Emissions of Air Pollutants and Emission Control Technologies

- Sources of air pollution
- Emission inventories
- Emission control technologies

Primary and Secondary Pollutants

- Primary pollutants: they are emitted directly into the atmosphere
  - Nitrogen oxides (NO_x, i.e., NO and NO_2), sulfur dioxide (SO_2), volatile organic compounds (VOC, for example, formaldehyde, benzene), etc.

- Secondary pollutants: they are formed in the atmosphere via chemical reactions
  - Ozone (O_3) formed from NO_x and VOC, nitrogen dioxide (NO_2), formaldehyde (HCHO), sulfuric acid (H_2SO_4), nitric acid (HNO_3), etc.

Processes Leading to Emissions of Air Pollutants

Pollutants formed during combustion

- from air constituents
- from substances present in the fuel and emitted during combustion possibly under an oxidized form

Pollutants emitted by volatilization

Pollutants emitted via mechanical processes

Pollutants produced via natural processes and emitted via natural or anthropogenic processes

Emissions of Air Pollutants
Combustion

- Pollutants formed during combustion from air constituents
  - Nitrogen oxides (NO_x): NO and NO_2

$$N_2 + O \Rightarrow NO + N$$
$$N + O_2 \Rightarrow NO + O$$
$$N + OH \Rightarrow NO + H$$
$$\ldots$$

Emissions of Air Pollutants
Combustion

- Pollutants formed from substances present in the fuel (hydrocarbons, coal… + impurities such as sulfur, mercury…)
  - Carbon dioxide (CO_2)
  - Carbon monoxide (CO)
  - Volatile organic compounds (benzene, formaldehyde…)
  - Semi-volatile and non-volatile organic compounds (polycyclic aromatic hydrocarbons, dioxins et furans…)
  - Soot particles
  - Sulfur oxides (SO_2 and SO_3)
  - Halogenated compounds (HCl)
  - Mercury (Hg^0, $HgCl_2$…)
  - …

Emissions of Air Pollutants
Volatilization

- Pollutants emitted by volatilization
  - Volatile organic compounds (fuels, paints, cleaning products…)
  - Elemental mercury (land, oceans…)
  - Reemission of compounds deposited on land (POP, mercury…)

Emissions of Air Pollutants Mechanical Processes

- Pollutants emitted by mechanical processes
  - Metals (brake pad abrasion, tire wear, road wear, industrial activities…)
  - Dust (agricultural activities, construction activities, resuspension due to traffic…)

Emissions of Air Pollutants
Natural Processes

- Pollutants emitted by natural processes
  - Volatile organic compounds emitted by vegetation (isoprene, methyl-butenol, monoterpenes, sesquiterpenes, terpenoides…)
  - Methane
  - Sulfur compounds (dimethylsulfur from oceans, H_2S from geothermal sources, SO_2 from volcanoes)
  - Nitrogen compounds (ammonia, nitrous oxide (N_2O) …) emitted from the Earth's surface ; NO_2 emitted by lightning in altitude
  - Wind-blown dust
  - Sea salt
  - Substances emitted from wild fires (CO_2, CO, NO_x, VOC, particles…)
  - …

Emissions
Local Sources versus Remote Sources

- Local emissions: on-road traffic, residential heating, industries, etc.

- Remote emissions: agriculture, other cities, maritime traffic, air traffic, etc.

Emissions
Man-made versus Natural

Anthropogenic emissions: those due to human activities; for example, traffic, industries, residential heating, agriculture, man-made biomass burning, etc.

Natural emissions: those that occur without human activities; for example, biogenic emissions from vegetation, sea salt, desert dust from Sahara, wild fires, volcanic eruptions, etc.

Emissions
Major Source Categories

On-road traffic:

- diesel vehicles: nitrogen oxides and particles
- gasoline vehicles and motorbikes: nitrogen oxides and organic compounds

Residential and business (heating, cleaning…): nitrogen oxides, organic compounds, and particles

Industries: sulfur dioxide, nitrogen oxides, volatile organic compounds, and particles

Agriculture: ammonia, particles

Vegetation : volatile organic compounds

Sulfur Dioxide (SO_2)

- Global annual emissions*

– Industry:	82 Tg
– Residential:	8 Tg
– Agriculture:	<1 Tg
– Transportation:	12 Tg
– Biomass fires:	3 Tg
– Natural sources:	19 Tg

* in Tg (10^{12} g)

Nitrogen Oxides (NO and NO_2)

- Global annual emissions*
  - Industry: 57 Tg
  - Agriculture: 6 Tg
  - Transportation: 49 Tg
  - Biomass fires: 25 Tg
  - Natural sources: 53 Tg

* in Tg (10^{12} g) of nitrogen dioxide (NO_2)

Ammonia (NH_3)

- Global annual emissions*
  - Industry & residential: 7 Tg
  - Agriculture: 47 Tg
  - Transportation: 1 Tg
  - Biomass fires: 6 Tg
  - Natural sources: 16 Tg

* in Tg (10^{12} g)

Carbon Monoxide (CO)

- Global annual emissions
  - Industry: 145 Tg
  - Residential 232 Tg
  - Agriculture: 75 Tg
  - Transportation: 177 Tg
  - Biomass fires: 413 Tg
  - Natural sources: 140 Tg

- Formation in the atmosphere
  - Methane oxidation: 700 Tg
  - Oxidation of other VOC: 400 Tg

Volatile Organic Compounds (VOC)

- Global annual emissions*
  - Industry: 69 Tg
  - Residential: 36 Tg
  - Agriculture: 4 Tg
  - Transportation: 27 Tg
  - Biomass fires: 251 Tg
  - Natural sources: 1000 Tg

* in Tg (10^{12} g) of equivalent CH_4; VOC emissions listed here do not include those of methane, which is not very reactive

Fine Particles ($PM_{2.5}$)

- Annual global emissions
  - Industry: 13 Tg
  - Residential: 18 Tg
  - Agriculture: 8 Tg
  - Transportation: 3 Tg
  - Biomass fires: 36 Tg
  - Natural sources (sea salt, wind erosion of soils, volcanoes, pollens…): 460 Tg

- Formation in the atmosphere
  - Human activities: 350 Tg
  - Natural sources: 250 Tg

Chemical Speciation and Particle Size Distribution

- **Nitrogen oxides (NO_x)**: The fractions of NO (nitric oxide) and NO_2 (nitrogen dioxide) vary among sources.

- **Volatile organic compounds (VOC)**: They differ in terms of chemical reactivity and toxicity; therefore, inventories of total VOC emissions do not reflect the potential impacts of those emissions.

- **Particles (PM)**: The size distribution and chemical composition of atmospheric particulate matter are very important to assess their health and environmental impacts; therefore, particle emission inventories do not necessarily reflect the potential impacts of those particles.

Emission Inventories

The fundamental equation to estimate air pollutants emitted from a source is as follows:

$$S_{ij} = EF_{ij} \text{ x } A_j$$

Activity (units/s) of source *j*

Emission rate (g/s) or air pollutant *i* from source *j*

Emission factor (g/unit of activity) for air pollutant *i* emitted from source *j*

Emission Inventories
Source Activity

The activity of a source is defined differently depending on the source type. For example:

- On-road traffic: kilometers travelled by the vehicle fleet per hour
- Residential heating: amount of fuel consumption per year

For biogenic sources (vegetation), the emission rate is calculated as a function of temperature and solar radiation.

For air pollutants emitted from some industrial sources (e.g., SO_2 and NO_x emitted from fossil-fuel fired power plants), the emission rate is measured directly in the stack.

Emission Inventories
Emission Factors

Emission factors may be obtained in several ways:

- Measurements at the source (for a given source category)

- Estimate from a mass balance (e.g., concentration of an element in coal)

- Simulation (e.g., chemical speciation of mercury emitted from power plants)

Emission Inventories
Spatial Distribution

Once emission rates have been calculated, they must be distributed spatially over the domain of interest.

Spatial distribution:

- Point sources: They can be located exactly
- Area sources: Surrogate factors are used to spatially distribute the total emissions (e.g., population for residential emissions).
- Line sources: They may be located exactly and are then assigned to a given grid cell of a geographical information system (GIS)

Chemical Speciation

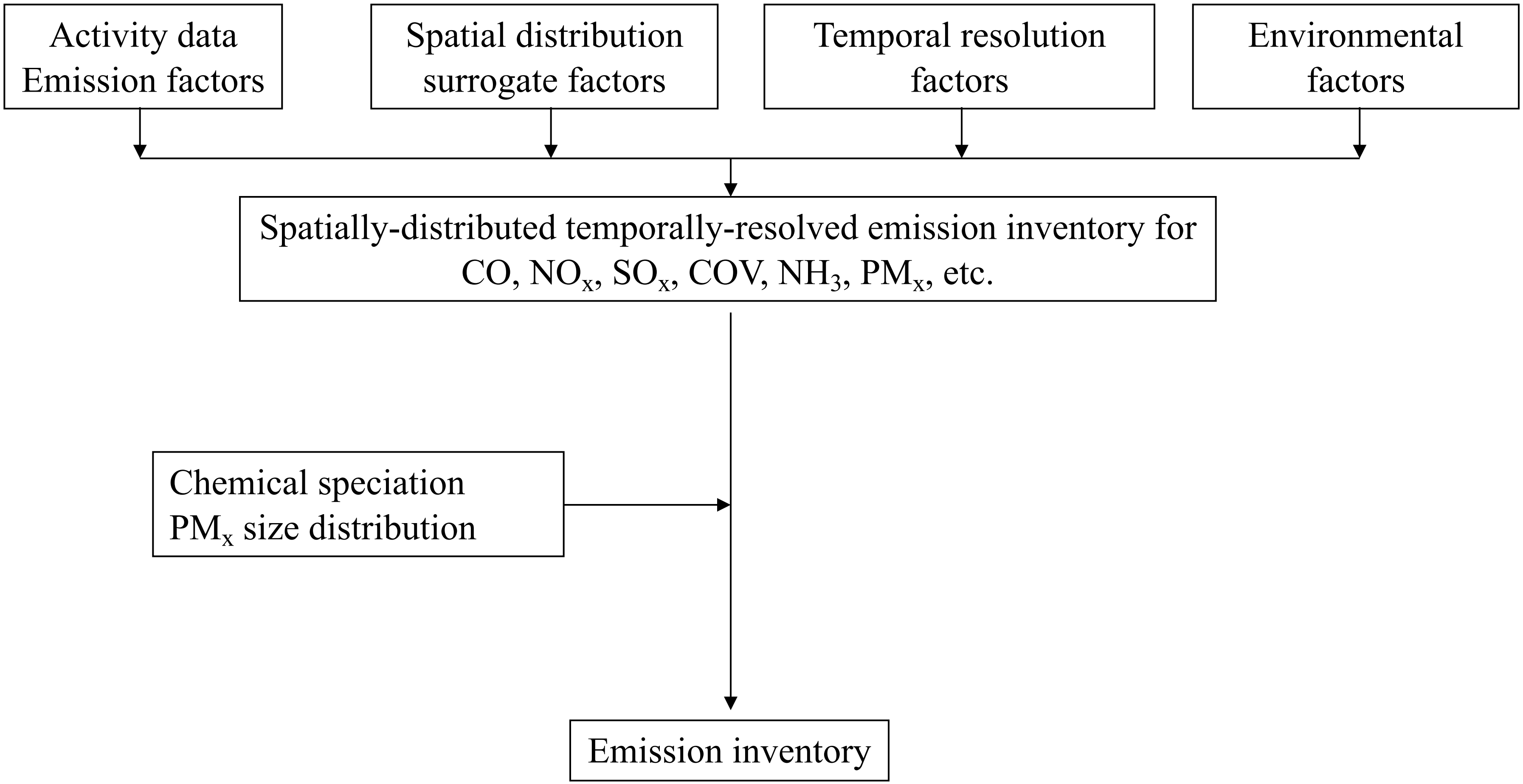
- Nitrogen oxides (NO_x): NO and NO_2
- Sulfur oxides: SO_2 and H_2SO_4
- Volatile organic compounds (VOC):
  - Speciation according to emitted molecules
  - Lumping using "model" species
- Particles: black carbon, sulfate, etc.

Particle Size Distribution

- Typically, limited to the regulated size fractions:
  - $PM_{2.5}$
  - PM_{10} (or PM_{10} - $PM_{2.5}$)

- Occasionally, with a finer size resolution corresponding to the model size distribution (see Chapter 9)

Development of an Emission Inventory



Emission Control

The fundamental equation to estimate air pollutant emissions from a source is modified to include a term that quantifies the emission control fraction:

$$S_{ij} = EF_{ij} \times A_j \times (1 - CF_{ij})$$

Emission control factor
for air pollutant *i* emitted from source *j*

Emission Control of Gaseous Pollutants

- The main approaches used to control gaseous pollutant emissions are:
  - Mass transfer:
    - Absorption in a liquid: e.g., HCl and SO_2 dissolved in water
    - Adsorption on a solid substrate: e.g., organic pollutants and mercury emitted from incinerators adsorbed on activated carbon
  - Chemical transformation: e.g., SO_2 and NO_x emitted from power plants

Chemical Transformation

- The chemical transformation of the pollutant leads either to a pollutant that can be extracted from the effluent stream more readily or to a non-toxic chemical species that can be emitted to the atmosphere.

  - Emission control of SO_2: Flue gas desulfurization system (FGD)

    $SO_2 \Rightarrow Ca(SO_4)_2$

  - Emission control of NO_x: Selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR)

    $NO_x + NH_3 \Rightarrow N_2$ (with or without a catalyst)

Efficiencies of Emission Control Systems for Gaseous Pollutants

Efficiencies of emission control systems used for
SO_2 and NO_x emitted from coal-fired power plants

Emission control system	Pollutant	Efficiency
Flue gas desulfurization (FGD)	SO_2	75 to 90 %
Selective non-catalytic reduction (SNCR)	NO_x	30 to 80 %
Selective catalytic reduction (SCR)	NO_x	90 %

Emission Control of Particulate Pollutants

- The main approaches to control particulate emissions are:
  - Sedimentation or inertial deposition
  - Filtration
  - Electrostatic migration

Emission Control of Particulate Pollutants Processes

- The physical processes that govern particulate emission control are the following:
  - Sedimentation
  - Impact by inertia and/or interception
  - Brownian diffusion
  - Migration in an electrical field (electrophoresis)

Emission Control of Particulate Pollutants
Cyclones

- Cyclones
  - Such devices use mostly inertia of particles in a stream to collect those particles on the wall of the device or on droplets injected within the device and collected at the bottom.

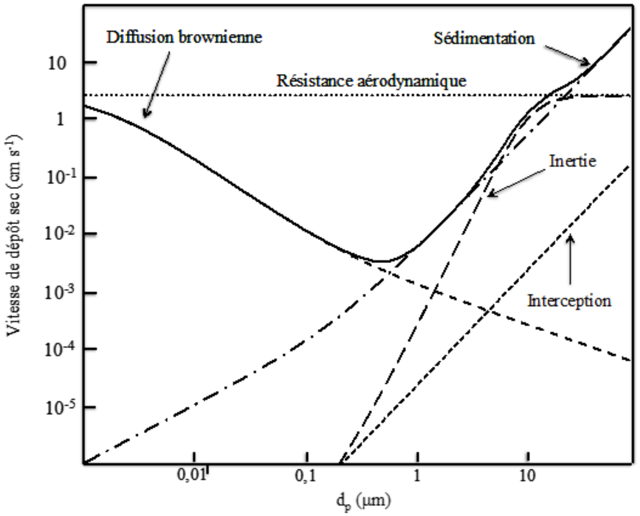
Emission Control of Particulate Pollutants
Electrostatic Precipitators (ESP)

- Electrostatic precipitators
  - An electrical discharge is sent in the effluent to charge particles electrically.
  - The charged particles migrate toward the system walls, which act as electrodes (electrophoresis).
  - The system is shaken regularly so that the particles collected on the walls fall at the bottom of the device.

Emission Control of Particulate Pollutants
Filters

Filters collect particles according to the same physical processes as those that lead to atmospheric dry deposition on natural and man-made surfaces: impact by inertia and interception and brownian diffusion.

Filters (e.g., baghouse for a power plant) collect particles with good efficiency (except fine particles). A process such as vibration, air injection or mechanical cleaning must be used to remove the collected particles and collect them at the bottom of the device.



Deposition velocity of particles on a surface

Emission Control of Vehicle Exhaust
Regulated Pollutants

- Carbon monoxide (CO)
- Lead (Pb)
- Sulfur dioxide (SO_2)
- Nitrogen oxides (NO_x)
- Volatile organic compounds (VOC), including formaldehyde (HCHO) in the U.S. and benzene (C_6H_6) in Europe
- Particulate matter (PM) in terms of mass and, in Europe, number

Emission Control of Vehicle Exhaust
Regulation of Content in Fuel

- Lead (Pb) was used as tetraethyl lead to reduce knocking in engines. It was banned from fuels and replaced by organic compounds.

- Sulfur (S) content in fuels is now regulated for on-road vehicles:
  - 10 ppm for gasoline and 15 ppm for diesel in the U.S.
  - 10 ppm for both gasoline and diesel in France

Emission Control of Vehicle Exhaust Gaseous Pollutants

- Carbon monoxide (CO): catalytic converter (platinum or palladium)

$$2\ CO + O_2 \rightarrow 2\ CO_2$$

- Volatile organic compounds (VOC): two-way catalytic converter

$$2\ C_nH_{2n+2} + (3n+1)\ O_2 \rightarrow 2n\ CO_2 + 2(n+1)\ H_2O$$

- Nitrogen oxides (NO_x): three-way catalytic converter (inefficient for diesel engines, because the exhaust is too oxygen-rich)

$$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$$

Emission Control of Vehicle Exhaust Gaseous Pollutants

- Nitrogen oxides (NO_x): For diesel engines, several approaches are used.
  - Exhaust gas recirculation (EGR): The recirculation of exhaust gases into the combustion chamber lowers the oxygen content and temperature, thereby lowering NO_x formation. However, it may decrease engine performance and increase PM formation.
  - NO_x trap: NO_x are trapped and converted to N_2 when a fuel-rich exhaust is used to regenerate the system. Several catalysts are used e.g., (platinum, barium, and rhodium). The efficiency is about 70 % within a temperature range of about 17 to 35 ° C; much less outside this temperature range.
  - Selective catalytic reduction (SCR): Urea $(NH_2)_2C{=}O$ is used to convert NO_x to N_2 using a catalyst (e.g., vanadium oxide). The efficiency is about 90 %; it is more costly than the NO_x trap.

Emission Control of Vehicle Exhaust Particulate Pollutants

- Diesel particle filter (DPF): The DPF collects the particles, but it must be regenerated from time to time to prevent clogging. Regeneration may be active (incineration at high temperature) or passive (incineration at a lower temperature using a catalyst or a gaseous oxidant)

- Continuous regeneration trap (CRT): Passive regeneration occurs by (1) converting NO to NO_2 (the gaseous oxidant) and (2) oxidizing carbonaceous PM to CO_2 on a catalyst. Active regeneration is needed from time to time. NO_2 emissions increase.

- Additivated DPF: The catalyst is added in the fuel and O_2 is the gaseous oxidant. Active regeneration is needed from time to time. There is no increase in NO_2 exhaust.