

# “Transport of Chemicals in the Atmosphere”

## Module 4: The Atmosphere, Lecture 2

*Chemical Fate and Transport in the Environment*, 2<sup>nd</sup> edition. H.F. Hemond and E.J. Fechner-Levy. Academic Press. London. 2000.

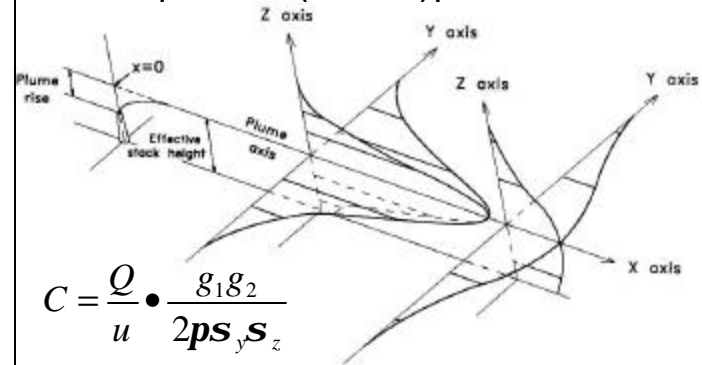
## 4.4 Transport of Chemicals in the Atmosphere

- Physical transport and chemical reaction rates are both needed to predict downwind concentrations of air pollutants.
- It is important to compare chemical reaction rates with advective velocities and mixing rates.
  - If chemical transformations are relatively slow compared to mixing rates, it may be appropriate to use simple box models in which air volumes are considered well mixed.
  - When chemicals are transported significant distances in the time it takes for the chemical reactions to reach equilibrium, then advection-dispersion-reaction equation solutions are most useful.

### 4.4.2 Local-Scale Outdoor Air Pollution

- The smallest spatial scale at which outdoor air pollution is of concern corresponds to the air volume affected by pollutant emissions from a single point source.
- Chemicals are carried downwind by advection, while turbulent (Fickian) transport cause the concentrations to become more diluted.
- Possible to predict the distance to and the concentration at which the plume from an elevated emission reaches the ground (classically considered the worst-case scenario).

#### Pasquill-Gifford (Gaussian) plume model:



$$C = \frac{Q}{u} \cdot \frac{g_1 g_2}{2ps_y s_z}$$

$$g_1 = \exp\left(-0.5y^2/s_y^2\right)$$

$$g_2 = \exp\left(-0.5 \cdot (z - H)^2 / s_z^2\right) + \exp\left(-0.5 \cdot (z + H)^2 / s_z^2\right)$$

## Plume Rise

H is the effective stack height. It includes the physical stack height plus the plume rise. Plume rise occurs for emissions that are physically ejected with an upward momentum, and/or when the gases are less dense than the surrounding air (usually because they are heated).

The plume rise can be calculated using Brigg's plume rise model:

$$\Delta H = 1.6 F_b^{1/3} x^{2/3} / u \quad F_b = g \frac{d^2 V}{4} \left( \frac{T_s - T_a}{T_s} \right)$$

$F_b$  is the buoyancy flux parameter and  $x$  is the distance downwind where the plume rise is being estimated. The wind speed is  $u$ ,  $V$  is the emission velocity,  $d$  is the stack diameter,  $T_s$  is the absolute stack gas temperature and  $T_a$  is the absolute ambient air temperature.

$$V = \frac{0.8 \text{ m}^3 / \text{sec}}{\pi (0.2 \text{ m})^2} = 6.4 \text{ m} / \text{sec}$$

$$F_b = g \frac{d^2 V}{4} \left( \frac{T_s - T_a}{T_s} \right) = \frac{9.81 \text{ m}}{\text{sec}^2} \cdot \frac{(0.4 \text{ m})^2}{4} \cdot \frac{6.4 \text{ m}}{\text{sec}} \cdot \frac{353 \text{ K} - 283 \text{ K}}{353 \text{ K}} = \frac{0.5 \text{ m}^4}{\text{sec}^3}$$

$$\Delta H = 1.6 F_b^{1/3} x^{2/3} / u = (1.6) \left( \frac{0.5 \text{ m}^4}{\text{sec}^3} \right)^{1/3} (30 \text{ m})^{2/3} \left( \frac{1}{2 \text{ m} / \text{sec}} \right) = 6 \text{ m}$$

## Example Problem 4-7

- A small industrial furnace emits  $0.8 \text{ m}^3/\text{sec}$  of exhaust gases at a temperature of  $80^\circ \text{C}$ . The outside temperature is  $10^\circ \text{C}$  and the wind speed is  $2 \text{ m}/\text{sec}$ . The stack is  $20 \text{ m}$  tall, with a diameter of  $40 \text{ cm}$ . What is the total plume height at the edge of the property,  $30 \text{ m}$  downwind?

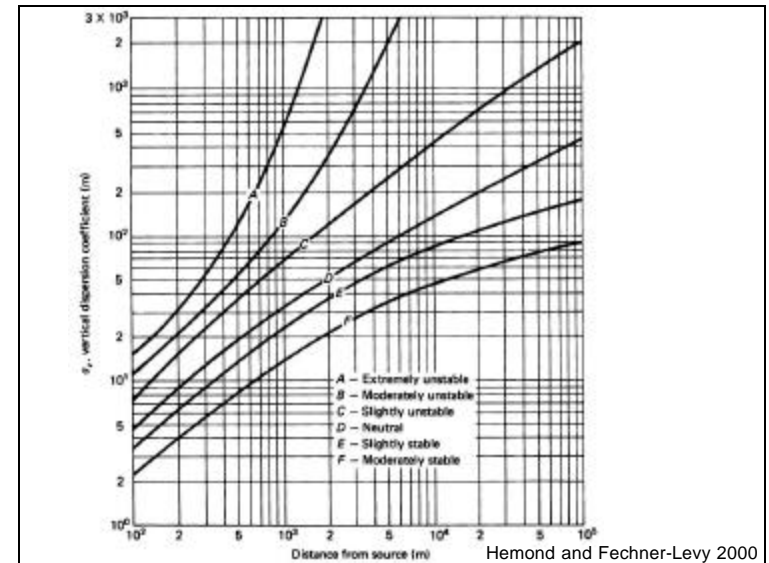
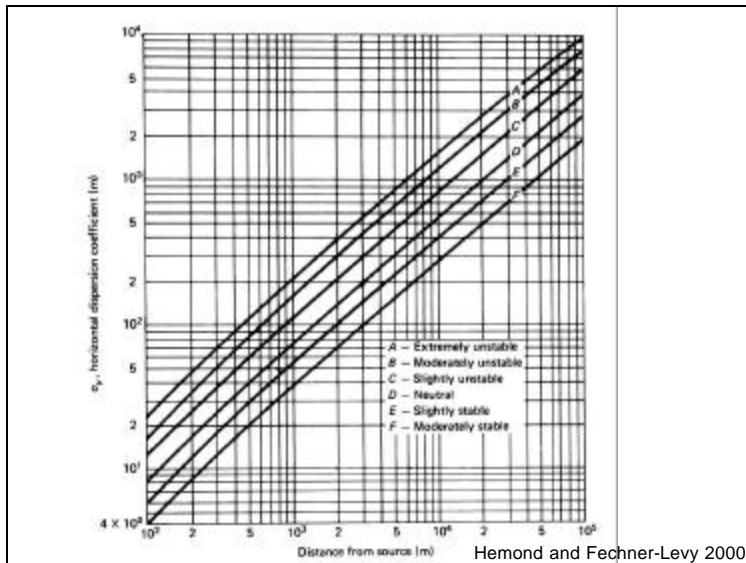
## Pasquill Stability Categories

Dispersion is expressed in standard deviation terms ( $\sigma_y$  and  $\sigma_z$ ) and not Fickian dispersion coefficients ( $D_y$  and  $D_z$ ). In one-dimensional Fickian transport of a chemical in a fluid,  $\sigma^2 = Dt$ , and therefore  $\sigma$  increases with distance, as  $D$  is constant. They also are highly dependent on meteorological conditions (especially atmospheric stability). The following table shows the stability classes for different conditions:

Pasquill Stability Categories Hemond and Fechner-Levy 2000

Surface wind speed (m/sec)	Insolation			Night	
	Strong	Moderate	Slight	Thinly overcast or $\geq 4/8$ low cloud	$\approx 3/8$ cloud
<2	A	A-B	B	—	—
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Strong insolation corresponds to sunny midday conditions in midsummer (England). Slight insolation corresponds to sunny midday conditions in midwinter (England). Neutral (D) should always be used for overcast conditions, and for the hour before sunset and for the hour after sunrise.



Formulae for  $\sigma_x$  and  $\sigma_z$  Recommended by Briggs

Pasquill stability category	$\sigma_x$ (m)	$\sigma_z$ (m)
Open country conditions		
A	$0.22 x / (1 + 0.0001 x)^{0.5}$	$0.20 x$
B	$0.16 x / (1 + 0.0001 x)^{0.5}$	$0.12 x$
C	$0.11 x / (1 + 0.0001 x)^{0.5}$	$0.08 x / (1 + 0.0002 x)^{0.5}$
D	$0.08 x / (1 + 0.0001 x)^{0.5}$	$0.06 x / (1 + 0.0015 x)^{0.5}$
E	$0.06 x / (1 + 0.0001 x)^{0.5}$	$0.03 x / (1 + 0.0003 x)$
F	$0.04 x / (1 + 0.0001 x)^{0.5}$	$0.016 x / (1 + 0.0003 x)$
Urban conditions		
A, B	$0.32 x / (1 + 0.0004 x)^{0.5}$	$0.24 x \cdot (1 + 0.001 x)^{0.5}$
C	$0.22 x / (1 + 0.0004 x)^{0.5}$	$0.20 x$
D	$0.16 x / (1 + 0.0004 x)^{0.5}$	$0.14 x / (1 + 0.0003 x)^{0.5}$
E, F	$0.11 x / (1 + 0.0004 x)^{0.5}$	$0.08 x / (1 + 0.0015 x)^{0.5}$

Hemond and Fechner-Levy 2000

## Example Problem 4-8

- A smokestack with an effective height of 25 m emits sulfur dioxide ( $\text{SO}_2$ ) at a rate of 10 kg/hr. What is the contribution of this stack to ground-level  $\text{SO}_2$  concentrations at a school yard 8 km downwind, if wind speed is 4.5 m/sec on a sunny midwinter day. Assume an unlimited mixing height.

The stability classification is estimated to be C for this condition,  $\sigma_y$  is approximately 700 m and  $\sigma_z$  is approximately 400 m. Also  $y=0$  directly downwind and  $z=0$  for ground level conditions.

$$\frac{Q}{u} = \frac{10 \text{ kg/hr}}{(4.5 \text{ m/sec} \cdot 3600 \text{ sec/hr})} = 6.2 \times 10^{-4} \text{ kg/m}$$

$$g_1 = \exp(-0.5 y^2 / s_y^2) = \exp(-0.5 \cdot (0 \text{ m})^2 / (700 \text{ m})^2) = 1$$

$$g_2 = \exp(-0.5 \cdot (z - H)^2 / s_z^2) + \exp(-0.5 \cdot (z + H)^2 / s_z^2) \\ = \exp(-0.5 \cdot (-25 \text{ m})^2 / (400 \text{ m})^2) + \exp(-0.5 \cdot (25 \text{ m})^2 / (400 \text{ m})^2) = 2$$

$$C_{\text{schoolyard}} = 6.2 \times 10^{-4} \text{ kg/m} \cdot \frac{(1) \cdot (2)}{2p \cdot 700 \text{ m} \cdot 400 \text{ m}} = 7 \times 10^{-10} \text{ kg/m}^3$$

It is possible to use the equations for open country or rural conditions to calculate  $\sigma_y$  and  $\sigma_z$ :

$$s_y = \frac{0.11 \cdot 8000}{(1 + 0.0001 \cdot 8000)^{0.5}} = 660 \text{ m} \quad s_z = \frac{0.08 \cdot 8000}{(1 + 0.0002 \cdot 8000)^{0.5}} = 400 \text{ m}$$

The concentration in the schoolyard for these rural conditions would be about  $8 \times 10^{-10} \text{ kg/m}^3$  (close to the above calculation).

Similarly, for urban conditions :

$$s_y = \frac{0.22 \cdot 8000}{(1 + 0.0004 \cdot 8000)^{0.5}} = 860 \text{ m} \quad s_z = 0.2 \cdot 8000 = 1600 \text{ m}$$

The concentration in the schoolyard for these urban conditions would be about  $1 \times 10^{-10} \text{ kg/m}^3$  ("rough" urban surfaces increase turbulence and therefore diffusion).

## Low Mixing Heights

- If the mixing height, L, is low enough to restrict the ascension of a plume, it may be appropriate to assume that the plume becomes fully mixed vertically beneath L and spreads only horizontally. The following equation can be used to estimate the concentration under this condition:

$$C = \frac{Q}{u} \cdot \frac{g_1}{2ps_y} \cdot \frac{1}{L}$$

Direct measurements of atmospheric turbulence can be used to more accurately estimate the dispersion coefficients. The following equations include turbulent intensity in the lateral and vertical directions:

$$i_y = \frac{s_v}{u} \quad i_z = \frac{s_w}{u}$$

$i_y$  and  $i_z$  are unitless measures of turbulent intensity and  $\sigma_v$  and  $\sigma_w$  are the standard deviations of the wind velocity in the y and z directions with respect to time, while u is the wind speed.

The  $\sigma_y$  and  $\sigma_z$  values are then calculated, using semiempirical functions for  $f_y$  and  $f_z$  from the following table:

$$s_y = i_y \cdot f_y \cdot x \quad s_z = i_z \cdot f_z \cdot x$$

Formulae for  $f_y$  and  $f_z$

Pasquill stability category	$f_y$	$f_z$
Rural conditions		
A, B	$1/(1 + 0.0001 x)^{0.5}$	1
C	$1/(1 + 0.0001 x)^{0.5}$	$1/(1 + 0.0002 x)^{0.5}$
D	$1/(1 + 0.0001 x)^{0.5}$	$1/(1 + 0.0015 x)^{0.5}$
E, F	$1/(1 + 0.0001 x)^{0.5}$	$1/(1 + 0.0003 x)$
Urban conditions		
A, B	$1/(1 + 0.0004 x)^{0.5}$	$(1 + 0.001 x)^{0.5}$
C	$1/(1 + 0.0004 x)^{0.5}$	1
D	$1/(1 + 0.0004 x)^{0.5}$	$1/(1 + 0.0003 x)^{0.5}$
E, F	$1/(1 + 0.0004 x)^{0.5}$	$1/(1 + 0.0015 x)^{0.5}$

Hemond and Fechner-Levy 2000

## Example Problem 4-9

- A smelter stack in a rural area emits very fine particles containing heavy metals. Wind speed is 5.5 m/sec and the insolation is slight. The emission rate for nickel is approximately 0.1 g/sec at an effective height of 120 m. The measured standard deviation of the vertical air velocity is 0.15 m/sec, while the standard deviation of the perpendicular wind vector is 0.25 m/sec. What is the nickel concentration at ground level directly downwind, 8 km from the stack?

The Pasquill stability category is D and the calculated  $\sigma_z$  and  $\sigma_y$  values are:

$$i_z = \frac{s_w}{u} = \frac{0.15 \text{ m/sec}}{5.5 \text{ m/sec}} = 0.027$$

$$f_z = \frac{1}{(1 + 0.0015x)^{0.5}} = \frac{1}{(1 + 0.0015 \cdot 8000 \text{ m})^{0.5}} = 0.28$$

$$s_z = i_z \cdot f_z \cdot x = (0.027) \cdot (0.28) \cdot (8000 \text{ m}) = 61 \text{ m}$$

$$i_y = \frac{s_v}{u} = \frac{0.25 \text{ m/sec}}{5.5 \text{ m/sec}} = 0.045$$

$$f_y = \frac{1}{(1 + 0.001x)^{0.5}} = 0.75$$

$$s_y = i_y \cdot f_y \cdot x = (0.045) \cdot (0.75) \cdot (8000 \text{ m}) = 271 \text{ m}$$

$$g_1 = \exp(-0.5y^2 / s_y^2) = \exp[-0.5(0)^2 / (271m)^2] = \exp(0)$$

$$g_2 = \exp(-0.5 \cdot (z - H)^2 / s_z^2) + \exp(-0.5 \cdot (z + H)^2 / s_z^2)$$

$$C = \frac{Q}{u} \cdot \frac{g_1 g_2}{2ps_y s_z}$$

$$= \frac{0.1g / \text{sec}}{5.5m / \text{sec}} \cdot \frac{\exp(0) \cdot \left( \exp \frac{-0.5 \cdot (-120m)^2}{(61m)^2} + \exp \frac{-0.5 \cdot (120m)^2}{(61m)^2} \right)}{2p \cdot (271m) \cdot (61m)}$$

$$= 4.9 \times 10^{-8} g / m^3$$

## Chapter 4 Homework Problems

**Problem 4-21**

**Problem 4-29**

**Problem 4-42**