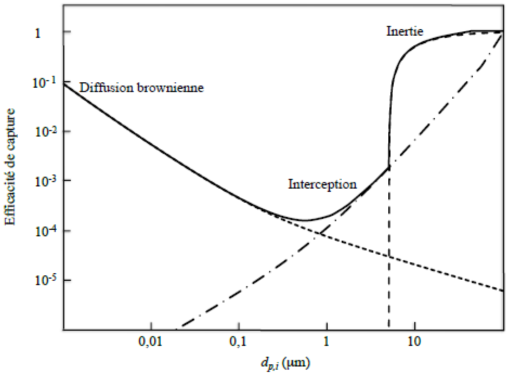
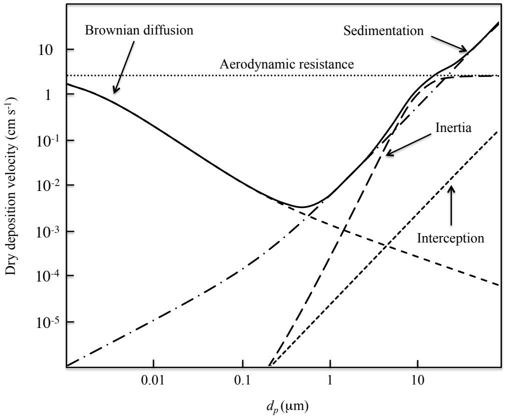
Transfer of Pollutants between the Atmosphere and Surfaces

- Dry deposition
- Wet deposition
- Reemissions and natural emissions
  - General considerations
  - Reemissions of particles by on-road traffic
  - Wind-blown dust
  - Sea-salt emissions





Atmospheric Dry Deposition

- Atmospheric dry deposition is defined as the transfer of mass from the atmosphere to surfaces by processes other than wet precipitation. It involves various processes:
  - Sedimentation
  - Diffusion toward a surface
  - Adsorption on a surface
  - Absorption (including dissolution) into a liquid film
  - Chemical reaction on a surface

Transfer from the Atmosphere to Surfaces

- The two fundamental processes are
  - Gravity: sedimentation of particles (dominant for coarse particles)
  - Various diffusion processes: combination of turbulent diffusion followed by molecular diffusion (for gases), brownian diffusion (for particles, dominant for ultrafine particles), and impacts by inertia and/or interception (for particles, dominant for fine particles)

Sedimentation

- The acceleration of a moving particle in the atmosphere is governed by two forces, which are gravity and the resistance of the air (friction).

$$m_p \frac{\mathrm{d}v_s}{\mathrm{d}t} = \underbrace{m_p\, g}_{\text{gravity}} - \underbrace{m_{air}\, g}_{\substack{\text{force of}\\ \text{Archimedes}}} - \underbrace{Fo_{St}}_{\text{friction (Stokes)}}$$

$m_p >> m_{air}$; therefore, the buoyancy force of Archimedes may be neglected

- When the friction of the particle against the air becomes commensurate with gravity, one obtains the fall velocity of the particle from the following equation:

$$\boxed{m_p\, g - Fo_{St} = 0}$$

Sedimentation

- For Re << 1 (particles), the particle sedimentation velocity is given by:

$$v_s^f = \frac{\rho_p \boxed{d_p^2} g \, c_c}{18 \, \mu_{\mathrm{v},a}}$$

where ρ_p is the particle density, $\mu_{\mathrm{v},a}$ is the dynamic viscosity of the air, d_p is the diameter of the particle, and c_c is the Cunningham correction factor, which is a function of the particle size.

- For fine particles, the sedimentation velocity decreases as the diameter decreases (proportional to the square of the diameter) and, therefore, becomes negligible for fine and ultrafine particles.

Sedimentation

- For Re >> 1 (raindrops; formula of Kessler, 1995 ; d_{gp} is in m and v_s^f in m/s):

$$\boxed{v_s^f = 130\sqrt{d_r}}$$

- For large coarse particles and raindrops, the terminal fall velocity increases with the diameter, but not proportionally because of the drag coefficient (c_D), which is a function of the particle/drop diameter. For raindrops, the fall velocity is approximately proportional to the square-root of the diameter.

Dry Deposition

- Dry deposition by diffusion processes is mostly function of the following characteristics:
  - Atmospheric turbulence: it determines the atmospheric flux that transfers the pollutant toward the surface.
  - The pollutant properties: solubility and chemical reactivity for gases; size, density, and shape for particles
  - The characteristics of the surface: wetness, roughness, reactivity, surface area, etc.

Diffusion

- Turbulent diffusion: it brings the pollutant in proximity of the surface.
- Diffusion in a laminar regime (i.e., near the surface, ~ a few mm):
  - Gases: molecular diffusion
  - Fine particles: brownian diffusion, impact by interception and/or inertia

Deposition on the Surface

- Particles: One typically assumes that the particles remains on the surface after contact, but a bouncing coefficient may be used.

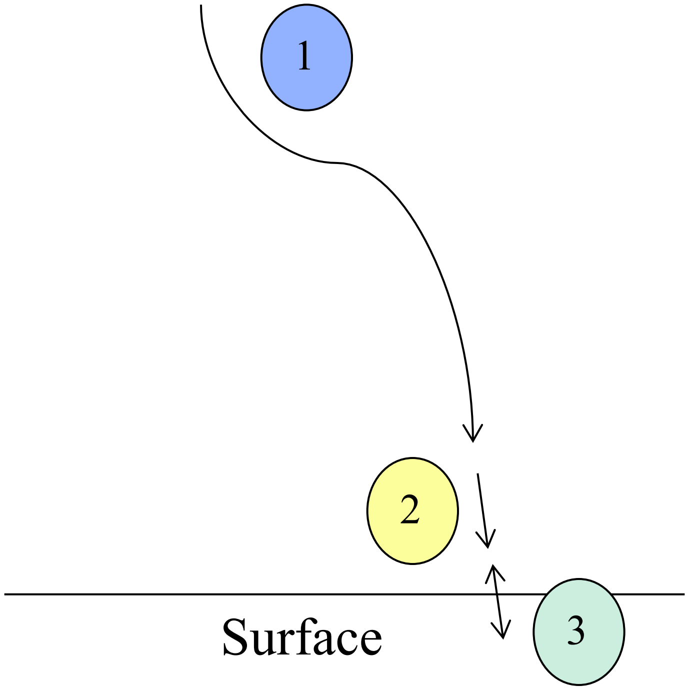
- Gases: The gas molecule deposits by adsorption, absorption (for example, dissolution in a liquid) or chemical reaction on the surface

Dry Deposition Processes

(1) Vertical turbulent transfer in the atmosphere

(2) Transfer by diffusion (molecular for gases, brownian for particles) in a very thin (a few millimeters) quasi-laminar layer above the surface

(3) Deposition by interception or inertia (for particles), adsorption, absorption or reaction (for gases)

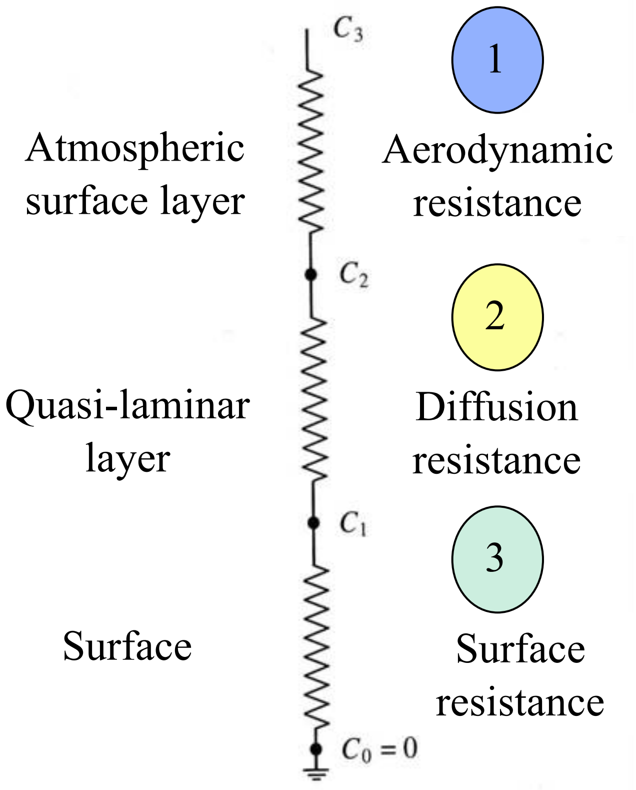


Resistance Approach

This approach for dry deposition by diffusion processes is based on an analogy with electrical resistances in series.

Each stage is represented by a resistance to the deposition process.

Resistances are expressed in units of s/cm and the inverse of the total resistance is the dry deposition velocity.



Atmospheric surface layer

1 Aerodynamic resistance

Quasi-laminar layer

2 Diffusion resistance

Surface

3 Surface resistance

Resistance Approach

The dry deposition flux, F_d (g m^{-2} s^{-1}), is defined as the product of a dry deposition velocity, v_d (m s^{-1}), and the pollutant concentration, C (g m^{-3})

$$F_d = v_d\,C$$

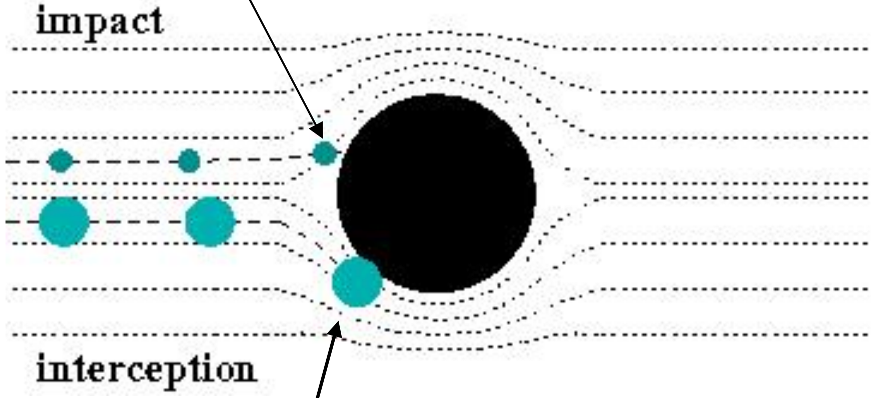
Gaseous pollutants: $1 / v_d = r_t = r_a + r_b + r_c$

Fine particles: $1 / v_d = r_t = r_a + r_b$

In this latter case, the sedimentation velocity is neglected and the surface resistance is considered to be zero (interception, inertia, and brownian diffusion are treated jointly in the diffusion resistance r_b)

Dry Deposition of Fine Particles

Impact by **inertia**: proportional to the mass of the particle, therefore, proportional to the volume (d_p^3) and particle density



Impact by **interception**: proportional to the cross-sectional surface area of the particle, i.e., d_p^2

Sedimentation + Deposition by Diffusion

Particles with a non-negligible sedimentation velocity (Venkatram and Pleim, 1999):

$$F_d = \underbrace{K\,\mathrm{d}C/\mathrm{d}z}_{\text{diffusion}} \;+\; \underbrace{v_s\,C}_{\text{sedimentaton}}$$

$$\boxed{v_d = \frac{v_s}{\left(1 - \exp\left(-r_t\, v_s\right)\right)}}$$

For a large coarse particle: $v_s >> 1/r_t \Rightarrow v_d = v_s$

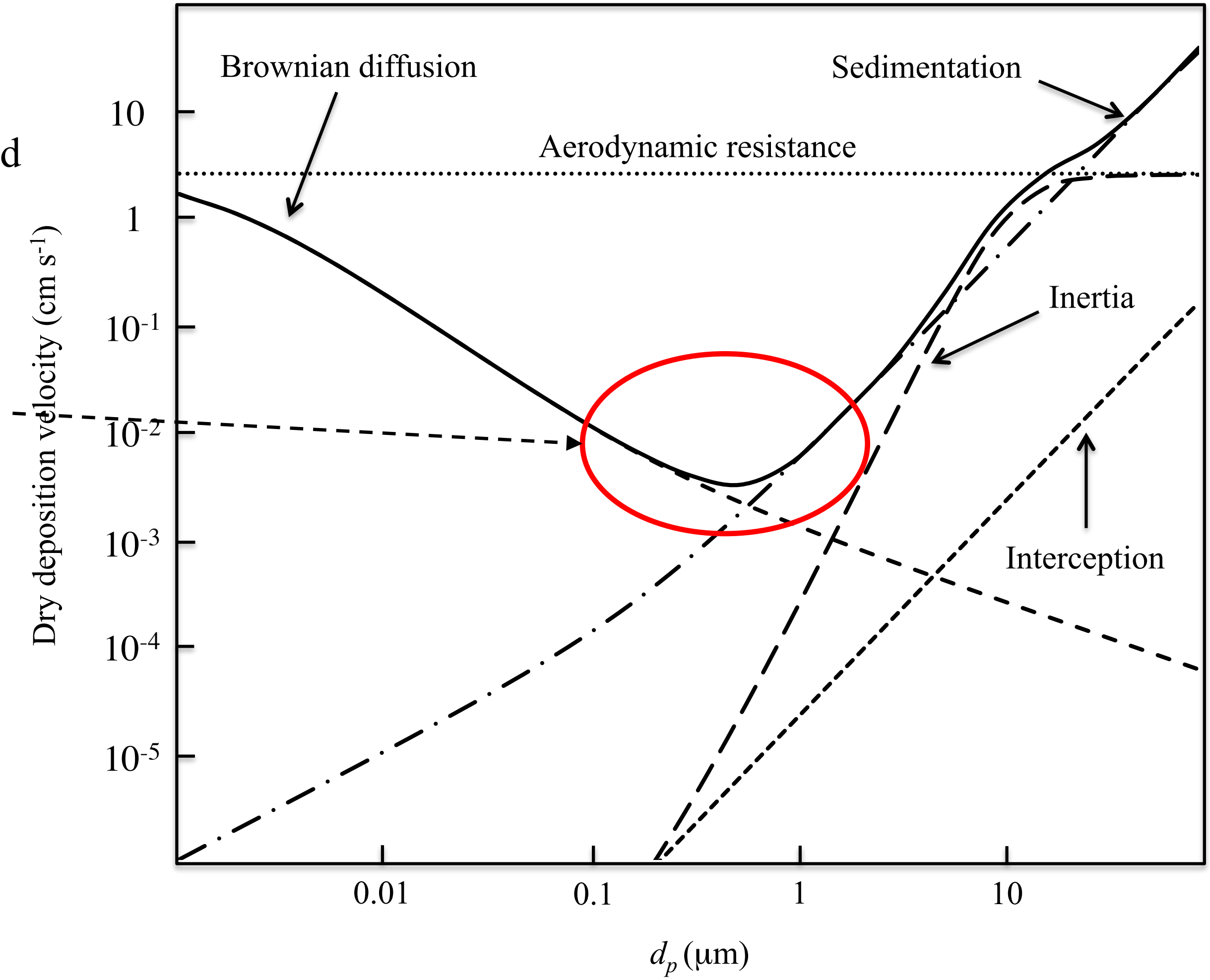
For a fine particle: $v_s << 1/r_t \Rightarrow v_d = 1/r_t$

Dry Deposition of Particles

The dry deposition velocities of particles depend on
(1) meteorological conditions and surface characteristics and
(2) particle size.

Fine particles (i.e., those with a diameter between 0.1 and 1 μm have the lowest dry deposition velocities.

The sedimentation velocity is important only for large coarse particles.



Reduction of Particulate Emissions by Filtration

Particle filters (e.g., baghouses, diesel particle filters) collect particles using the same processes as those involved in atmospheric processes: impact by inertia and interception, brownian diffusion.

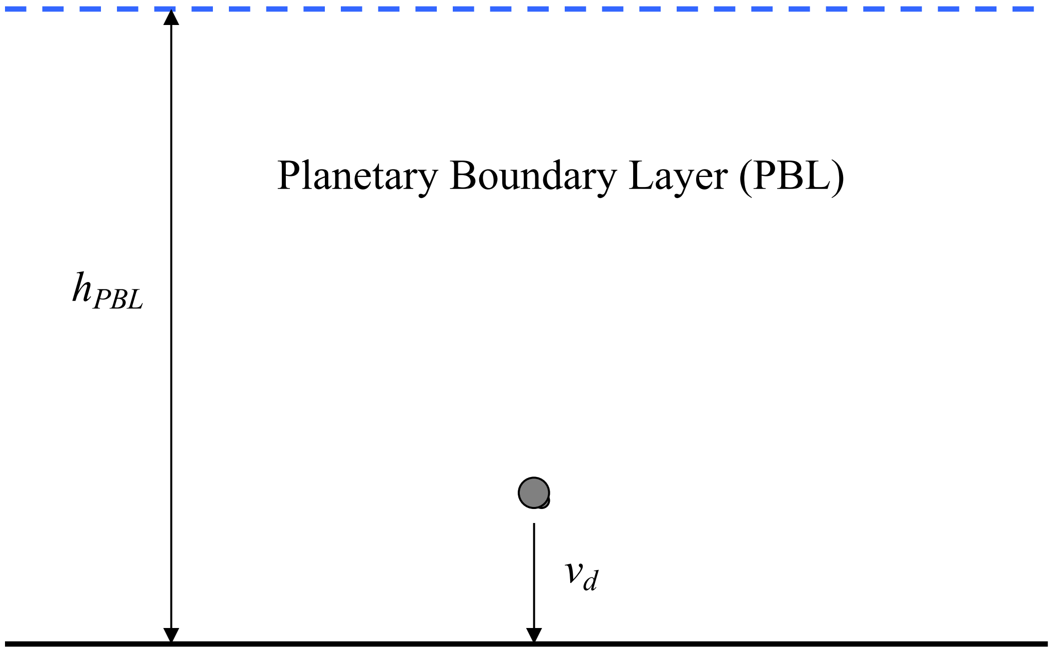
In electrostatic precipitators (ESP), electrostatic forces play the major role.

Inhalation of Particles
Influence of Particle Size

The same deposition processes as those taking place in the atmosphere occur in the respiratory tract: therefore, particles with a diameter between 0.1 and 1 μm penetrate the deepest into the lungs.

However, ultrafine particles (those with a diameter less than 0.1 μm) have a greater probability to deposit within the lungs than fine particles (i.e., those with a diameter greater than 0.1 μm).

Dry Deposition
Mass Balance within the Planetary Boundary Layer



Dry deposition flux:

$$F_d = v_d\, C$$

Change with time of the concentration within the boundary layer:

$$dC/dt = -\, v_d\, C / h_{PBL}$$

$$\boxed{C = C_0 \exp(-\,(v_d / h_{PBL})\, t)}$$

Atmospheric Wet Deposition

- Wet deposition may be defined as the transfer of mass from the atmosphere to surfaces via precipitation:
  - Rain
  - Snow
  - Hail
  - Fog settling
  - Mountain cloud impact

Pollutant Scavenging

- The two fundamental processes are:
  - The scavenging of gaseous and particulate pollutants within the cloud: rainout
  - The scavenging of gaseous and particulate pollutants by raindrops below the cloud base: washout

Wet Deposition Flux
Scavenging of Pollutants below the Cloud

The change with time of the concentration of an atmospheric pollutant (gas or particle) due to precipitation scavenging is as follows:

$$C(t) = C_0 \exp(- \Lambda\, t)$$

where C_0 is the pollutant concentration at the beginning of the precipitation event.

The wet deposition flux is given by the following expression:

$$\boxed{F_w(t) = C(t)\, \Lambda\, h_c}$$

where h_c is the height of the cloud base above ground level (i.e., the height of the air column scavenged by precipitation).

Scavenging Coefficient of Gaseous Pollutants

- The scavenging coeffiient depends on precipitation intensity:

$$\boxed{\Lambda = (6\, k_m\, I_p) / (d_r\, v_{s,r})}$$

I_p: precipitation intensity; $(\pi/6)\, d_r^3\, v_{s,r}^f\, N_{rp}$
d_r: raindrop diameter
$V_{s,r}$: fall velocity of raindrops
N_{gp}: number of raindrops per unit volume of air for that precipitation event
k_m: mas transfer coefficient of the gaseous pollutant in the air

However, precipitation intensity depends on raindrop size and the mass transfer coefficient also depends on raindrop size. Therefore, the scavenging coefficient is less than proportional to precipitation intensity.

Wet Deposition Flux
Scavenging Coefficient of Nitric Acid

Precipitation intensity	1 mm/h	5 mm/h	10 mm/h	20 mm/h
HNO_3	5×10^{-5} s^{-1}	1.5×10^{-4} s^{-1}	2×10^{-4} s^{-1}	3.5×10^{-4} s^{-1}

Wet Deposition of Particles

- Scavenging of fine particles occurs via various processes:

  Within the cloud:

    - formation of cloud droplets from atmospheric particles (Aïtken nucleation particles and fine particles)
    - collision of particles with cloud droplets

  Below the cloud:

    - scavenging by collision of particles with raindrops

Scavenging Coefficient of Particles

The scavenging coefficient is as follows:

$$\boxed{\Lambda = (3/2)\, I_p\, E(d_r, d_p) / d_r}$$

I_p: precipitation intensity ; $(\pi/6)\, d_r^3\, v_{s,r}^f\, N_{rp}$

d_r: raindrop diameter

d_p: particle diameter

$V_{s,r}$: fall velocity of the raindrop

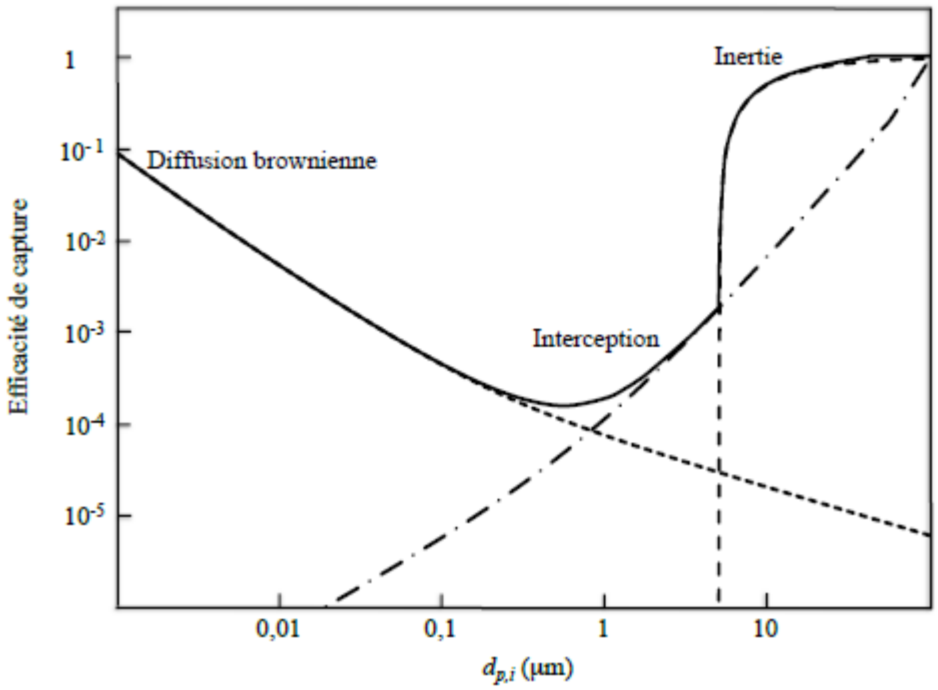
$E(d_r, d_p)$: collision efficiency of particles and raindrops (<1)

N_{rp}: number of raindrops per unit volume of air for that precipitation event

However, precipitation intensity depends on raindrop size and the collision efficiency depends also on raindrop size. Therefore, the scavenging coefficient is less than proportional to precipitation intensity.

Scavenging Coefficient of Particles

Collision efficiency of raindrops and particles



Brownian diffusion dominates for ultrafine particles, i.e. those particles of diameter < 0.1 μm.

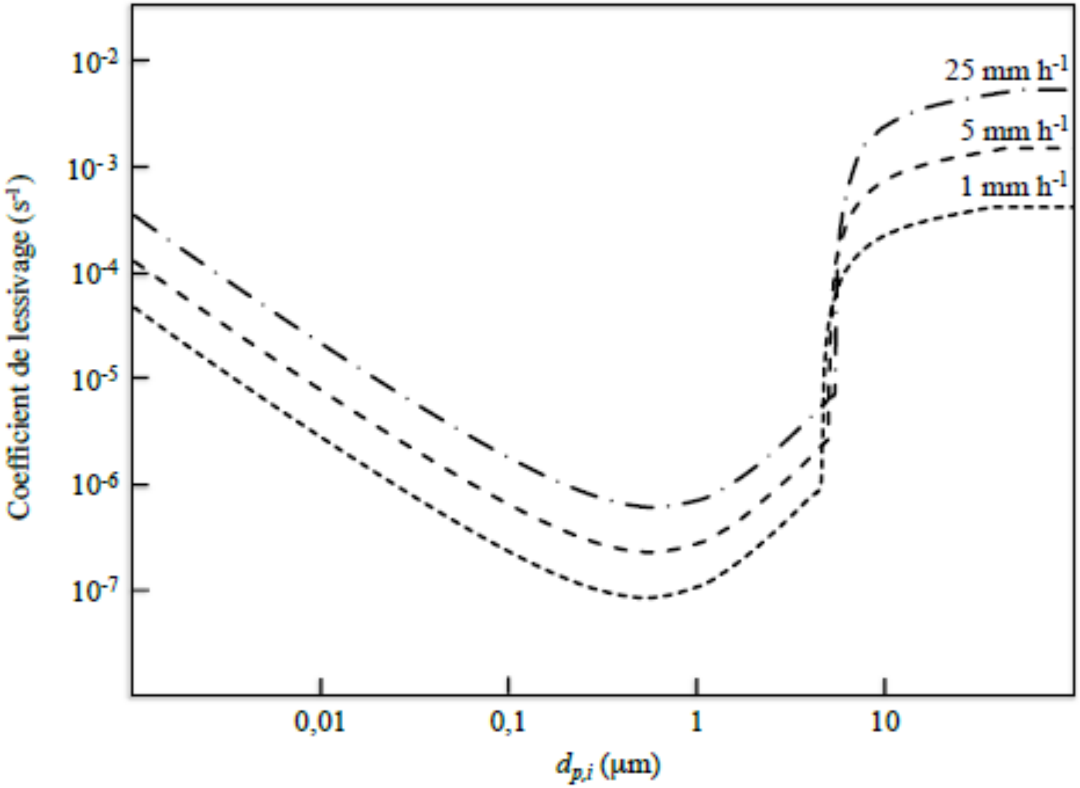
Interception becomes important for fine particles with diameter in the range of 0.1 to 2.5 μm and coarse particles up to 5 μm diameter.

Inertia dominates for coarse particles with diameter > 5 μm.

The collision efficiency tends toward 1 for particles of diameter > 10 μm.

Scavenging Coefficient of Particles

- Example of scavenging coefficients for particles (precipitation intensity between 1. 5 and 25 mm/h)



Scavenging Coefficients

Precipitation intensity	1 mm/h	5 mm/h	10 mm/h	20 mm/h
HNO_3	5×10^{-5} s^{-1}	1.5×10^{-4} s^{-1}	2×10^{-4} s^{-1}	3.5×10^{-4} s^{-1}
Fine particles (diameter = 2.5 μm)	3×10^{-7} s^{-1}	8×10^{-7} s^{-1}	1×10^{-6} s^{-1}	2×10^{-6} s^{-1}

Dry and Wet Deposition

- Wet deposition occurs intermittently (mostly when it rains); it rains only 2 to 5 % of the time in the mid-latitudes.

- Dry deposition occurs all the time; however, the dry deposition flux is typically smaller (per unit time) than the wet deposition flux when it rains.

- Wet deposition affects the entire atmospheric column below cloud base.

- Dry deposition affects mostly the pollutants located near the surface (typically within the mixing layer) and it is more efficient in areas with complex surfaces (e.g., vegetation, built areas).

Reemissions and Natural Emissions

- Reemissions
  - Grasshopper effect
  - Resuspension of particles by on-road traffic

- Wind-driven natural emissions
  - Wind-blown dust
  - Sea-salt emissions

Grasshopper Effect

- Semi-volatile pollutants such as persistent organic pollutants (POP) have a volatility that varies with temperature. They will deposit more readily when the temperature is low as they are mostly present in the particulate phase. When the ambient temperature increases, their gas/particle partitioning will tend to shift toward the gas phase and they will be reemitted as gases.
- A succession of deposition and reemission steps of a semi-volatile pollutant is called the "grasshopper effect", because the pollutant may be transported over long distances (several thousands of kilometers) via a series of deposition/reemission "hops".
- The reemission of a pollutant may also occur following a chemical transformation; e.g., N_2O from soils and Hg^0 from soils and water bodies.

Resuspension of Particles by On-road Traffic

- Vehicles leads to resuspension of particles present on the roadway.
- One assumes that the majority of this particulate mass deposited on the roadway consists of coarse particles resulting from wear of brake-pads, tires, and road surface.
- The NORTRIP model (Denbigh et al., 2013) uses a mass balance based on deposition of particles on the roadway and resuspension of particles by traffic:

$$\boxed{\frac{\mathrm{d}M_{l,r}}{\mathrm{d}t} = F_{l,r} - S_{l,r}}$$

$M_{l,r}$: Mass of particles on the roadway per unit length

$F_{l,r}$: Deposition rate particles onto the roadway per unit length

$S_{l,r}$: Resuspension rate of particles from the roadway per unit length and runoff of particles during rain events

Resuspension of Particles by On-road Traffic

- The resuspension rate of particles from the roadway, $S_{l,r}$, is proportional to the particulate mass present on the roadway, $M_{l,r}$, the number and type of vehicles (trucks, passenger cars) travelling on the roadway, and the fraction of particles resuspended per vehicle (a function of vehicle type, vehicle speed, and moisture on the road).

$$\boxed{S_{l,r} = M_{l,r} \sum_{v=1}^{2} N_v f_v(v_v)}$$

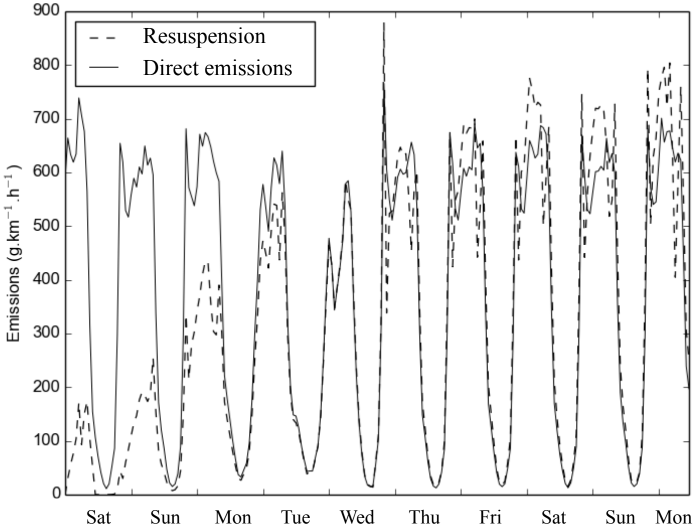
N_v: Number of vehicles of type v travelling per unit time

f_v: Fraction of particles resuspended per vehicle

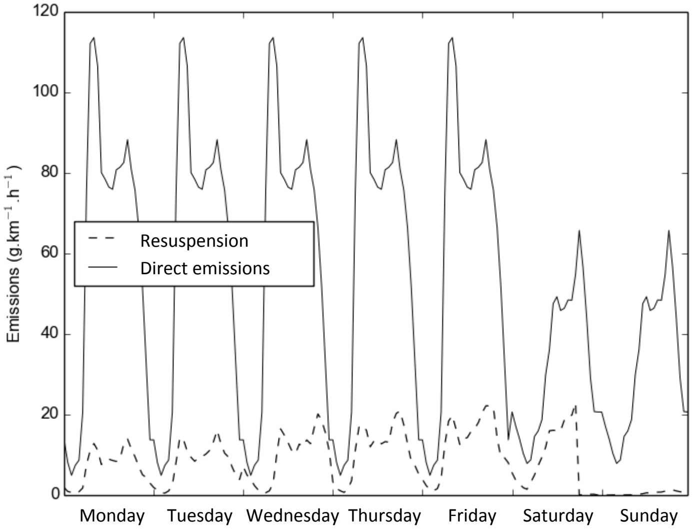
v_v: Vehicle speed

Resuspension of Particles by On-road Traffic

Comparison of direct particle emissions from vehicles and particle resuspension by traffic



Urban freeway
$v_v = 69 \text{ km h}^{-1}$
dry conditions



Suburban boulevard
$v_v = 32 \text{ km h}^{-1}$
wet conditions

Source: adapted from Thouron, 2017

Wind-blown Dust

- Resuspension of particles from an erodible surface by wind erosion (aeolian resuspension) may contribute significantly to atmospheric particle concentrations and these particles may be transported over long distances.

- The aeolian resuspension process consists first in a hydrodynamic lifting of particles available at the surface. These particles may subsequently deposit back to the surface, especially if they are large particles. This saltation leads to impacts of particles on the surface and generates smaller particles, which become available for resuspension.

Wind-blown Dust

- The vertical flux of particles resuspended by wind erosion, F_e, may be calculated according the expression developed by Kok et al. (2011), based on a literature review of theory and experimental data.
- An upper limit of the resuspension vertical flux may be estimated for fine particles as follows:

$$\boxed{F_e = 4.4\,\mathrm{x}\,10^{-5}\, f_{er}\, f_{clay}\, \frac{\rho_a\,(u_*^2 - u_{*t}^2)}{u_{*st}}}$$

f_{er}: erodible fraction of the soil

f_{clay}: clay fraction of the soil

ρ_a: density of the air

u_*: friction velocity

u_{*t}: threshold friction velocity for soil erosion

u_{*st}: threshold friction velocity at standard conditions

Sea-salt Emissions

- Sea and ocean waves lead to the formation of sea salt droplets in suspension in the air. The evaporation of those droplets may lead to the formation of sea salt aerosol particles. Wave formation depends strongly on wind speed.

- Different processes are involved in the formation of sea salt droplets. Fine particles ($d_p < 1$ mm) result from he bursting of bubbles. Other processes lead to the formation of larger particles that settled back rapidly to the sea surface.

- Sea salt particle formation may be important and may affect PM concentrations in coastal areas.

Sea-salt Emissions

- Monahan et al. (1986) have developed one of the first algorithms that have been widely used to simulate sea salt particle formation. The emission flux may be written as the density function of the particle vertical flux emitted from the sea surface, F_s, as a function of particle diameter.

$$\boxed{\frac{\mathrm{d}F_s}{\mathrm{d}d_p} = \mathrm{function}(u_{10},\ d_p,\ T_{ss},\ s_s)}$$

u_{10}: wind speed at 10 m

d_p: sea-salt particle diameter

T_{ss}: sea surface temperature

s_s: salinity