CE 213A
Introduction to Environmental Science

L10: Unit 2: A. Air Pollution
Pollutant Transport & Modeling

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Schedule : LEC Mon Wed Fri 5:10 – 6 pm

Pollutant transport phenomenon and modeling

Factors affecting levels observed – Meteorological parameters

An air pollution problem involves three parts:

- The pollution source
- The movement or dispersion of the pollutant
- The recipient

The transport of the pollutant is determined by meteorological conditions

Source   Transport   Recipient
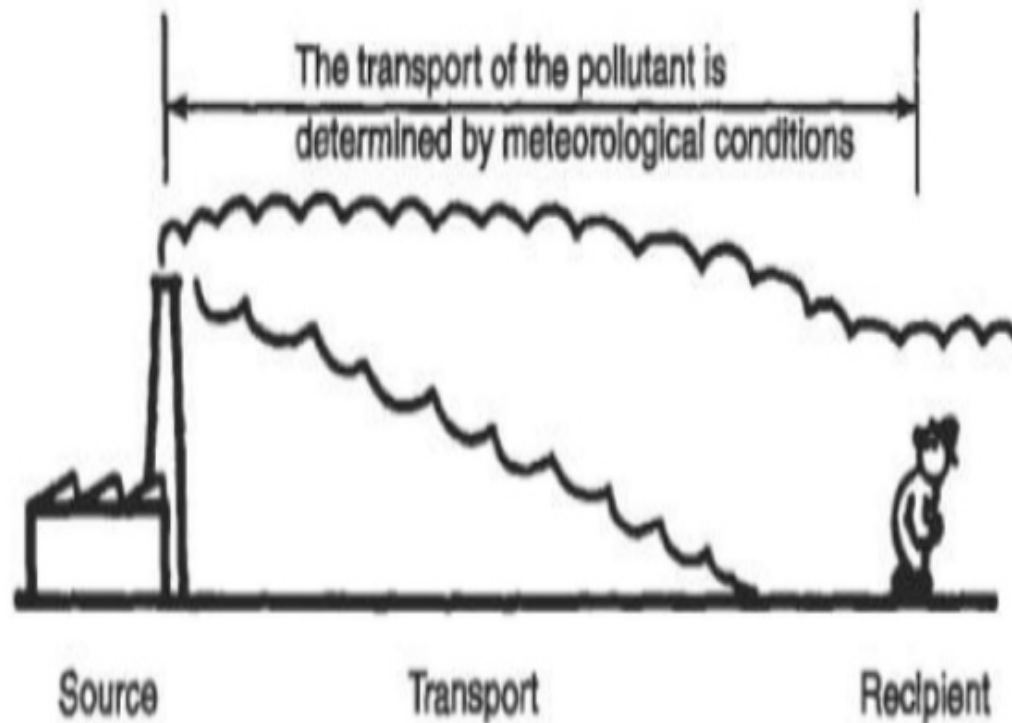
Basic concepts and mechanisms of Transport phenomena

Flux

Advection, Diffusion and Dispersion

Ref. Nazaroff, Ch. 4

Contaminant flux:

Transport of both molecules and particles is commonly quantified in terms of flux density or simple flux.
- Flux is a <u>vector quantity</u>, comprising both a magnitude and a direction.
- The flux vector points in the direction of net contaminant motion, and the magnitude indicates the rate at which the contaminant is moving.
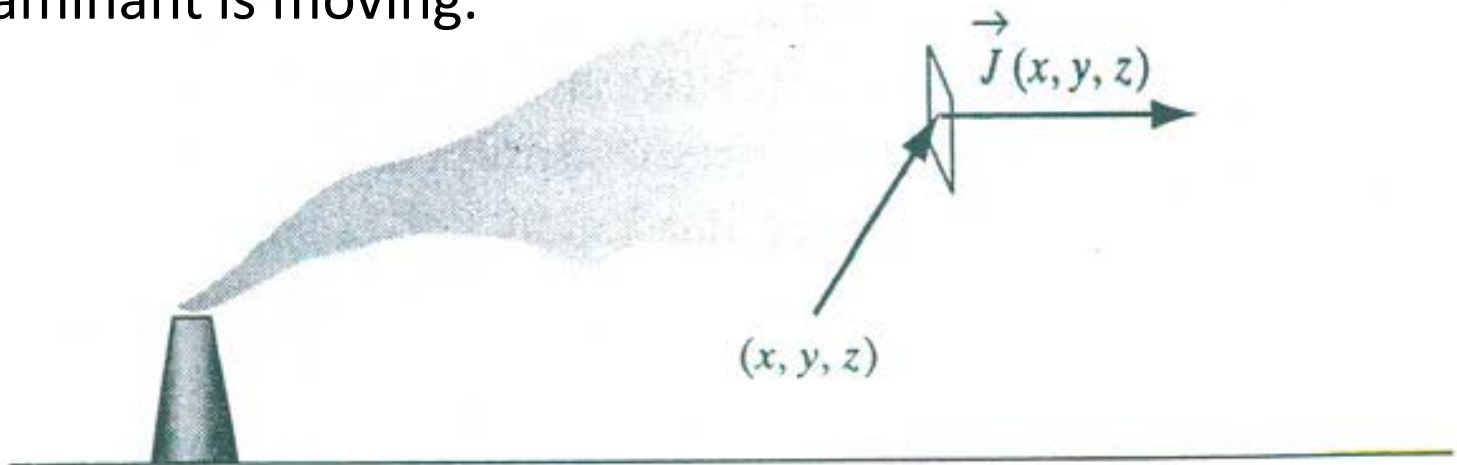
$$\vec{J}(x, y, z)$$

(x, y, z)

Figure 4.A.1 Flux, $\vec{J}$, is a vector quantity whose value varies with position (x, y, z). The contaminant flux vector points in the direction of transport, and its magnitude is the quantity transported (usually

Dominant mechanism that cause transport of molecules and particles in environmental fluids

Transport mechanism	Species[a]	Description	1-D flux[b]
Advection	m, p	Movement with fluid	$J_a = CU$
Gravitational settling	p	Transport induced by gravity	$J_g = Cv_t$
Molecular diffusion or Brownian motion[c]	m, p	Transport caused by random thermal motion	$J_d = -D\dfrac{dC}{dx}$
Turbulent diffusion	m, p	Transport caused by apparently random fluid velocity fluctuations in turbulent flow	$J_t = -\varepsilon_t\dfrac{dC}{dx}$
Shear-flow dispersion	m, p	Transport caused by nonuniform fluid flow with position	$J_s = -\varepsilon_s\dfrac{dC}{dx}$
Hydrodynamic dispersion (porous media)	m, p	Transport caused by nonuniform flow through porous material	$J_h = -\varepsilon_h\dfrac{dC}{dx}$
Electrostatic drift[d]	m, p[e]	Movement of charged species in an electric field	$J_e = Cv_e$
Inertial drift	p	Transport associated with acceleration of a fluid	$J_f = Cv_f$

[a] m = molecule, p = particle.

[b] C = species concentration, U = fluid velocity, v_t = settling velocity, D = molecular or Brownian diffusivity, ε_t = turbulent diffusivity, ε_s = shear-flow dispersivity, ε_h = dispersion coefficient, v_e = electrostatic drift velocity, v_f = inertial drift velocity, J = flux.

[c] Molecular diffusion and Brownian motion apply to molecules and particles, respectively; both occur from the same fundamental process.

[d] See §7.C.

[e] Electrostatic drift applies to charged species only.

Advection, diffusion and dispersion

1. **Advection**

- transport of material caused by the <u>net flow of the fluid</u> in which that material is suspended.
- Whenever a fluid is in motion, all contaminants in the fluid, including both molecules and particles, are advected along with the fluid.
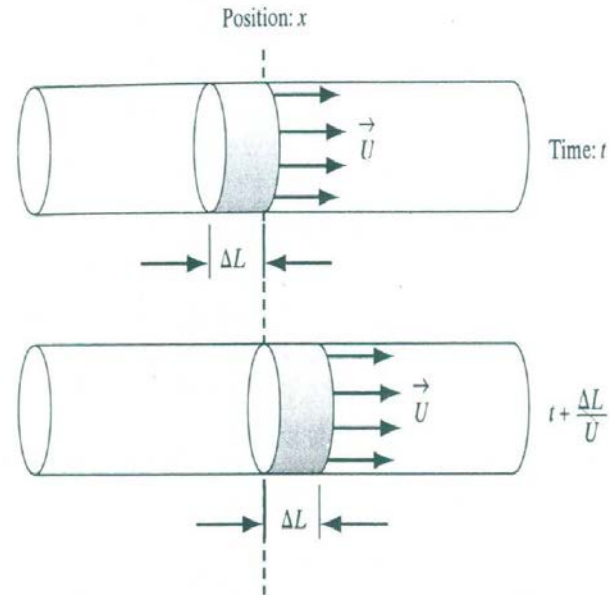

Figure 4.A.2 Advective flux of contaminant through a tube. The two pictures represent the same tube at two points in time, t and $t + \Delta t$, where $\Delta t = \Delta L/U$.

per time:

$$J_a = \frac{C \times \Delta L \times A}{A(\Delta L/U)} = CU \tag{4.A.1}$$

In general, the three-dimensional advective flux vector is the product of the contaminant concentration and the fluid velocity:

$$\vec{J_a}(x, y, z) = C(x, y, z) \times \vec{U}(x, y, z) \tag{4.A.2}$$

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2.   Molecular diffusion

The random motion of fluids causes a <u>net movement of species from regions of high concentration to regions of low concentration</u> this phenomenon is known as molecular diffusion

Fick's law for molecular diffusion

$$J_d \propto -\frac{\Delta C}{\Delta x} \qquad (4.A.3)$$

where J_d is the diffusive flux density (moles per cross-sectional area of the tube per time), ΔC is the change in concentration of ethylbenzene molecules across the tube, and Δx is the tube length. The minus sign appears in this relationship to remind us that the diffusive flux proceeds in the direction of decreasing concentration.

By introducing the proportionality constant, D, this expression can be converted to an equation:

$$J_d = -D\frac{\Delta C}{\Delta x} \qquad (4.A.4)$$

The constant, D, is called the *diffusion coefficient*, or *diffusivity*. It is a property of the diffusing species (ethylbenzene in this case), the fluid through which it is diffusing

Table 4.A.2 Measured Diffusion Coefficients for Species in Air at 1 atm

Species	Formula	T (K)	D (cm^2 s^{-1})	Reference[a]
Ammonia	NH_3	273	0.198	Bretsznajder, 1971
		273	0.216	McCabe et al., 1993
Benzene	C_6H_6	273	0.077	McCabe et al., 1993
		298.2	0.096	Cussler, 1984
Carbon dioxide	CO_2	273	0.138	McCabe et al., 1993
		317.2	0.177	Cussler, 1984
Ethanol	C_2H_5OH	273	0.102	McCabe et al., 1993; Cussler, 1984
		313	0.147	Reid et al., 1987 (pressure $=$ 1 bar)
Helium	He	276.2	0.624	Cussler, 1984
Hydrogen	H_2	273	0.611	Cussler, 1984; McCabe et al., 1993
Methane	CH_4	273	0.196	Cussler, 1984
Methyl alcohol	CH_3OH	273	0.133	McCabe et al., 1993
n-Octane	C_8H_{18}	273	0.051	McCabe et al., 1993
Naphthalene	$C_{10}H_8$	273	0.051	McCabe et al., 1993
		303	0.087	Reid et al., 1987
Oxygen	O_2	273	0.178	Cussler, 1984; McCabe et al., 1993
Toluene	C_7H_8	273	0.071	McCabe et al., 1993
		299.1	0.086	Cussler, 1984
Water	H_2O	273	0.219	Bretsznajder, 1971; McCabe et al., 1993
		289.1	0.282	Cussler, 1984
		298.2	0.260	Cussler, 1984
		312.6	0.277	Cussler, 1984
		313	0.292	Reid et al., 1987

[a]When two sources disagree by less than 5 percent, only one value is listed.

Table 4.A.3 Measured Diffusion Coefficients for Species in Water

Species	Formula	T (K)	D (cm^2 s^{-1})	Reference[a]
Benzene	C_6H_6	298	1.02×10^{-5}	Cussler, 1984
Hydrogen	H_2	298	3.36×10^{-5}	Bretsznajder, 1971
		298	4.50×10^{-5}	Cussler, 1984
Air		298	2.00×10^{-5}	Cussler, 1984
Methane	CH_4	275	0.85×10^{-5}	Reid et al., 1987
Carbon dioxide	CO_2	298	2.00×10^{-5}	Reid et al., 1987
Methanol	CH_3OH	288	1.26×10^{-5}	Reid et al., 1987
		298	0.84×10^{-5}	Cussler, 1984
Ethanol	C_2H_5OH	288	1.00×10^{-5}	Reid et al., 1987
		298	0.84×10^{-5}	Cussler, 1984
Ethylbenzene	C_8H_{10}	293	0.81×10^{-5}	Reid et al., 1987
Oxygen	O_2	298	2.60×10^{-5}	Bretsznajder, 1971
Vinyl chloride	C_2H_3Cl	298	1.34×10^{-5}	Reid et al., 1987

[a]When two sources disagree by less than 5 percent, only one value is listed.

3.   Dispersion

Effect of dispersion on Pollutant conc. Downwind of a localized source

Slow dispersion   Rapid dispersion

Wind →   Wind →

Side view

Top view

Peak concentration high,   Peak concentration low,
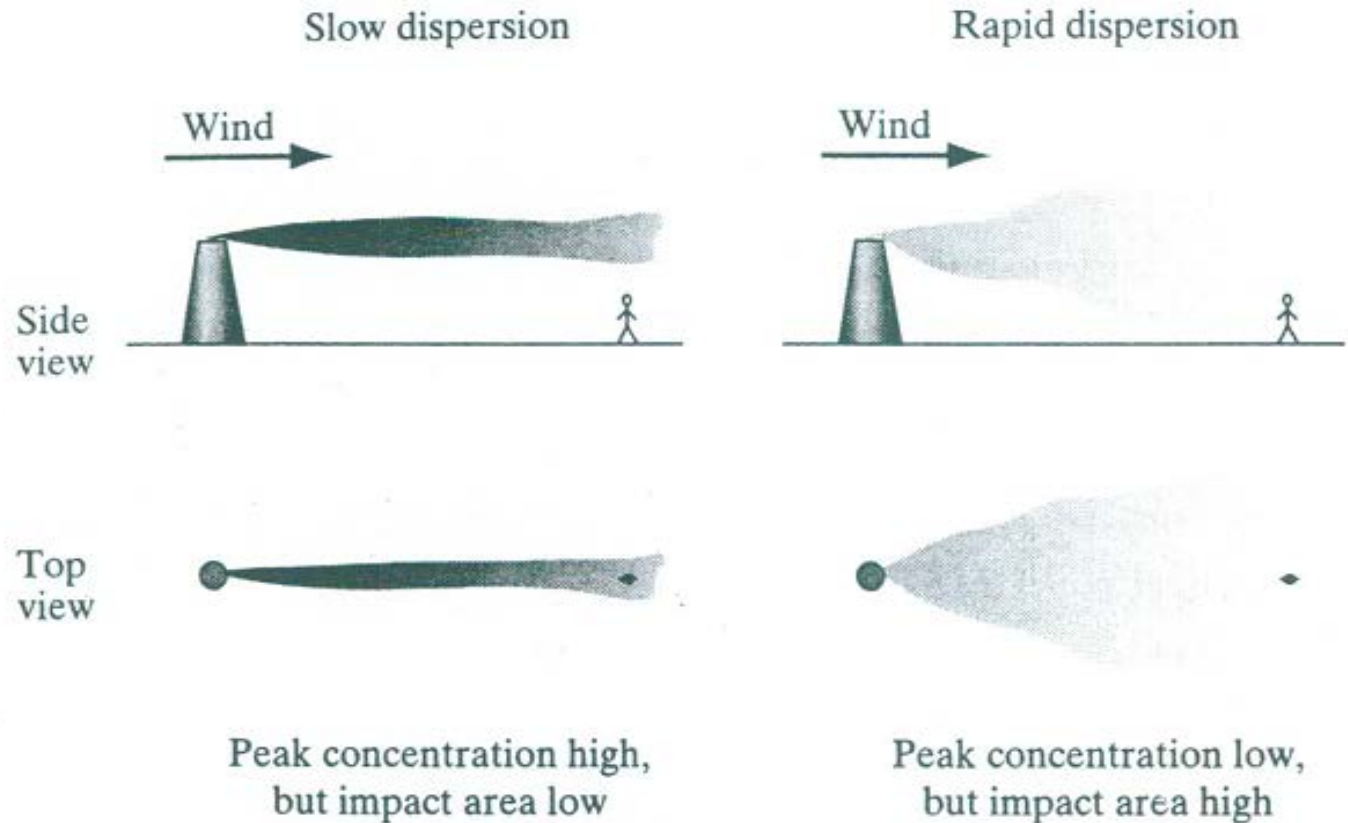but impact area low   but impact area high

Figure 4.A.5 Effect of dispersion on pollutant concentrations downwind of a localized source. If the release rate of pollutants and mean wind speed are the same in the left- and right-hand frames, then the total flow of pollutants is the same in the two cases. Rapid dispersion leads to smaller peak concentrations but a larger impact area.

Many atmospheric factors influence the way air pollution is dispersed, including wind direction and wind speed, type of terrain and heating effects.

Dispersion

- Spreading due to:

  - pore to pore variation in velocity

  - velocity variation within the pores

$$q_M = -D_M \frac{\partial c}{\partial x}$$

Concentration gradient

Mechanical dispersion coefficient

$$D_M = \alpha \cdot v_a$$

Pore velocity

Dispersivity

In complex flow fields, it is impossible (or at least impractical) to describe fluid velocity exactly as a function of space and time. Without this information, dispersion cannot be accurately described in terms of the fundamental mechanisms of advection and molecular diffusion. As an alternative, dispersion can be treated as a random process, analogous to molecular diffusion, by applying Fick's first law of diffusion with the molecular diffusion coefficient replaced by a dispersion coefficient. So in one dimension, we would write

$$J_{\text{dispersion}} = -\varepsilon \frac{dC}{dx} \qquad (4.A.10)$$

where ε is a *dispersion coefficient*, obtained through a combination of empirical data and theoretical equations.
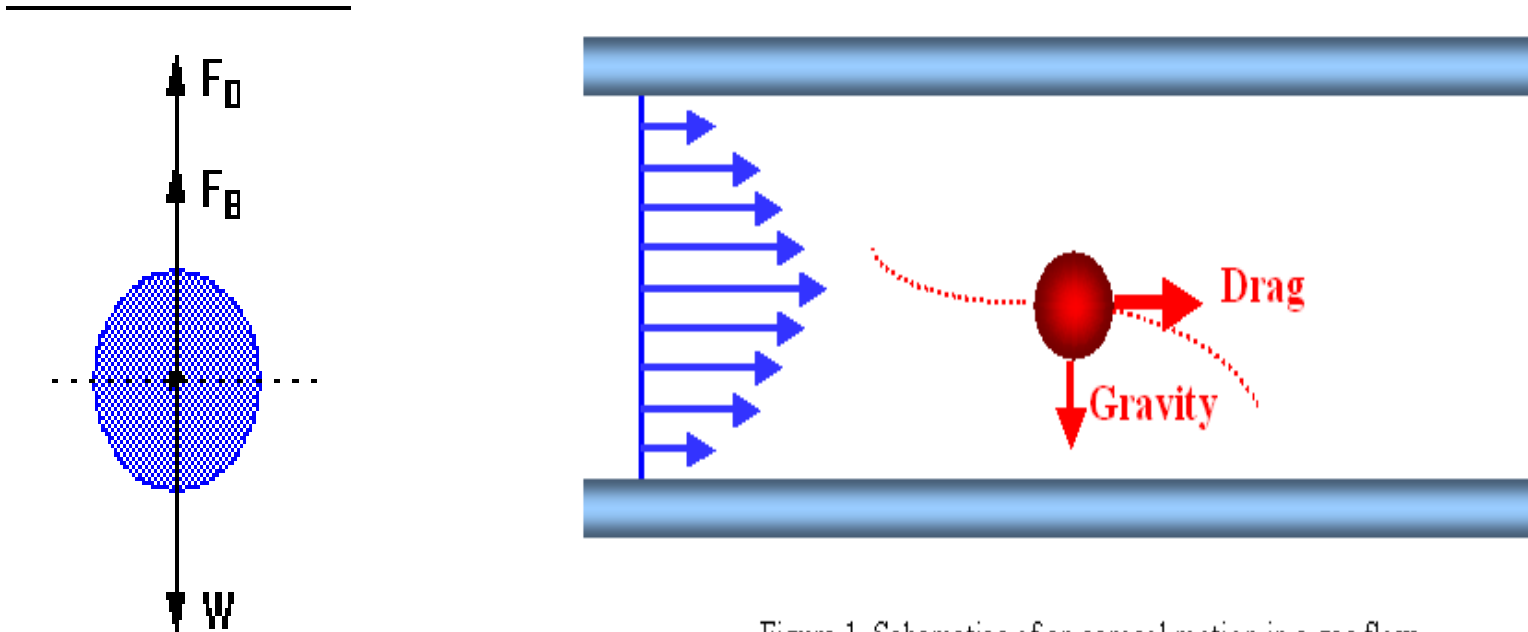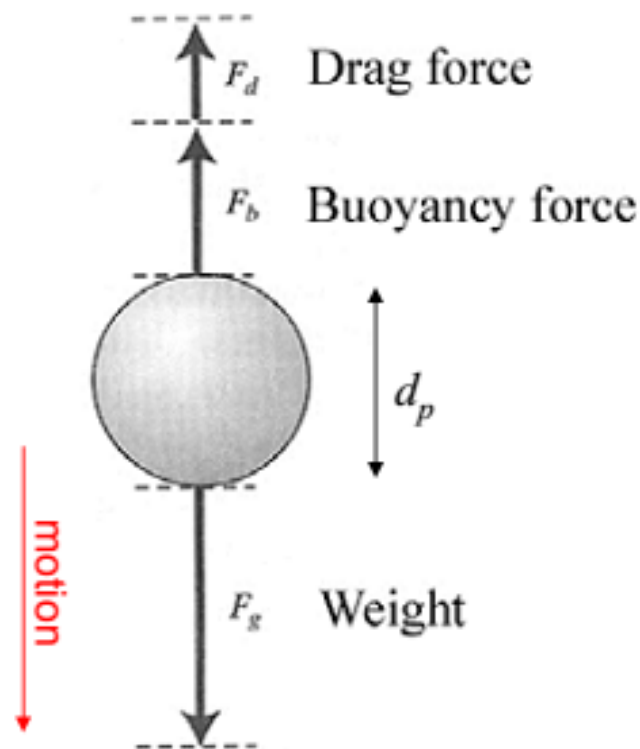
Particle Motion

Figure 1. Schematics of an aerosol motion in a gas flow.

Gravitational settling

(Nazaroff & Alvarez-Cohen, Section 4.B.2)

When moving relatively to a fluid,
a particle is subject to 3 forces:
- its own weight
- a buoyancy force
- a drag force.

After a brief period of acceleration,
A terminal velocity is reached, and
a balance is achieved between these 3 forces:

$$F_g = F_b + F_d$$

F_d Drag force

F_b Buoyancy force

d_p

motion

F_g Weight

weight of particle: $F_g = m_{\text{particle}}\, g = \rho_p \dfrac{\pi d_p^3}{6} g$

buoyancy force: $F_b = m_{\text{displaced fluid}}\, g = \rho_f \dfrac{\pi d_p^3}{6} g$

drag force: $F_d = C_d \dfrac{\pi}{4} d_p^2 \dfrac{1}{2} \rho_f V_p^2$

Note the difference: ρ_p = density of material making up the particle, ρ_f = fluid density.

Drag on Particles

Mechanisms that cause particle movement relative to a fluid are always opposed by drag force. The magnitude of the drag force increases as the particle velocity relative to the fluid increases. The drag force on a spherical particle is usually computed by the expression
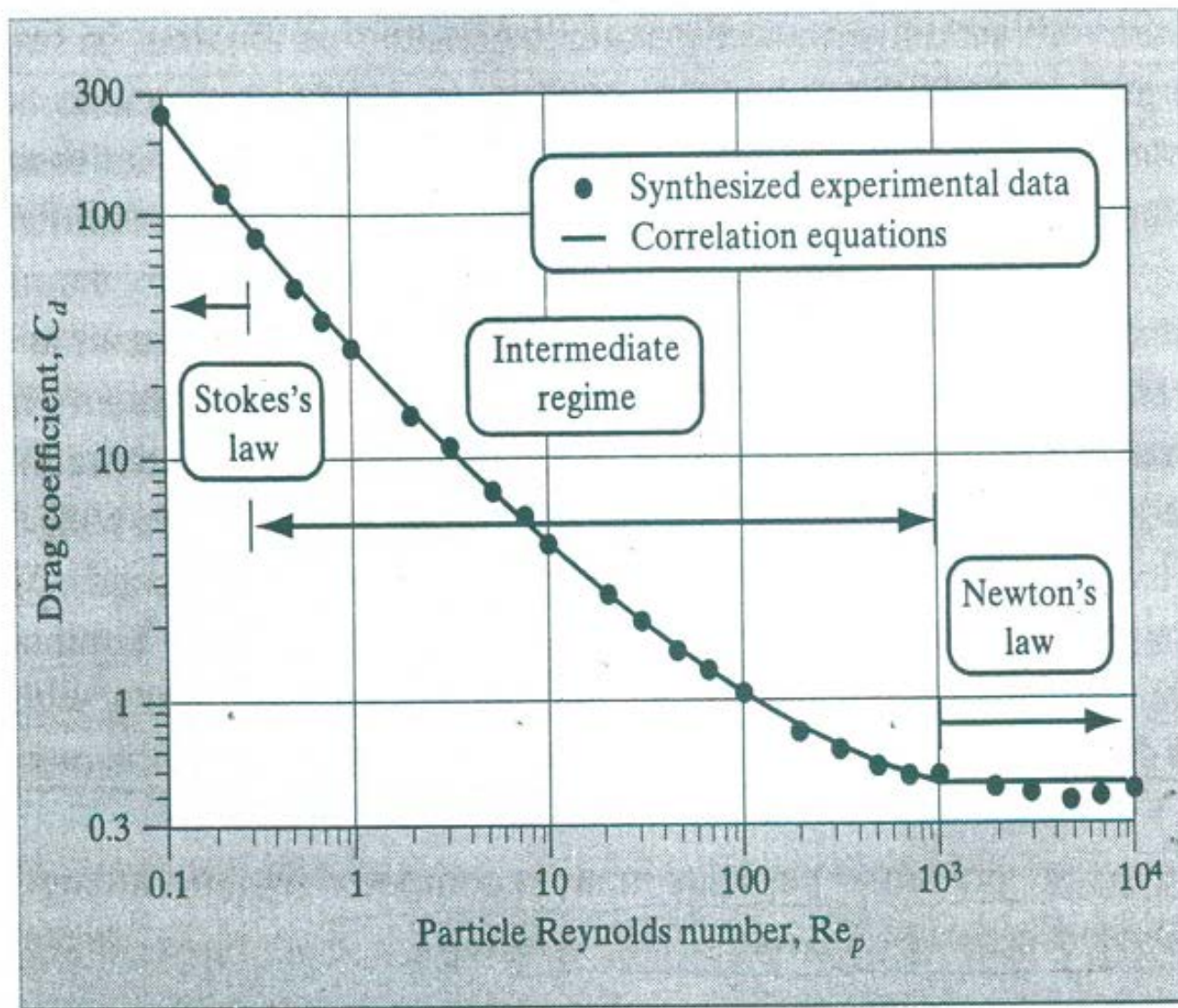
$$\checkmark \quad F_d = \left(\frac{\pi}{4}d_p^2\right)\left(\frac{1}{2}\rho_f V_\infty^2\right)C_d \tag{4.B.1}$$

where d_p represents particle diameter, ρ_f is the density of the fluid, V_∞ is the speed of the particle relative to the fluid, and C_d is the *drag coefficient*. As shown in Figure 4.B.1, the drag coefficient is a function of the Reynolds number of the particle, which is defined by

$$\checkmark \quad \mathrm{Re}_p = \frac{d_p V_\infty}{\nu} = \frac{d_p V_\infty \rho_f}{\mu} \tag{4.B.2}$$

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Reynold's number

- https://www.youtube.com/watch?v=Yv0RB71BQ_4

Figure 4.B.1 Drag coefficient as a function of particle Reynolds number for smooth, spherical, nonaccelerating particles in a uniform fluid flow. The experimental data are from Lapple and Shepherd (1940). The correlation equations are described in the text.

✱ Given a particle Reynolds number, we can determine the drag coefficient from the data in the figure, or from the following equations (Perry and Green, 1984):

$$C_d = \frac{24}{Re_p} \qquad\qquad Re_p < 0.3 \qquad\qquad \text{Stokes's law} \qquad (4.B.3)$$

$$C_d = \frac{24}{Re_p}(1 + 0.14\,Re_p^{0.7}) \quad 0.3 < Re_p < 1000 \qquad \text{Intermediate regime} \quad (4.B.4)$$

$$C_d = 0.445 \qquad\qquad 1000 < Re_p < 350,000 \quad \text{Newton's law} \qquad (4.B.5)$$

Two intrinsic properties of fluids contribute to drag: viscosity and density. When the particle Reynolds number is low (laminar flow, Stokes's law regime), the drag force depends only on viscosity, as can be seen by substituting equations 4.B.3 and 4.B.2 into 4.B.1:

$$F_d = 3\pi\mu d_p V_\infty \qquad Re_p < 0.3 \qquad\qquad (4.B.6)$$

As a particle moves through a stationary fluid, some fluid molecules are drawn along with the particle because of viscous interactions, causing drag. At low Re_p, this contribution dominates.

✱ At high particle Reynolds numbers, the drag force, as described by Newton's law, depends on the density of the fluid, but not on its viscosity.

$$F_d = 0.173\,\rho_f d_p^2 V_\infty^2 \qquad 1000 < Re_p < 350,000 \qquad\qquad (4.B.7)$$

Diffusivity of Particles in Air and Water

The Brownian diffusivity of particles is determined by an equation known as the *Stokes-Einstein relation*,

$$D = \frac{kT}{f} \tag{4.B.18}$$

where k is Boltzmann's constant (1.38×10^{-16} erg K^{-1}, where the erg is an energy unit equivalent to 1 g cm^2 s^{-2}), T is temperature (K), and f is the friction coefficient computed according to Stokes's law ($3\pi\mu d_p C_c^{-1}$), including the Cunningham slip correction factor if the particle is in air (equations 4.B.9–10). Example 4.B.3 illustrates the application of equation 4.B.18. Figure 4.B.6 shows the Brownian diffusivity of particles in air and water as a function of particle size. As the particles become very small, their diffusivities approach those of large molecules, ~0.1 cm^2 s^{-1} in air and ~10^{-5} cm^2 s^{-1} in

Meteorological Parameters

- Wind speed
- Wind direction
- Temperature

Modeling Approaches

- Two broad families of air pollution models are currently used: Statistical and Deterministic

1. **Statistical Models**:

   o They use tools from probability and statistics to <u>analyze measured pollutant concentrations</u>.

   o Their main **goal** is to make <u>near-term predictions</u>.

   o They tend to have large data requirements.

      E.g. It is used to answer the following question: Given predicted weather conditions tomorrow, what are the expected air pollutant levels?

   o **Advantage:** Require no more than a superficial knowledge of the underlying chemistry physics of air pollution.

   o **Limitation:** They are <u>incapable</u> of predicting the consequences of significantly changed conditions

2. **Deterministic Models:**

- o They are based on the <u>principle of material science</u> .

- *o* Their main aim is to describe the chain of <u>cause-and-effect processes</u> that link emissions from sources to concentrations at receptors.

- o They generally ***require*** information on meteorological conditions and pollutant emissions as ***input***.

- o They predict concentrations, taking account of the most important atmospheric transport and transformation processes.

They can be further divided into 2 main groups:

i) Gaussian Plume Models

ii) Transport and Transformation Models

i.   Gaussian Plume Models:

- o   They are used to <u>predict the relationship</u> between emissions from a <u>single</u> source (or small group of sources) and downwind concentrations.

- o   The greatest strength of this model is the ease of use.

- o   They are useful mainly for <u>source-oriented assessments</u> of pollutants emitted from localized sources.

- o   Their ***weakness*** include (a) some "leaps of faith" in deriving the models from first principles, (b) limited applicability in complex terrains, and (c) the <u>inability to accommodate any chemistry beyond first-order decay.</u>

ii.   Transport and Transformation Models:

- o   They generally predict species concentrations while taking into consideration <u>all important emission sources</u>.

- o   Whereas Gaussian plume models use approximate analytical solutions, they employ numerical methods to solve the governing equations.