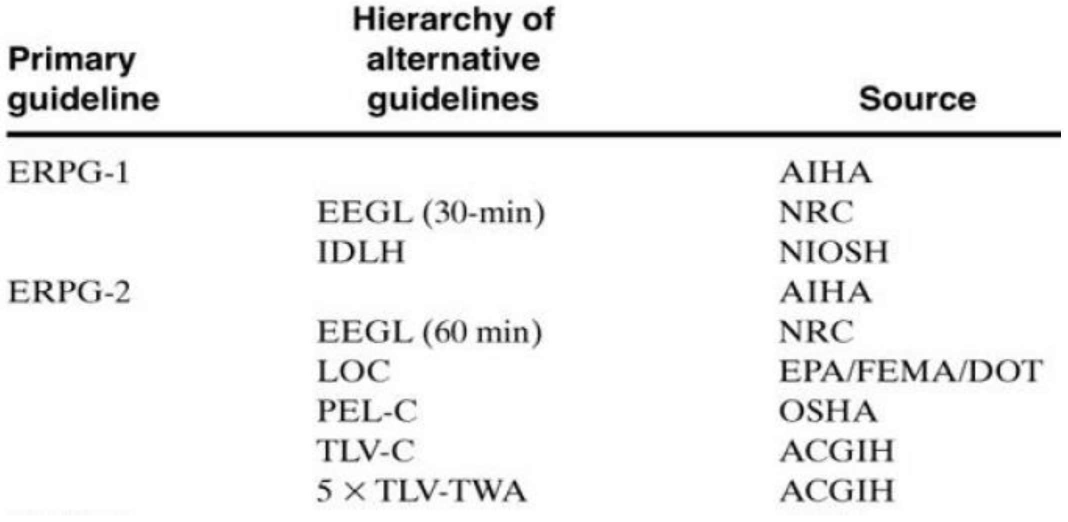
Chemical name	Toxic endpoint (mg/L)	Chemical name	Toxic endpoint (mg/L)
Gases		Liquids (*continued*)	
Ammonia (anhydrous)	0.14	Cyclohexylamine	0.16
Arsine	0.0019	Dimethyldichlorosilane	0.026
Boron trichloride	0.010	1,1-Dimethylhydrazine	0.012
Boron trifluoride	0.028	Epichlorohydrin	0.076
Chlorine	0.0087	Ethylenediamine	0.49
Chlorine dioxide	0.0028	Ethyleneimine	0.018
Cyanogen chloride	0.030	Furan	0.0012

[a] EPA, *RMP Offsite Consequence Analysis Guidance* (Washington, DC: US Environmental Protection Agency, 1996).

- In general, the most directly relevant toxicologic criteria currently available, particularly for developing emergency response plans, are ERPGs, SPEGLs, and EEGLs.
- These were developed specifically to apply to general populations and to account for sensitive populations and scientific uncertainty in toxicologic data.
- For incidents involving substances for which no SPEGLs or EEGLs are available, IDLH levels provide alternative criteria.
- However, because IDLH levels were not developed to account for sensitive populations and because they were based on a maximum 30-min exposure period, the EPA suggests that the identification of an effect zone should be based on exposure levels of one-tenth the IDLH level.
- For example, the IDLH level for chlorine dioxide is 5 ppm.
- Effect zones resulting from the release of this gas are defined as any zone in which the concentration of chlorine dioxide is estimated to exceed 0.5 ppm.
- Of course, the approach is conservative and gives unrealistic results; a more realistic approach is to use a constant dose assumption for releases less than 30 min using the IDLH level.

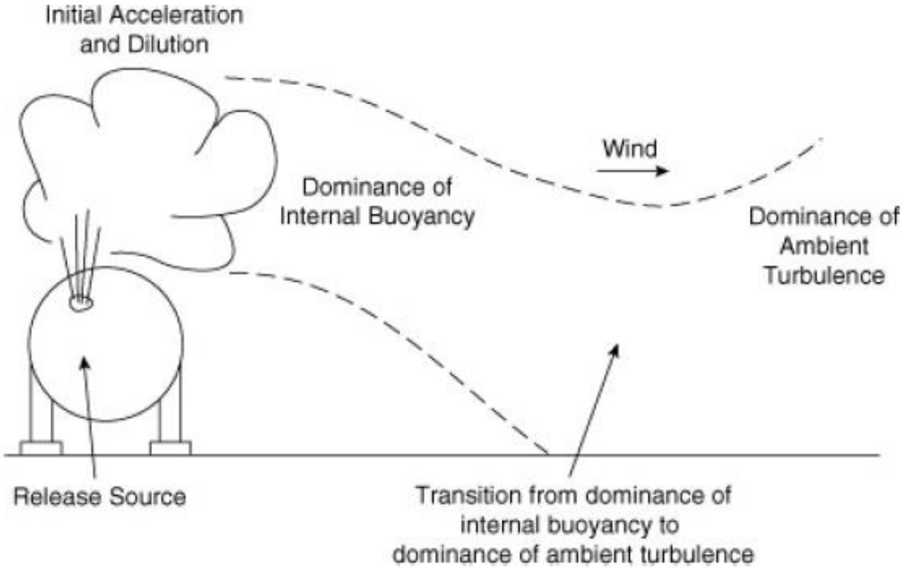
- The use of TLV-STELs and ceiling limits may be most appropriate if the objective is to identify effect zones in which the primary concerns include more transient effects, such assensory irritation or odor perception.
- In general, persons located outside the zone that is based on these limits can be assumed to be unaffected by the release.
- Craig et al. provided a hierarchy of alternative concentration guidelines in the event that ERPG data are not available.
- These methods may result in some inconsistencies because the different methods are based on different concepts. Good judgment should prevail.

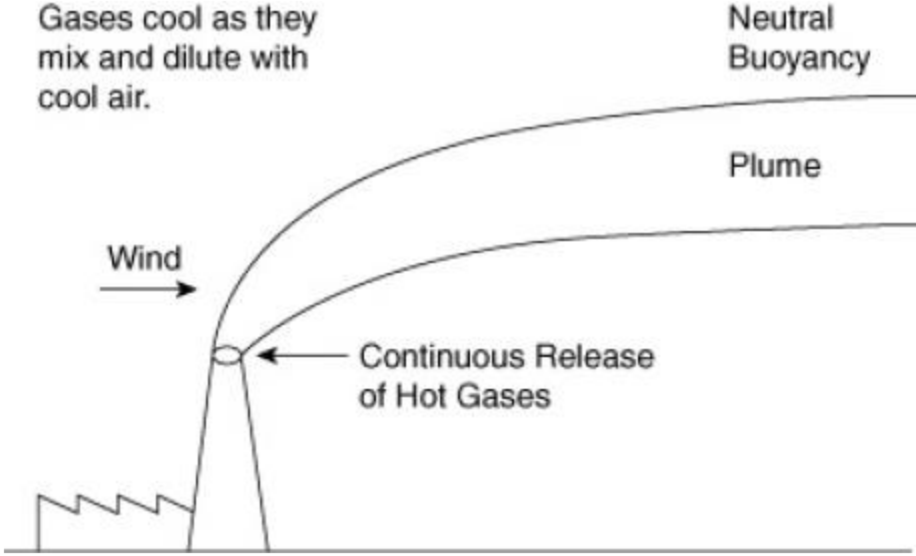
Recommended Hierarchy of Alternative Concentration Guideli



Primary guideline	Hierarchy of alternative guidelines	Source
ERPG-1		AIHA
	EEGL (30-min)	NRC
	IDLH	NIOSH
ERPG-2		AIHA
	EEGL (60 min)	NRC
	LOC	EPA/FEMA/DOT
	PEL-C	OSHA
	TLV-C	ACGIH
	5 × TLV-TWA	ACGIH

Effect of Release Momentum and Buoyancy

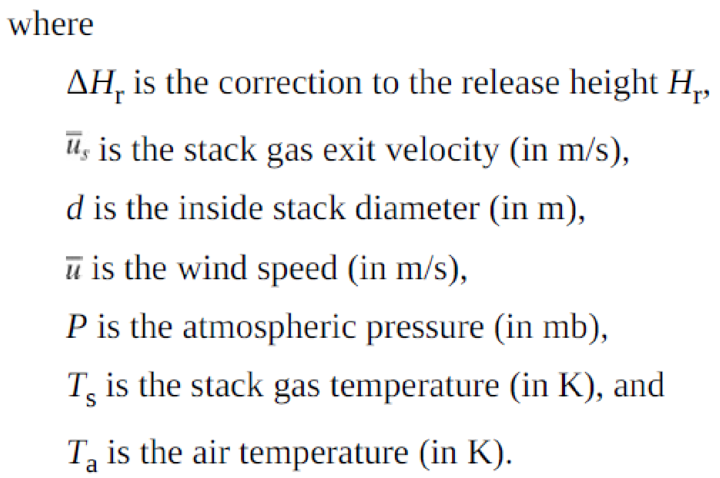




- Release characteristics of a puff or plume depend on the initial release momentum and buoyancy.
- The initial momentum and buoyancy change the effective height of release.
- A release that occurs at ground level but in an upward spouting jet of vaporizing liquid has a greater effective height than 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.

- Both effects are demonstrated by the traditional smokestack release shown in Figure.
- The material released from the smokestack contains momentum, based on its upward velocity within the stack pipe, and it is also buoyant, because its temperature is higher than the ambient temperature.
- Thus the material continues to rise after its release from the stack.
- The upward rise is slowed and eventually stopped as the released material cools and the momentum is dissipated.
- For smokestack releases ‘Turner’ suggested using the empirical Holland formula to compute the additional height resulting from the buoyancy and momentum of the release:

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



where

ΔH_r is the correction to the release height H_r,

$\overline{u}_s$ is the stack gas exit velocity (in m/s),

d is the inside stack diameter (in m),

$\overline{u}$ is the wind speed (in m/s),

P is the atmospheric pressure (in mb),

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

T_a is the air temperature (in K).

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

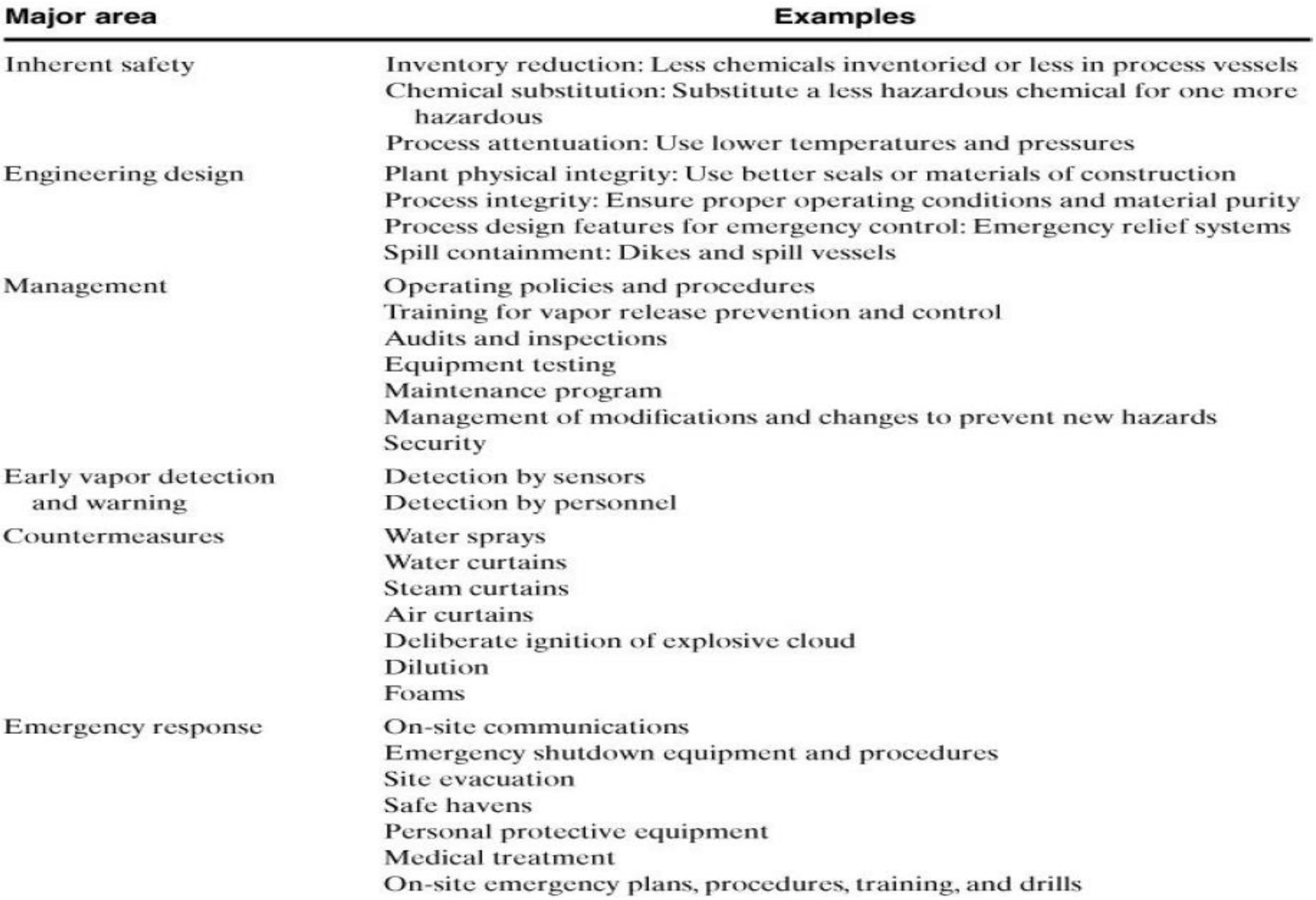
(1) In a preventive way by reducing the likelihood of an event that could generate a hazardous vapor cloud or

(2) In a protective way by reducing the magnitude of the release and/or the exposure of local persons or property.

- The release mitigation procedure is part of the consequence modeling procedure.
- After selection of a release incident, a source model is used to determine either the release rate or the total quantity released.
- This is coupled to a dispersion model and subsequent models for fires or explosions.
- Finally, an effect model is used to estimate the impact of the release, which is a measure of the consequence.
- 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.

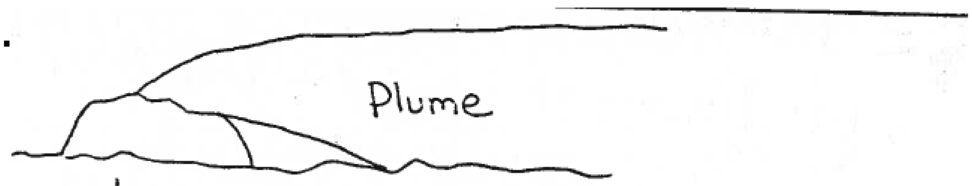
- Table contains a number of measures to mitigate a release.
- The example problems presented in this chapter demonstrate that a small release can result in significant downwind impact.
- In addition, this impact can occur minutes after the initial release, reducing the time available for an emergency response procedure.
- Clearly, it is better to prevent the release in the first place.
- Inherent safety, engineering design, and management should be the first issues considered in any release mitigation procedure.

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

5-3. A burning dump emits an estimated 3 g/s of oxides of nitrogen. What is the average concentration of oxides of nitrogen from this source directly downwind at a distance of 3 km on an overcast night with a wind speed of 7 m/s? Assume that this dump is a point ground-level source.

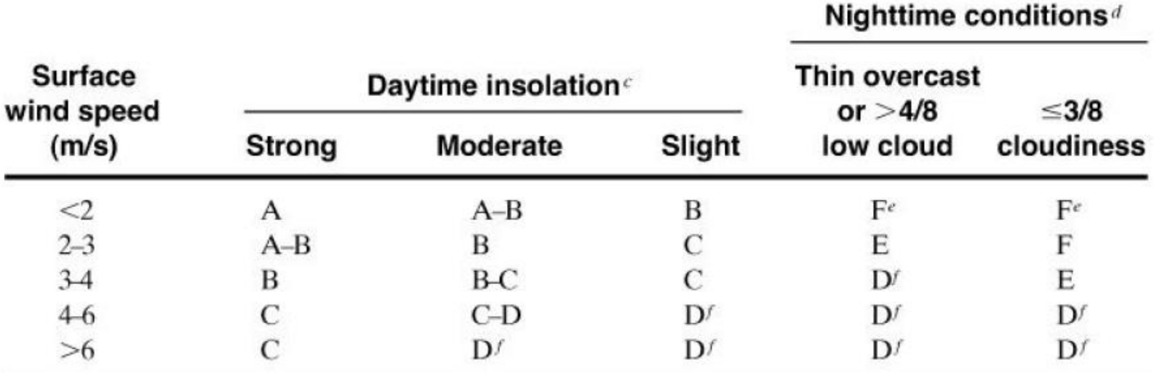


Burning Dump releasing 3 g/sec NO_x

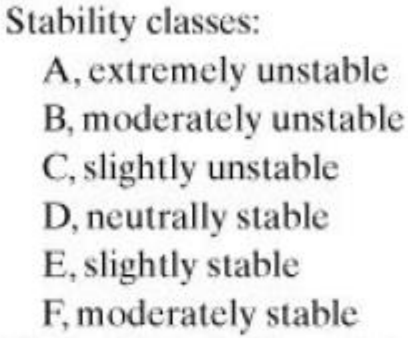
$x = 3\ km = 3000\ m$ downwind

$\bar{u} = 7\ m/s$, overcast night

From Table 5-1, neutral stability, class D applies.



Surface wind speed (m/s)	Daytime insolation[c]			Nighttime conditions[d]	
	Strong	Moderate	Slight	Thin overcast or >4/8 low cloud	≤3/8 cloudiness
<2	A	A–B	B	F[e]	F[e]
2–3	A–B	B	C	E	F
3–4	B	B–C	C	D[f]	E
4–6	C	C–D	D[f]	D[f]	D[f]
>6	C	D[f]	D[f]	D[f]	D[f]



Stability classes:
- A, extremely unstable
- B, moderately unstable
- C, slightly unstable
- D, neutrally stable
- E, slightly stable
- F, moderately stable

Not stated if rural or urban.
If rural, then from Table 5-2

$$\sigma_y = 0.08x(1+0.0001x)^{-1/2}$$
$$= (0.08)(3000m)[1+(0.0001)(3000m)]^{-1/2}$$
$$= 210\,m$$
$$\sigma_z = 0.06x(1+0.0015x)^{-1/2}$$
$$= (0.06)(3000m)[1+(0.0015)(3000m)]^{-1/2}$$
$$= 76.8\,m$$

Pasquill-Gifford stability class	**σ_y (m)**	**σ_z (m)**
Rural conditions		
A	$0.22x(1+0.0001x)^{-1/2}$	$0.20x$
B	$0.16x(1+0.0001x)^{-1/2}$	$0.12x$
C	$0.11x(1+0.0001x)^{-1/2}$	$0.08x(1+0.0002x)^{-1/2}$
D	$0.08x(1+0.0001x)^{-1/2}$	$0.06x(1+0.0015x)^{-1/2}$
E	$0.06x(1+0.0001x)^{-1/2}$	$0.03x(1+0.0003x)^{-1}$
F	$0.04x(1+0.0001x)^{-1/2}$	$0.016x(1+0.0003x)^{-1}$
Urban conditions		
A–B	$0.32x(1+0.0004x)^{-1/2}$	$0.24x(1+0.001x)^{+1/2}$
C	$0.22x(1+0.0004x)^{-1/2}$	$0.20x$
D	$0.16x(1+0.0004x)^{-1/2}$	$0.14x(1+0.0003x)^{-1/2}$
E–F	$0.11x(1+0.0004x)^{-1/2}$	$0.08x(1+0.0015x)^{-1/2}$

If urban,

$$\sigma_y = 0.16x(1+0.0004x)^{-1/2}$$
$$= (0.16)(3000\,m)[1+(0.0004)(3000m)]^{-1/2}$$
$$= 324\,m$$
$$\sigma_z = 0.14x(1+0.0003x)^{-1/2}$$
$$= (0.14)(3000m)[(1)+(0.0003)(3000m)]^{-1/2}$$
$$= 305\,m$$

The concentration along the centerline of the plume directly downwind is given at *y* = *z* =0:

$$\langle C\rangle(x,0,0) = \frac{Q_m}{\pi\sigma_y\sigma_z u}.$$

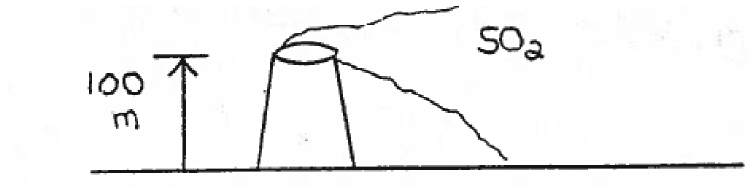
For rural release

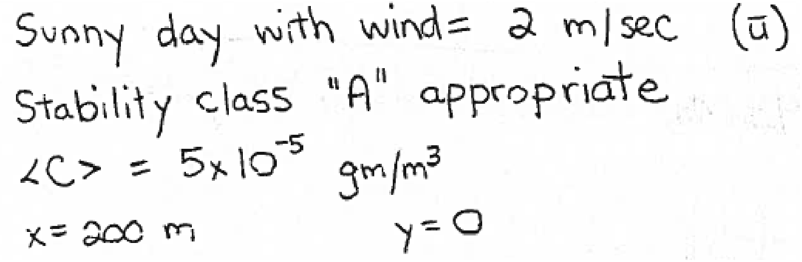
$$\langle C\rangle = \frac{3\,gm/s}{(3.14)(210m)(76.8m)(7m/s)}$$
$$= 8.46\times10^{-6}\,gm/m^3$$

For urban

$$\langle C\rangle = \frac{3\,gm/s}{(3.14)(324m)(305m)(7m/s)}$$
$$= 1.38\times10^{-6}\,gm/m^3$$

5-4. A trash incinerator has an effective stack height of 100 m. On a sunny day with a 2 m/s wind the concentration of sulfur dioxide 200 m directly downwind is measured at 5.0 × 10–5 g/m3. Estimate the mass release rate (in g/s) of sulfur dioxide from this stack. Also estimate the maximum sulfur dioxide concentration expected on the ground and its location downwind from the stack.

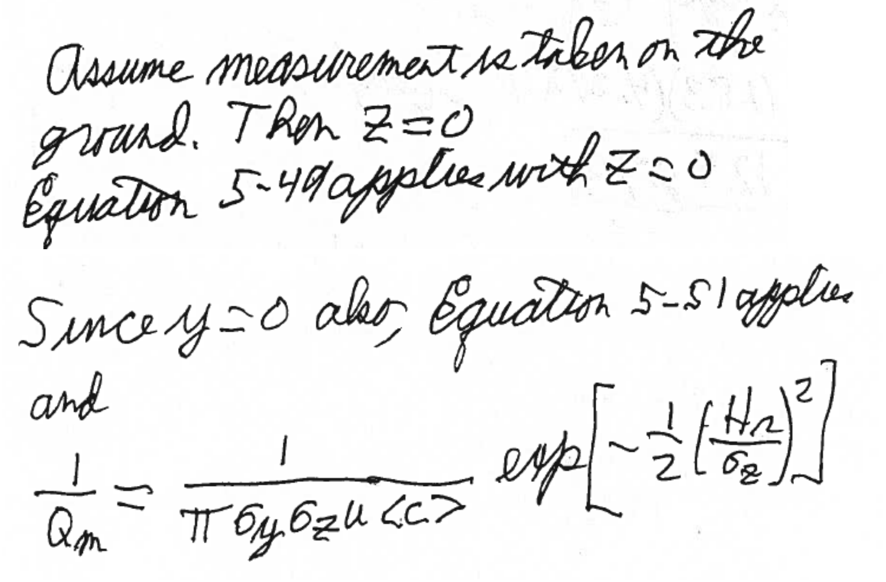



Sunny day with wind = 2 m/sec ($\bar{u}$)

Stability class "A" appropriate

$\langle C \rangle = 5 \times 10^{-5}$ gm/m^3

$x = 200$ m $y = 0$


Assume measurement is taken on the ground. Then $Z = 0$

Equation 5-49 applies with $Z = 0$

Since $y = 0$ also, Equation 5-51 applies

and

$$\frac{1}{Q_m} = \frac{1}{\pi \sigma_y \sigma_z u \langle C \rangle} \exp\left[-\frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right]$$

Case 13: Plume with Continuous Steady-State Source at Height *H*r above Ground Level and Wind Moving in *x* Direction at Constant Velocity *u*

$$\langle C\rangle(x, y, z) = \frac{Q_m}{2\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{\exp\left[-\frac{1}{2}\left(\frac{z - H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z + H_r}{\sigma_z}\right)^2\right]\right\}.$$

The ground-level centerline concentrations are found by setting *y* = *z* = 0:

$$\langle C\rangle(x, 0, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right].$$

Use Table 5-2 to compute σ_y and σ_z

Assume rural conditions

$$\sigma_y \simeq 0.22x(1 + 0.0001x)^{-1/2}$$

$$= (0.22)(200\,m)\left[1 + (0.0001)(200\,m)\right]^{-1/2}$$

$$= 43.6\,m$$

$$\sigma_z \simeq 0.20x \simeq (0.20)(200\,m) \simeq 40\,m$$

Then

$$\frac{1}{Q_m} = \left[\frac{1}{(3.14)(43.6\,m)(40\,m)(2\,m/s)(5 \times 10^{-5}\,gm/m^3)}\right]$$

$$\times \exp\left[-\left(\frac{1}{2}\right)\left(\frac{100\,m}{40\,m}\right)^2\right]$$

$$= (1.83)(4.39 \times 10^{-2})(gm/s)^{-1}$$

$$\boxed{Q_m \simeq 12.4\,gm/s}$$