## **Atmospheric Particles**

- General considerations on atmospheric particles
- Dynamics of atmospheric particles
- Equilibrium thermodynamics
- Secondary inorganic fraction of particulate matter
- Organic fraction of particulate matter
- Emission control strategies
- Case studies



## Photochemical "Smog"

"Smog": Smoke + fog

Pollutants + solar radiation => **photochemical** pollution

Photochemical smog:

- Gaseous pollutants (ozone, nitrogen dioxide, formaldehyde, acroleine ...)

- Particles

## **Atmospheric Particles**

- Atmospheric particles are solid or liquid particles (or a combination of a solid core with a liquid coating) in suspension in the air
- Particles and the surrounding gas phase are called aerosols
- An ensemble of atmospheric particles is generally called PM for "Particulate Matter"
- Particles vary in size, chemical composition, and shape

## **Atmospheric Particles**

- Some particles are emitted directly into the atmosphere as particles (soot, soil dust, sand, sea salt, pollen...): these are **primary particles**.
- Some particles (or fractions of particles) are formed by chemical reaction in the atmosphere from gases (sulfate, nitrate, ammonium, organic compounds...); these reactions can occur in the gas phase or in the aqueous phase: these are secondary particles or **secondary PM**.
- A particle may include a primary core and a secondary coating.

## **Atmospheric Particles: Chemical Composition**



Data source: Source apportionment of airborne particles in the Île-de-France region, AIRPARIF, 2011.

#### **Atmospheric Particles: Chemical Composition**



Data source: Wang et al., 2015; Dumka et al., 2017

## **Atmospheric Particles: Size and Shape**

Atmospheric particles may have various sizes and shapes

- Primary particles, such as soot, dust, and sea salt typically have a fractal shape
- Secondary liquid particles typically have a spherical shape

## **Regulations for Atmospheric Particles**

USA	TSP	$PM_{10}$	PM <sub>2,5</sub>	PM <sub>0,1</sub> ?
	1970	1987	1997	
Europe	Black	smoke	PM <sub>10</sub>	PM <sub>2,5</sub> PM <sub>0,1</sub> ??
	1980		1999	2008

TSP: Total suspended particulates

Black smoke: Soot particles

 $PM_{10}$ : Particulate matter with an aerodynamic diameter equal to or less than 10  $\mu$ m  $PM_{2.5}$ : Particulate matter with an aerodynamic diameter equal to or less than 2.5  $\mu$ m  $PM_{0.1}$ : Particulate matter with an aerodynamic diameter equal to or less than 0.1  $\mu$ m

## **Atmospheric Particles**

- Some particles (or fractions of particles) are formed by **chemical reaction** in the atmosphere from gases (sulfate, nitrate, ammonium, organic compounds...); these reactions can occur in the gas phase or **in the aqueous phase**: these are secondary particles or secondary PM.
- If the cloud evaporates, then some of the droplet chemical species form an atmospheric particle.

Size distribution of particle volume (or mass) and number concentrations

Assumptions: Mass concentration:  $M_p = 1 \ \mu g/m^3$ ; particle density:  $\rho_p = 1 \ g/cm^3$ :

Volume concentration:  $V_p = M_p / \rho_p = 1 \ \mu g/m^3 / (10^{-6} \ \mu g/\mu m^3) = 10^6 \ \mu m^3/m^3$ 

Number concentration:  $N_p = V_p / v_p$ ;  $v_p = \pi d_p^3 / 6$ ;  $v_p$  and  $d_p$  are the volume and diameter of a single particle.

For 
$$d_p = 0.5 \ \mu\text{m}$$
:  $N_p = 6 \ \text{x} \ 10^6 \ / \ (\pi \ 0.5^3) = 1.5 \ \text{x} \ 10^7 \ \text{particles/m}^3$ 

For 
$$d_p = 0.05 \ \mu\text{m}$$
 :  $N_p = 6 \ \text{x} \ 10^6 \ (\pi \ 0.05^3) = 1.5 \ \text{x} \ 10^{10} \ \text{particles/m}^3$ 

Distribution of the number concentration of particles as a function of size



Diameter (µm)

Distribution of the mass or volume concentration of particles as a function of size



 $PM_{10}$ : Mass concentration of PM with an aerodynamic diameter equal to or less than 10  $\mu$ m  $PM_{2.5}$ : Mass concentration of PM with an aerodynamic diameter equal to or less than 2.5  $\mu$ m



#### **The General Dynamic Equation**



Change in the particle number concentration,  $n(v_p)$ , as a function of time, t

#### Nucleation

$$J_n = 1.6 \,\mathrm{x} \, 10^{-14} \, \left( N_{H_2 SO_4} \right)^2$$

The nucleation rate depends on the saturation vapor pressure of the gas molecules that nucleate to create a new particle.



#### Nucleation

Nucleation increases the number (a lot) and the mass (little) of particles in the atmosphere.



$$\frac{\partial n_p(v_p)}{\partial t} = -\frac{\partial I_v n_p(v_p)}{\partial v_p}$$
$$I_v = \frac{\mathrm{d}v_p}{\mathrm{d}t}$$

 $I_v$  is the growth rate of a particle of volume v (or the shrinkage rate due to evaporation if negative).



## **Condensation / Evaporation Continuum Regime (Large Particles)**

$$\frac{\mathrm{d}v_p}{\mathrm{d}t} = \pi \, d_p^2 \, \frac{2D_m}{d_p} \, v_m \left( C_s - C_{g,e} \right) = 2 \, \pi \, d_p \, D_m \, v_m \left( C_s - C_{g,e} \right)$$

 $v_p$ : volume of the particle

 $d_p$ : diameter of the particle

*t*: time

 $D_m$ : diffusion coefficient of the molecule in the air

 $v_m$ : volume of a molecule

 $C_g$ : concentration of the condensing gas

 $C_{g'e}$ : concentration of the gas at thermodynamic equilibrium at the particle surface

The growth rate of the particle volume by condensation is proportional to the diffusion rate  $(2 D_m/d_p)$ , the particle surface area  $(\pi d_p^2)$ , and the concentration gradient of the condensing gas molecules.

## **Condensation / Evaporation Free Molecular Regime (Ultrafine Particles)**

$$\frac{\mathrm{d}v_p}{\mathrm{d}t} = \frac{\pi}{4} d_p^2 \left(\frac{8k_B T}{\pi m_g}\right)^{\frac{1}{2}} v_m \left(C_g - C_{g,e}\right)$$

 $v_p$ : volume of the particle

*t*: time

 $C_g$ : concentration of the condensing gas molecules

 $C_{g,e}$ : concentration of the gas at thermodynamic equilibrium at the particle surface

 $v_m$ : volume of a molecule

 $m_g$ : mass a of a gas molecule

*k*<sub>*B*</sub>: Boltzmann constant

T: temperature

The growth rate of the particle volume by condensation of gas molecules is proportional to the thermal velocity of the gas molecules  $[\overline{c} = 1.6 \ (k_B T/m_g)^{1/2}]$ , the particle cross-sectional surface area; and the concentration gradient of the condensing gas molecules.

## **Condensation / Evaporation Transition Regime (Fine Particles)**

$$\frac{\mathrm{d}v_p}{\mathrm{d}t} = \frac{2\pi d_p D_m}{1 + \left(\frac{1.33\mathrm{Kn} + 0.71}{1 + \mathrm{Kn}}\right)\mathrm{Kn}} v_m \left(C_g - C_{g,e} \exp\left(\frac{4\sigma_p v_m}{d_p k_B T}\right)\right)$$
  

$$\sigma_p: \text{ surface tension } v_m: \text{ volume of a molecule } Kelvin \text{ effect } k_B: \text{ Boltzmann constant } T: \text{ temperature } \mathrm{Kn} = 2 \ \lambda / d_p: \mathrm{Knudsen number}$$
  

$$\lambda: \text{ mean free path in the air }$$

The growth rate of the particle volume is given by the Fuchs-Sutugin equation, which is proportional to  $d_p$  when  $d_p > 2 \lambda$  (continuum regime) and proportional to  $d_p^2$  when  $d_p < 2 \lambda$  (free molecular regime).

The exponential term represents the Kelvin effect, which leads to a partial pressure at equilibrium that is greater for a curved surface than for a flat surface.

## Condensation / Evaporation Growth Law for One Particle of Size $d_p$

Condensation of 1 ppb of sulfuric acid



## **Condensation / Evaporation Condensation Rate on a Population of Particles**



Condensation increases particulate mass in the accumulation mode; i.e., the fine particle mass.





The Kelvin effect is important for ultrafine particles because gases cannot condense on the smallest ultrafine particles.

Condensation and evaporation conserve the number of particles.

Condensation increases the total mass of particles.

Evaporation decreases the total mass of particles.



## Coagulation

$$\frac{\mathrm{d}n_p(v_p)}{\mathrm{d}t} = \frac{1}{2} \int_0^{v_p} \beta(v_p', v_p - v_p') n_p(v_p') n_p(v_p - v_p') \mathrm{d}v_p' - \int_0^\infty \beta(v_p, v_p') n_p(v_p) n_p(v_p') \mathrm{d}v_p'$$

 $\beta(v, v')$  is the coagulation coefficient between two particles of volumes v and v', respectively.



## **Coagulation Continuum Regime (Large Particles)**

$$\beta(v_{p,i}, v_{p,j}) = 2\pi (D_{p,i} + D_{p,j}) (d_{p,i} + d_{p,j})$$

 $v_{p,i}$ : volume of particle *i*  $D_{p,i}$ : coefficient of diffusion of particle *i* in air  $d_{p,i}$ : radius of particle *i* 

In the continuum regime, the coagulation coefficient is proportional to the diffusion velocity  $(2 (D_{p,i} + D_{p,j}) / (d_{p,i} + d_{p,j}))$ and the cross-section area of the two particles  $(\pi (d_{p,i} + d_{p,j})^2)$ .

## **Coagulation Free Molecular Regime (Ultrafine Particles)**

$$\beta(v_{p,i}, v_{p,j}) = \frac{\pi}{4} \left( \overline{c}_{t,i}^2 + \overline{c}_{t,j}^2 \right)^{1/2} \left( d_{p,i} + d_{p,j} \right)^2$$

 $v_{p,i}$ : volume of particle *i*  $d_{p,i}$ : diameter of particle *i*  $c_{t,i}$ : mean thermal speed of particle *i* 

In the free molecular regime, the coagulation coefficient is given by the kinetic theory of gases; it is proportional to the thermal velocity of the particles and the cross-sectional area of the two particles.

## **Coagulation Transition Regime (Fine Particles)**

$$\beta(v_{p,i}, v_{p,j}) = \frac{2\pi \left(D_{p,i} + D_{p,j}\right) \left(d_{p,i} + d_{p,j}\right)}{\left[\frac{d_{p,i} + d_{p,j}}{d_{p,i} + d_{p,j} + 2\left(g_i^2 + g_j^2\right)^{1/2}} + \frac{8\left(D_{p,i} + D_{p,j}\right)}{\left(\overline{c}_{t,i}^2 + \overline{c}_{t,j}^2\right)^{1/2} \left(d_{p,i} + d_{p,j}\right)}\right]}$$

 $v_{p,i}$ : volume of particle *i*  $D_{p,i}$ : coefficient of diffusion of particle *i* in air  $d_{p,i}$ : diameter of particle *i*  $g_i$ : coefficient function of the diameter of particle *i* and of the free mean path of particles in the air

 $\overline{c_{t,i}}$ : mean thermal speed of particle *i* 

The coagulation coefficient is given by the Fuchs equation, which tends toward the continuum regime solution when  $d_p > 2 \lambda$  and the free molecular regime solution when  $d_p < 2 \lambda$  (where  $\lambda$  is the mean free path of the air).

#### **Coagulation Rate between Two Particles**



The Brownian coagulation rate is minimum for particles with the same size  $d_p$ .

Ultrafine particles will coagulate preferentially with larger particles.

Continuum regime

# **Coagulation Rates of a Particle with a Population of Particles**



Given a particle population in the atmosphere, the coagulation rate of a single particle depends on:(1) its coagulation rate with other particles(2) the number of those other particles



## Coagulation

Coagulation increases particulate mass in the accumulation mode; i.e., the fine particle mass.



## Coagulation

Coagulation decreases the number of particles.

Coagulation conserves the total mass of particles.



## **Deposition of Particles**



- Coarse particles deposit more easily on surfaces than particles in the 0.1 to 1 micron range.

- Ultrafine particles deposit more easily on surfaces than particles in the 0.1 to 1 micron range.

## **Sources and Deposition of Particles**

Emissions increase the number and the mass of particles in the atmosphere.

Nucleation increases the number and the mass of particles in the atmosphere.

Deposition decreases the number and the mass of particles.

#### **Representation of the Particle Size Distribution**


#### Log-normal Representation of the Size Distribution

Log-normal representation of the number concentration for a mode

$$\eta_{p,a}(d_p) = \frac{N_a}{\left(2\pi\right)^{1/2}\log(\sigma_a)} \exp\left(-\frac{\left(\log(d_p) - \log(d_{p,a,n})\right)^2}{2\left(\log(\sigma_a)\right)^2}\right)$$

 $N_a$ : Total number of particles in the mode (# cm<sup>-3</sup>)  $d_{p,a,n}$ : Median diameter of the mode for number (µm)  $\sigma_a$ : Standard deviation of the distribution



#### Log-normal Representation of the Size Distribution

Log-normal representation of the volume concentration for a mode

$$\upsilon_{p,a}(d_p) = \frac{V_a}{\left(2\pi\right)^{1/2}\log(\sigma_a)} \exp\left(-\frac{\left(\log(d_p) - \log(d_{p,a,v})\right)^2}{2\left(\log(\sigma_a)\right)^2}\right)$$

 $V_a$ : Total volume of particles in the mode (# cm<sup>-3</sup>)  $d_{p,a,v}$ : Median diameter of the mode for volume (µm)  $\sigma_a$ : Standard deviation of the distribution



# Sectional Representation of the Size Distribution

Sectional representation of the number and volume concentrations

$$N_{i} = \int_{d_{p,i-1}}^{d_{p,i}} n_{p,d}(d_{p}) \, \mathrm{d}d_{p}$$
$$V_{i} = \int_{d_{p,i-1}}^{d_{p,i}} n_{p,d}(d_{p}) \frac{\pi}{6} \, d_{p}^{3} \, \mathrm{d}d_{p}$$

 $N_i$ : Total number of particles in section  $i \ (\# \text{ cm}^{-3})$  $V_i$ : Total volume of particles in section  $i \ (\mu\text{m}^3 \text{ cm}^{-3})$  $n_{p,d}$ : Distribution of particle number as a function of diameter  $d_p \ (\# \mu\text{m}^{-1} \text{ cm}^{-3})$ 

# **Chemical Composition of Atmospheric Particles in Paris**



Source: Source apportionment of airborne particles in the Île-de-France region, AIRPARIF, 2011, www.airparif.asso.org.

# **Chemical Composition of Atmospheric Particles in Paris**



Source: Source apportionment of airborne particles in the Île-de-France region, AIRPARIF, 2011, www.airparif.asso.org.

# **Chemical Composition of Atmospheric Particles in Beijing, China, and Delhi, India**



The same chemical species are found in the urban background of various cities throughout the world, albeit with different relative fractions.

Sources: Wang et al., Aerosol Air Quality Res., 15, 2200-2211, 2015; Dumka, J. Atmos. Chem., 74, 423-450, 2017.

# Primary and Secondary Particles A Complicated System



## Primary and Secondary Particles A Complex System



#### Thermodynamics

Ideal gas law: P V = n R T*R*: ideal gas law constant (8.314 J/mol/K)

Saturation vapor pressure:

 $P_i^{sat}$ ;  $P_i > P_i^{sat} =>$  nucleation or condensation

Henry's law:  $\gamma_i c_i = H_i P_i$ 

Raoult's law:  $P_i = P_i^{sat} \gamma_i x_i$ 

# **Inorganic Particles**

- Primary particles (mostly coarse) :
  - Sea salt (NaCl...)
  - Soil dust, including alkaline particles (CaCO<sub>3</sub>...)
- Secondary particles (mostly fine)
  - Sulfate
  - Nitrate
  - Ammonium

# Sulfate

- Formed from gaseous sulfuric acid  $(H_2SO_4)$
- $H_2SO_4$  has a very low saturation vapor pressure; therefore,  $H_2SO_4$  goes rapidly to the particulate phase
  - Nucleation
  - Condensation on existing particles
- $H_2SO_4$  can be neutralized by ammonia (NH<sub>3</sub>)
  - Ammonium bisulfate NH<sub>4</sub>HSO<sub>4</sub>
  - Ammonium sulfate  $(NH_4)_2SO_4$
  - Letovicite  $(NH_4)_3H(SO_4)_2$

#### Nitrate

- Formed from gaseous nitric acid (HNO<sub>3</sub>)
- HNO<sub>3</sub> has a high saturation vapor pressure; therefore, HNO<sub>3</sub> will tend to remain in the gas phase.
- HNO<sub>3</sub> may go to the particulate phase
  - By dissolution in an aqueous particle (very small quantity)
  - By reaction with another compound, either gaseous (NH<sub>3</sub>), or particulate (sea salt, alkaline dust)

#### **Ammonium Nitrate**

• Formed from gaseous nitric acid (HNO<sub>3</sub>) and gaseous ammonia (NH<sub>3</sub>)

 $K_{eq} = [\text{HNO}_3]_g [\text{NH}_3]_g / [\text{NH}_4\text{NO}_3]_p$ 

• In the absence of other particles,  $NH_4NO_3$  is formed when  $K_{eq}$  exceeds a threshold value  $K_{eq,sat}$ 

#### **Ammonium Nitrate**

• In the case of a solid particle

 $K_{eq} = [\text{HNO}_3]_{\text{g}} [\text{NH}_3]_{\text{g}} = 3.35 \text{ x } 10^{-16} \text{ atm}^2 \text{ at } 25 \text{ }^{0}\text{C}$ 

• In the case of a liquid particle

 $K_{eq} = [\text{HNO}_3]_g [\text{NH}_3]_g / (\gamma_{\text{NH4}+} [\text{NH}_4^+]_{aq} \gamma_{\text{NO3}-} [\text{NO}_3^-]_{aq})$ 

#### **Other Particulate Nitrate**

• Reaction with sea salt

 $HNO_3(g) + NaCl(p) \implies NaNO_3(p) + HCl(g)$ 

• Reaction with alkaline dust

 $2 \text{ HNO}_3(g) + \text{CaCO}_3(p) \implies \text{Ca(NO}_3)_2(p) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$ 

#### Deliquescence

Sulfuric acid  $(H_2SO_4)$  is always in a liquid phase at ambient temperature.

The relative humidity of deliquescence is the humidity at which a salt goes from a solid phase to a liquid phase:

- 40 % for  $NH_4HSO_4$
- 80 % for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>
- 62 % for  $NH_4NO_3$

When humidity decreases, the salt becomes solid again (crystallization) at a humidity lower than that of deliquescence: it is called the phenomenon of hysteresis.

#### **Inorganic Particulate Matter**

- The chemical composition of inorganic particles is determined by the particulate and gaseous concentrations because the chemical system tends toward equilibrium among the different phases (solid, liquid, and gaseous).
- At equilibrium, the Gibbs energy is minimized.
- Software (numerical mathematical models) is available to calculate the chemical composition of inorganic particles knowing the composition of the gas phase (e.g., ISORROPIA, MARS, EQUISOLV...).

#### **Major Chemical Regimes**

- Oxidants (O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>)
   NO<sub>x</sub> or VOC limited
- Sulfate

- SO<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> limited

• Ammonium nitrate

- NH<sub>3</sub> or HNO<sub>3</sub> limited

#### **Non-linearity of Inorganic Aerosols**

Explanation of the effect of a decrease in SO<sub>2</sub> emissions on particulate nitrate:

$$SO_{2} \downarrow => Sulfate \downarrow => (NH_{4})_{2}SO_{4} \downarrow$$

$$(NH_{4})_{2}SO_{4} \downarrow => NH_{3} \uparrow => [HNO_{3}] [NH_{3}] \uparrow => NH_{4}NO_{3} \uparrow$$

$$Mass$$

$$conservation of$$

$$NH_{3} and NH_{4}^{+}$$

$$Gas/particle$$

$$equilibrium for$$

$$NH_{3} and HNO_{3}$$

#### **Reduction of Ammonium Nitrate**

• One may also define "available ammonia":

 $[NH_3]_a = [NH_3]_{total} - 2 x [Sulfate]$ 

and the precursor gas ratio:  $GR = [NH_3]_a / [HNO_3]_{total}$ If GR < 1; it is more efficient to reduce ammonia emissions than HNO<sub>3</sub> concentrations (and vice-versa).

Note: these criteria are approximate and one must perform the calculation to confirm which precursor (NH<sub>3</sub> or HNO<sub>3</sub>) must be preferentially reduced.

#### **Reduction of Ammonium Nitrate**

- Is it preferable to reduce nitric acid (HNO<sub>3</sub>) or ammonia (NH<sub>3</sub>) to reduce the concentration of particulate ammonium nitrate?
- One defines the "ammonia excess":

 $[NH_3]_e = [NH_3]_{total} - 2 [Sulfate] - [Nitrate]_{total}$ 

"Available ammonia" (in ppb) :  $[NH_3]_a = [NH_3]_{total} - 2$  [Sulfate]

 $[NH_3]_e = [NH_3]_a - [Nitrate]_{total}$ 

If  $[NH_3]_e < 0$ ; it is more efficient to reduce ammonia emissions than HNO<sub>3</sub> concentrations (and vice-versa).

#### **Reduction of Ammonium Nitrate**

• The same estimation can be done by using the ratio rather than the difference of the available ammonia and total nitrate:

The precursor gas ratio:  $GR = [NH_3]_a / [HNO_3]_{total}$ 

- If GR < 1; it is more efficient to reduce ammonia emissions than HNO<sub>3</sub> concentrations (and vice-versa).
- Note: these criteria are approximate and one must perform the calculation to confirm which precursor (NH<sub>3</sub> or HNO<sub>3</sub>) must be preferentially reduced

### Primary and Secondary Particles A Complex System



### Secondary Particles Ammonium Nitrate



#### **Summary for Secondary Inorganic Particles**

- A decrease in sulfate may lead to an increase in ammonium nitrate.
- A decrease in ammonium nitrate will be best obtained when reducing the limiting gaseous precursor (HNO<sub>3</sub> or NH<sub>3</sub>): estimated with GR for example.
- Decrease in  $NH_3$ : its lifetime is on the order of a week => long-range transport
- Decrease in  $HNO_3$ : one must account for oxidants, which convert  $NO_x$  into  $HNO_3$ ; it may necessary to reduce VOC in addition to  $NO_x$ .



# Change in $PM_{2.5}$ (µg/m<sup>3</sup>) due to a 15 % decrease in NO<sub>x</sub> emissions in the Paris Region



# Change in $PM_{2.5}$ (µg/m<sup>3</sup>) due to a 15 % decrease in NH<sub>3</sub> emissions in the Paris Region



# Change in $PM_{2.5}$ (µg/m<sup>3</sup>) due to a 30 % decrease in NH<sub>3</sub> emissions in France



### **Secondary Organic Aerosols**



- Precursors
  - Anthropogenic : aromatics, alkanes, alkenes, aldehydes
  - Biogenic : isoprene, monoterpenes, terpenoïdes, sesquiterpenes
- Oxidants: OH, NO<sub>3</sub>, and O<sub>3</sub> (for alkenes)
- Condensable compounds: acids, alcohols, aldehydes, ketones, ethers, nitrates, peroxides, etc.

#### **Volatility of Organic Compounds**



The volatility of organic compounds decreases with the number of carbon atoms and with the number of functional groups.

Number of carbon atoms

Data source: Schwarzenbach et al., 2003

#### **Absorption in Organic and Aqueous Phases**



#### **Secondary Organic Aerosols**



# **Experimental Studies of SOA Formation in Smog Chambers**

- General measurements
  - Amount of VOC that has reacted:  $\Delta$ [VOC]
  - Amount of organic particulate matter formed:  $\Delta M_o$
- Measurements of chemical species formed during VOC oxidation
  - Particulate phase
  - Gaseous phase

### **Secondary Organic Aerosols Formation from Aromatics**



Data source: Ng et al., 2007a. Other experiments have been conducted that can lead to significantly different yields for some of these compounds. Therefore, these yields must be seen in terms of comparison between high-NO<sub>x</sub> and low-NO<sub>x</sub> regimes or among VOC of a same category.

### Secondary Organic Aerosols Formation from Alkanes with 12 Carbon Atoms



Data source: Loza et al., 2014. Other experiments have been conducted that can lead to significantly different yields for some of these compounds. Therefore, these yields must be seen in terms of comparison between high- $NO_x$  and  $low-NO_x$  regimes or among VOC of a same category
#### Secondary Organic Aerosols Formation from Alkenes



Alkenes : number of carbon atoms

Data source: Matsunaga et al., 2009. Other experiments have been conducted that can lead to significantly different yields for some of these compounds. Therefore, these yields must be seen in terms of comparison between high-NO<sub>x</sub> and low-NO<sub>x</sub> regimes or among VOC of a same category.

#### Secondary Organic Aerosols Formation from Biogenic Compounds



Data source: Kroll et al., 2006; Jaoui et al., 2012; Eddingsaas et al., 2012; Lee et al., 2006; Ng et al., 2007b. Other experiments have been conducted that can lead to significantly different yields for some of these compounds. Therefore, these yields must be seen in terms of comparison between high-NO<sub>x</sub> and low-NO<sub>x</sub> regimes or among VOC of a same category.

## Secondary Organic Aerosols Formation from Biogenic Compounds

Compounds	SOA formation yield	Fraction of biogenic emissions	Combination SOA x emissions
Isoprene (C5)	4 %	50 %	2 %
Monoterpenes (C10)	40 %	15 %	6 %
Sesquiterpenes (C15)	90 %	3 %	3 %

## **Optimal Representation of SOA**

• The large number of condensable organic compounds does not allow a detailed representation of those molecular compounds in air quality models, even if those compounds have been identified experimentally or theoretically; a representation based on a limited number of surrogate compounds is necessary.

# Approaches for the representation of secondary organic aerosol species

- Two empirical surrogate compounds by reaction (Caltech), also referred to as the two-compound Odum method
- Empirical surrogate compounds characterized by their saturation vapor pressure (VBS method of Carnegie-Mellon University)
- Molecular surrogate compounds characterized by their thermodynamic properties (AER and CEREA)

#### **PM due to Vehicle Emissions**

PM emissions from vehicles

- Diesel (with and without a particle filter)
- Gasoline

Formation of secondary PM from gaseous emissions from vehicles

Source: Seigneur, JAWMA, 2009

# Diesel Engines PM Chemical Composition

- Unburned hydrocarbons from lubricating oils (C<sub>24</sub> to C<sub>32</sub> alkanes): > 95 %
- Unburned hydrocarbons from fuel (C<sub>15</sub> to C<sub>23</sub> alkanes): ~ 1 %
- Organic compounds from combustion products (for example, polycyclic compounds): < 1 %</li>
- Sulfate: a few %
- Metals: traces









## Diesel Engine with Particle Filter Chemical Composition

- Sulfate and ammonium
- Soot particles are collected by the filter and burned via oxidation.
- Organic compounds are negligible because of their oxidation to CO<sub>2</sub>.

No soot

Nucleation of a sulfuric acid particle  $H_2SO_4 - (H_2O)_n$ or a particle of ammonium sulfate

• •











## **Gasoline Engines Chemical Composition**

- Organic compounds
- No soot particles
- Sulfate
- Metals: traces









#### **Conceptual Model of the Formation of Particles from Vehicle Emissions**

In summary:

- Diesel vehicles without a particle filter (DFP) emit diesel particles (black carbon + organic compounds + sulfate +...), which are initially mostly ultrafine particles.

- Diesel vehicles with a DFP emit very little PM; however, they may emit SVOC that are PM precursors.

- Gasoline vehicles emit less PM than diesel vehicles without DFP, but more PM than diesel vehicles with DFP; furthermore, gasoline vehicles emit more VOC, which are precursors of SOA, than diesel vehicles.

## **Emission of Particles From Diesel Passenger Cars**

Two types of diesel particle filters (DPF), which differ in the technique used to regenerate the filter

- Catalyzed particle filter
  - Catalyzed oxidation of C to  $CO_2$  (and CO) is performed by  $NO_2$ , with some NO being oxidized to  $NO_2$
  - A problem is the higher fraction of  $NO_2$  in the  $NO_x$  emissions.
- Activated particle filter
  - Oxidation of C to  $CO_2$  (and CO) is performed by  $O_2$ , with the help of a fuel-borne catalyst, which is added to the fuel
  - There is no increase in NO<sub>2</sub> emissions.

#### **Importance of SVOC Emissions from Vehicles**

- Emissions of semi-volatile organic compounds (SVOC) are currently not taken into account in emission inventories.

- SVOC emissions are estimated to be about 150 % of primary organic aerosol (POA) emissions.

#### Formation and Evolution of Ultrafine Particles Emitted from Vehicles



Formation ofDispersion andultrafine particles andgrowth of ultrafineof their initialparticles near theevolution after theirroadwayexhaust

Dispersion and growth of e ultrafine particles into fine particles in the ambient environment

#### PM<sub>2.5</sub> in Los Angeles, California



Source : South Coast Air Quality Management District, www.aqmd.gov

#### **PM<sub>2.5</sub> in Paris**



Air quality standards: 10  $\mu$ g/m<sup>3</sup> for WHO, 12  $\mu$ g/m<sup>3</sup> in the U.S., and 25  $\mu$ g/m<sup>3</sup> in Europe

Source: AIRPARIF, http://www.airparif.asso.fr

#### Air Pollution Episode in March 2014 in Paris



#### Air Pollution Episode in December 2016 in Paris



Source : Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL) and LCSQA/Ineri