Lesson 2
MAIN AIR POLLUTANTS AND TRANSFORMATIONS

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> **POLLUTANT** is "any substance present in the air and likely to have harmful effects on human health and/or the environment as a whole" *European Directive 2008/50/EC on ambient air quality and cleaner air for Europe*

The most common gaseous air pollutants are inorganic, mainly oxides of nitrogen (N_2O, NO and NO_2), oxides of sulfur (SO_2) and oxides of carbon (CO).

Some other air pollutants of concern are hydrocarbons such as methane (CH_4), Volatile Organic Compounds (VOCs) and Particulate Matter (PM).

2.1. CARBON MONOXIDE (CO)

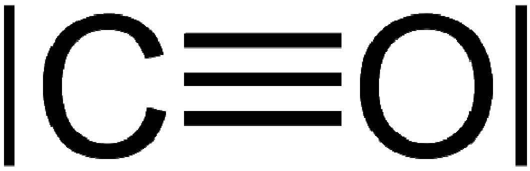
Characteristics

CO is a colorless, odorless, inflammable and **toxic gas**.

Lifetime ≈ 30 - 90 days

Background concentration ≈ 0.2 - 50 ppm (hourly average)

CO is one of the most abundant and widely distributed air pollutants.



Carbon monoxide by Yikrazul under Public Domain

Sources and sinks of CO

CO is produced by both natural and anthropogenic sources.

Global CO sources:

oxidation of CH_4 by ·OH radicals, biomass burning, wildfires and the oxidation of non-methanic hydrocarbons (NMHC).

Global CO sinks:

oxidation by ·OH radicals to CO_2. CO is also lost by deposition to soils.

Sources and sinks of CO in Tg CO·year^{-1}

sources	
Vegetation	60-160
Oceans	20-200
Oxidation of CH_4	400-1000
Oxidation of NMHC	200-600
Biomass burning	300-700
Fossil and domestic fuel	300-550
sinks	
Surface deposition	250-640
OH reaction	1500-2700

In **urban areas** the major source of CO is the incomplete combustion of fossil fuels in **vehicles** with internal combustion engines. Thus, the highest levels of this toxic gas tend to occur in congested urban areas during rush hours, when the greatest number of people are exposed.

Modern vehicles use catalytic converters to cut down on CO emissions by pumping excess oxygen into the exhaust gas.

A three-way catalytic converter by Bot
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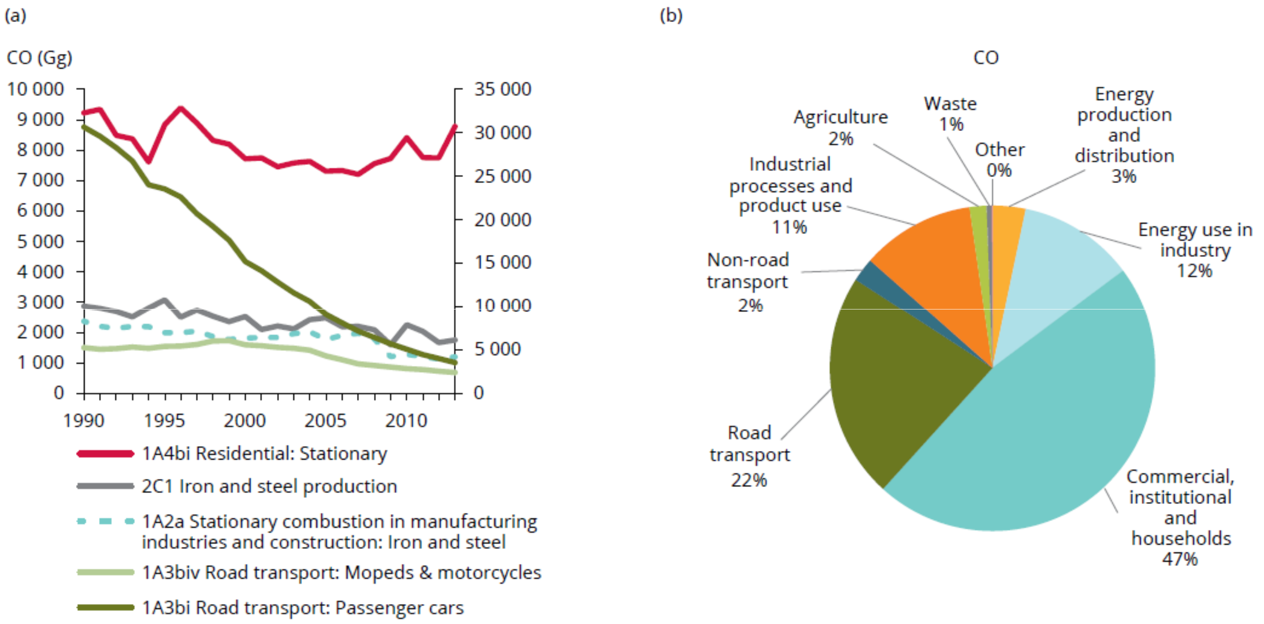


CO emissions in the EU-28: (a) trend in CO emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013

2.2. SULFUR DIOXIDE (SO_2)

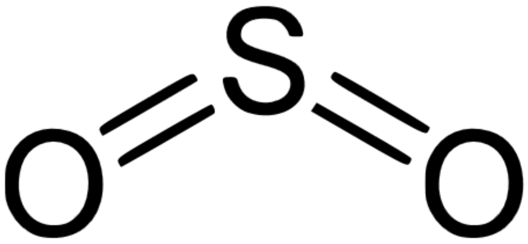
Characteristics

SO_2 is a colorless, non-flammable and non-explosive gas.

Lifetime ≈ 3 days

Ambient concentration 1 ppb - 2 ppm (24-hour average)

$[SO_2] > 0.3\text{-}1$ ppm → taste $SO_2 > 3$ ppm → pungent odor



Sulfur monoxide by Yikrazul under Public Domain

Sources and sinks of SO_2

Global SO_2 sources

SO_2 is produced in the air from 1) carbonile sulfide (COS), which is the most abundant sulfur compound present in the atmosphere, 2) hydrogen sulfide (H_2S), which is produced by sulfur- and sulfate-reducing bacteria in absence of oxygen and, 3) dimethyl sulfide (DMS), which is emitted by phytoplankton and other marine organisms over the oceans.

The atmosphere tends to oxidize these reduced sulfur compounds.

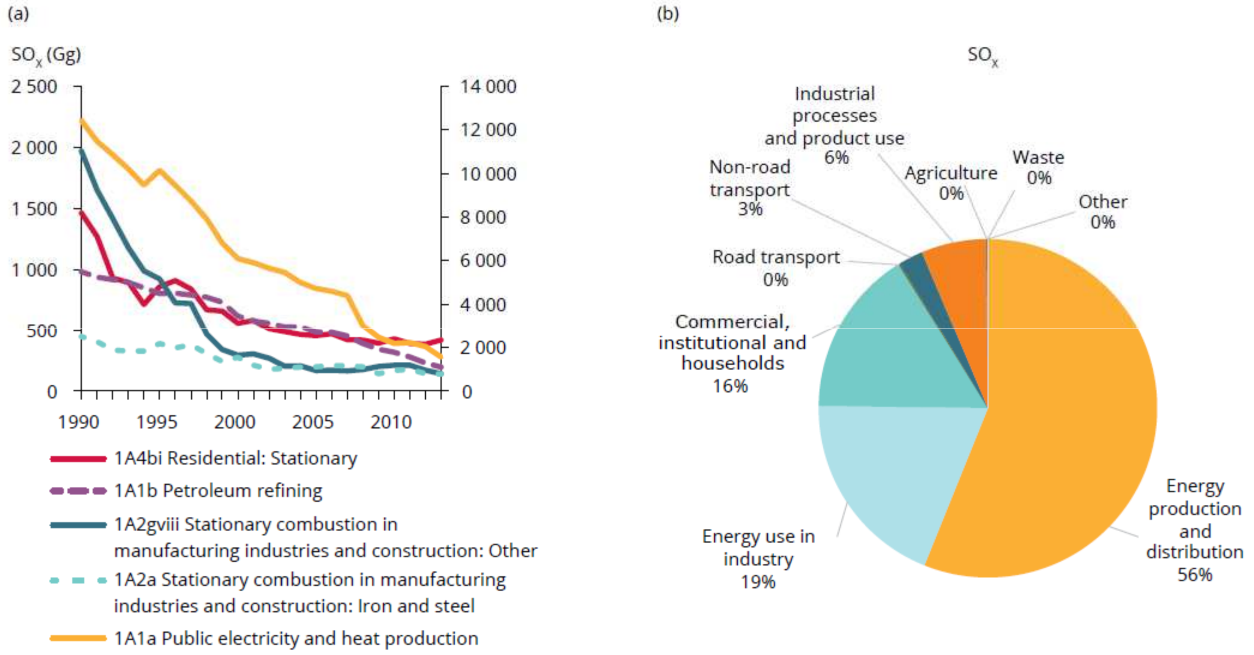
Global SO_2 sinks

Homogeneous and heterogeneous oxidation

The major antropogenic source of **anthropogenic SO_2** is the combustion of sulfur- carrying coal-fired power plants.

Power plant by B.Dmitrov licensed under CC BY-SA 2.0

In recent decades, the amount of SO_2 being released into the atmosphere has been reduced due to the decreasing use of coal for power generation and its replacement by natural gas.



SOX emissions in the EU-28: (a) trend in SOX emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013

GAS PHASE OXIDATION OF S (IV)

The free radicals produced from the degradation of hydrocarbons (hydroxyl radical **$^{\cdot}$OH**) oxidize SO_2 to reactive intermediates such as bisulfite ion (**HSO_3^-**) and sulfur trioxide (**SO_3**).

These intermediates combine rapidly with water vapor to form sulfuric acid (**H_2SO_4**), which can fall to Earth as acid rain or form fine sulfate particles: **SO_4^{-2}**.

$$SO_2(g) + \cdot OH + M \rightarrow HSO_3^-\ (g)$$

$$HSO_3(g) + O_2(g) \rightarrow SO_3\ (g) + \cdot HO_2\ (g)$$

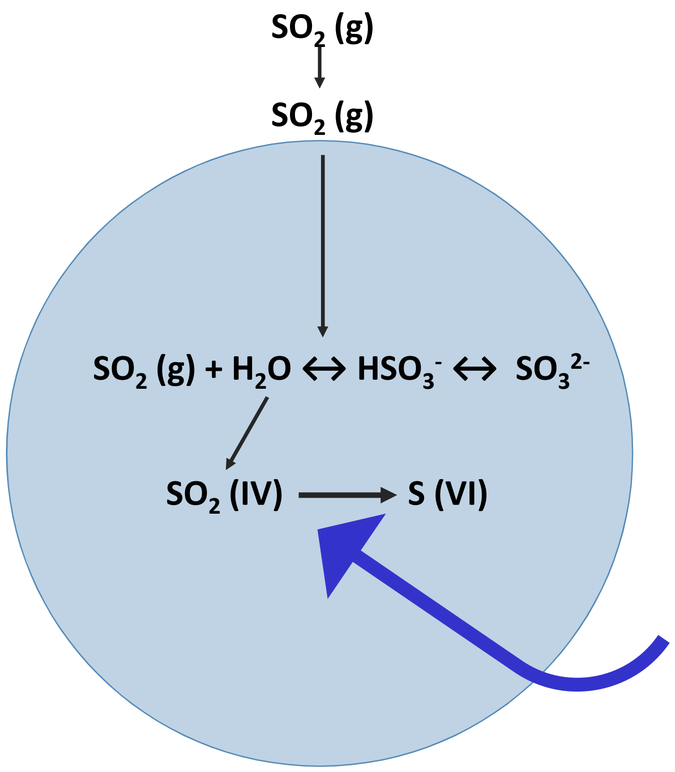
$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4\ (g)$$

AQUEOUS PHASE OXIDATION OF S (IV)

Whereas the homogeneous oxidation is the dominant mechanism by which S(IV) produces S (VI) when the relative humidity is < 70 %, a 2nd mechanism produces more rapidly S(VI) from S(IV) in cloud and rain droplets: this is referred to as heterogeneous oxidation.

This involves the transport and dissolving of SO_2 in water droplets, with the subsequent chemical reactions:

- Dissolution of SO_2 (g) into liquid-water drops to produce dissolved sulfur dioxide: **SO_2** (aq).
- In-drop conversion of dissolved sulfur dioxide SO_2 (aq) to sulfurous acid **H_2SO_3** (aq) and dissociation of H_2SO_3 (aq) to bisulfite ion (**HSO_3^-**) and sulfite ion (**SO_3^{2-}**)
- In-drop oxidation of HSO_3^- and SO_3^{2-} to sulfates (SO_4^{2-}).



SO_2 (g)

SO_2 (g)

$SO_2\text{ (g)} + H_2O \leftrightarrow HSO_3^- \leftrightarrow SO_3^{2-}$

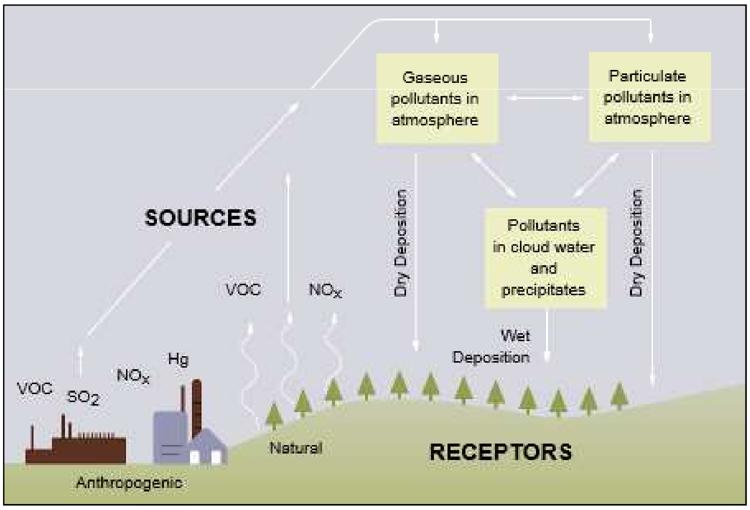
$SO_2\text{ (IV)} \longrightarrow \text{S (VI)}$

Oxidants

Oxygen (O_2)
Ozone (O_3)
Hydrogen peroxide (H_2O_2)

Heterogeneous oxidation of the SO_2

Thus, SO_2 contributes notably to **acid deposition.** It occurs when anthropogenically produced acid-containing gases, dissolutions or salts are deposited to the ground, vegetation, lakes or buildings in dry or wet form.

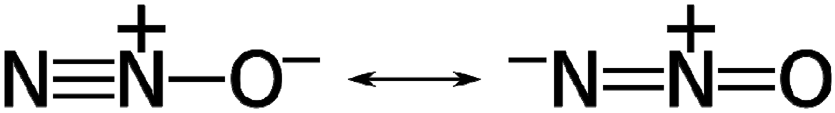


“Acid rain origins” by Zazou licensed under Public Domain

2.3. OXIDES OF NITROGEN

The oxides of nitrogen most commonly found in the atmosphere are the nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2).

N_2O, a commonly used anesthetic known as “laughing gas”, is produced mainly by natural processes, in particular microbiological reactions. It is relatively unreactive and it does not significantly influence important chemical reactions in the lower atmosphere. However, it is one of the main contributor to the greenhouse effect.



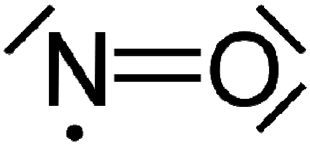
$$N\equiv\overset{+}{N}-O^{-} \longleftrightarrow {}^{-}N=\overset{+}{N}=O$$

“Nitrous oxide 2D-VB” by WhiteTimberwolf licensed under Public Domain

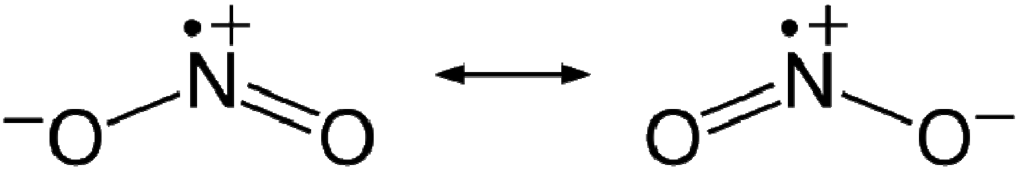
NO and **NO_2** are referred together as NO_x due to their interconvertibility in photochemical reactions.

NO is a colorless, odorless, non-flammable and toxic gas.

NO_2 is a reddish-brown gas with a pungent odor. Their hourly average concentrations are 0.02-1000 ppb and 1 ppb-0.5 ppm, respectively.



“Nitric oxide” by Yikreazul licensed under Public Domain



“Nitrogen dioxide resonance 2D” by B.Mills licensed under Public Domain

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Sources and sinks of NOx

On a global scale, NO is emitted naturally by microorganisms in soils, by natural combustion processes and storms with lightning strikes. Nevertheless, the major NO sources are anthropogenic. Well over 90% of all the man-made nitrogen oxides are formed when **oxygen** in the **air** and **nitrogen** in the **fuel** react at high temperatures during combustion: $N_2 + O_2 \rightarrow 2NO$

NO is rapidly oxidized to NO_2 by homogeneous reactions:

$$2NO + O_2 \rightarrow 2NO_2$$

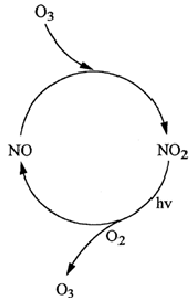
During the day, the NO_2 undergoes **photolysis.** Photolysis is a process in which the sunlight causes transformations of compounds.

$$NO_2 + h\nu \rightarrow NO + O$$

This reaction is one of the most important photochemical reactions in the lower atmosphere, since it produces highly active O, which regenerates tropospheric ozone and nitric oxide.

NO_2 photolytic cycle

$$\begin{array}{lll} NO + O_3 \rightarrow NO_2 + O_2 & & k_a \\ NO_2 + h\nu \rightarrow NO + O(^3P) & & k_b \\ O_2 + O + M \rightarrow O_3 + M & & k_c \end{array}$$



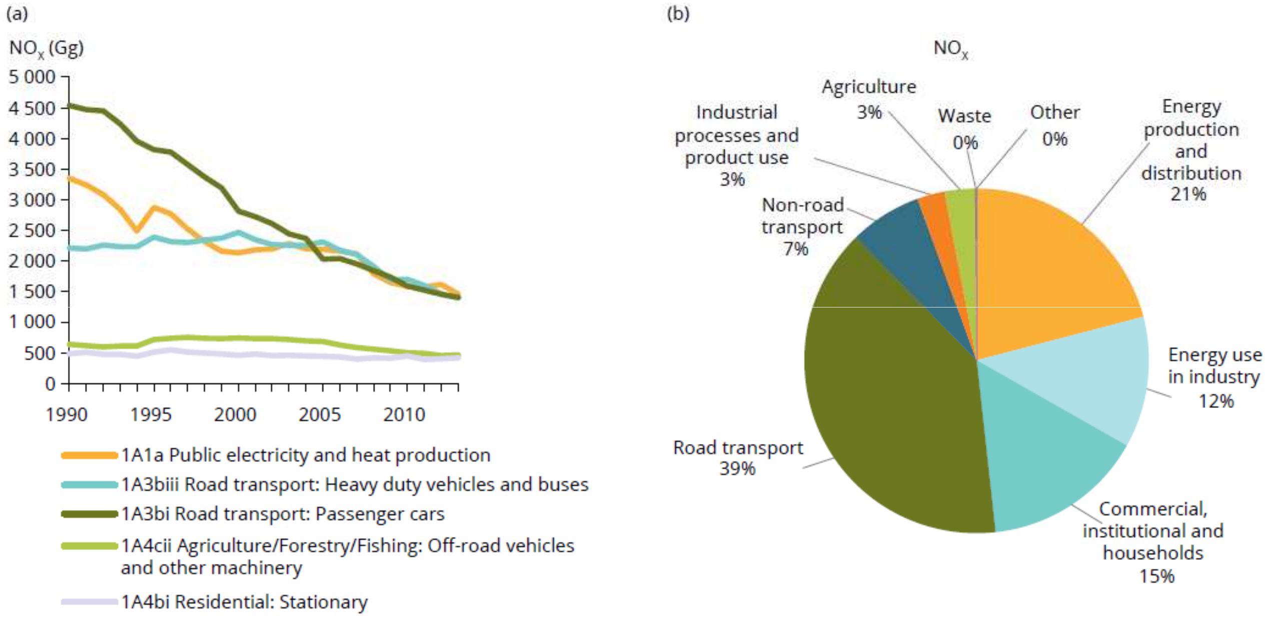
All three reactions noted above are very fast, and the combination would tend to maintain at **steady-state** a constant and low level of ozone. The **photostationary state** expression for ozone is:

$$[O_3] = \frac{k_b\ [NO_2]}{k_a\ [NO]}$$

During the daytime, NO_2 can be removed slowly from the photostationary state cycle, as it reacts with hydroxyl radicals, producing nitric acid:

$$NO_2 + \cdot OH \rightarrow HNO_3$$

Like sulfuric acid, nitric acid contributes to acid deposition. Nitric acid is soluble in water and it may react with basic compounds such as ammonia and form nitrate salts, which can be deposited over the Earth’s surface as acid gases, acid solutions or acid salts.

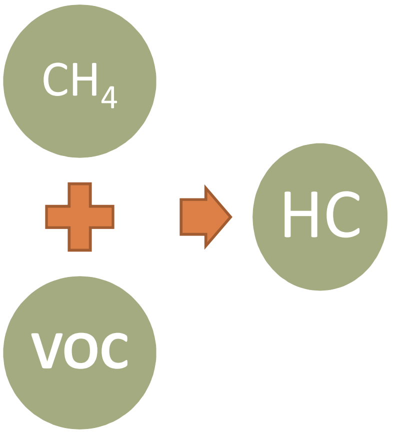


NO$_X$ emissions in the EU-28. (a) trend in NOX emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013

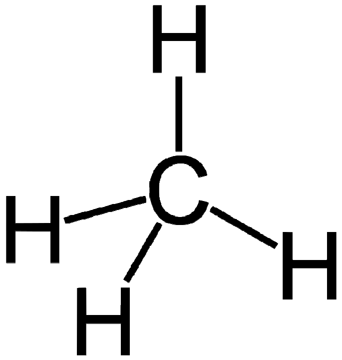
2.4. HYDROCARBONS

On a global scale most hydrocarbons (HC) are emitted from natural sources, principally vegetation and the decomposition of organic matter by bacteria.

Anthropogenic sources contribute to a considerably less significant fraction (1/7) of total ambient HC.



Methane is a colorless gas, odorless at low concentrations but with a sweetish chloroform-like odor at high concentration. It is the most long-lived (≈ 9-10 years), simple and abundant HC in the atmosphere (≈ 1.7 ppm)



“Methane 2D” by Palosirkka licensed under Public Domain

Effects

CH_4 has a negligible photochemical activity. As it is orders of magnitude less reactive than other HC it is usually excluded from reports, which refer to non-methane hydrocarbons (**NMHC**).

The main environmental concern with CH_4 is the role it plays as a greenhouse gas.

Sources of CH_4

Methane is emitted by natural sources such as decomposition of plant and animal matter by methane producing bacteria, cud-chewing animals, rice paddies and wetlands. The anthropogenic sources of methane are farming, production of fossil fuels, wet rice cultivation, biomass burning and landfills.

“Cow” by K. Hansen licensed under CC BY-SA 3.0

“Thailand rice” by Lakeway licensed under CC BY-SA 3.0

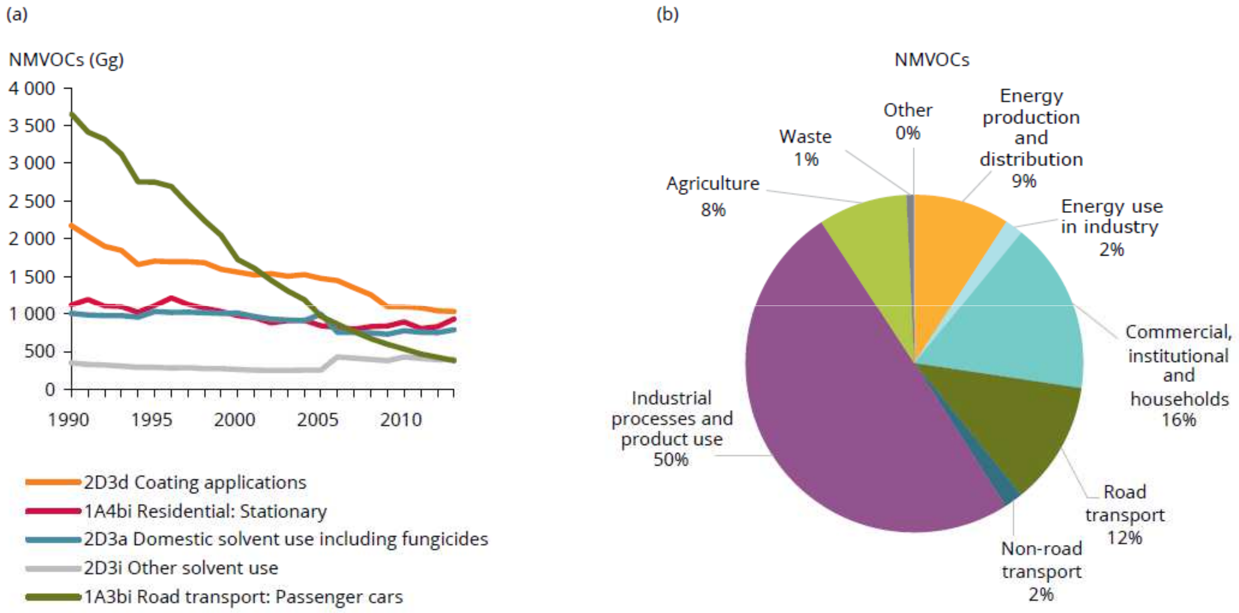
Volatile Organic Compounds (VOC) mean "organic compounds from anthropogenic and biogenic sources, other than methane, that are capable of producing photochemical oxidation by reactions with nitrogen oxides in the presence of sunlight" *Directive 2008/50/EC on ambient air quality and cleaner air for Europe*

The term **Non methanic Volatile Organic Compounds** (NMVOC) includes hydrocarbons (alkanes, alkenes y aromatics), oxygenated compounds (alcohols, aldehydes, ketones, acids and ethers) and halogenated compounds.

Sources of NMVOC

On a **global scale** natural NMVOC emissions are predominant. The largest source by far, is vegetation. However, on a **local scale**, anthropogenic emissions can be similar or even higher than the natural ones. The major anthropogenic sources of NMVOC in urban areas include solvent usage, combustion (motor vehicles + fossil fuel power plant emissions) and fuel storage and transport.

Fuel tank by Gnangarra licensed under CC BY 2.5



NMVOC emissions in the EU-28: (a) trend in NMVOC emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013

Photochemical smog

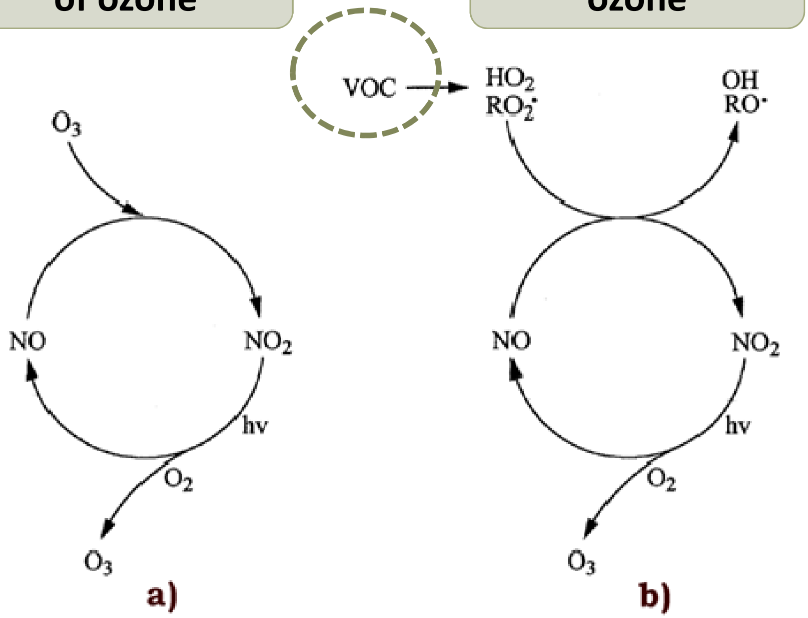
The term smog is a shorthand combination of “smoke-fog”. It is code word for *photochemical oxidant smog*.

Smog is characterized by a relatively high level of oxidants, which irritate the eyes and throat and damage plants.

Photochemical smog forms when NOx and VOCs react in the presence of solar radiation. Smog initiates when organic gases photolyze or are oxidized by different compounds to produce radicals. These radicals convert NO to NO_2, which photolyzes to O, which reacts with O_2 to form **ozone** (O_3) and other **oxidation products** such as peroxyacyl nitrate (PAN) and aldehydes. Of all these oxidation products O_3 is the most notorious one due to its high levels and its effects on human health, plants and materials.

NO net formation of ozone

Net formation of ozone



Schematics of the reactions involved in NO-to-NO_2 conversion and ozone formation. a) in the absence of VOCs and b) in the presence of VOCs

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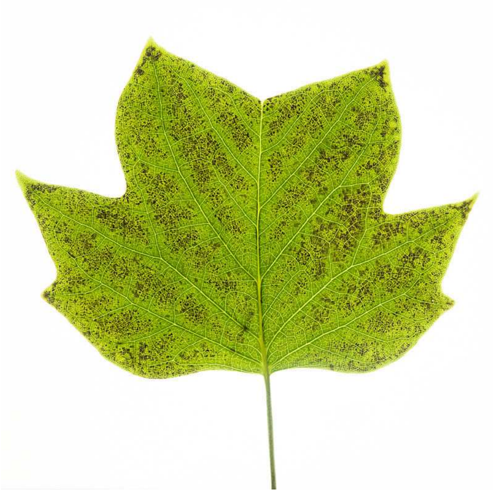


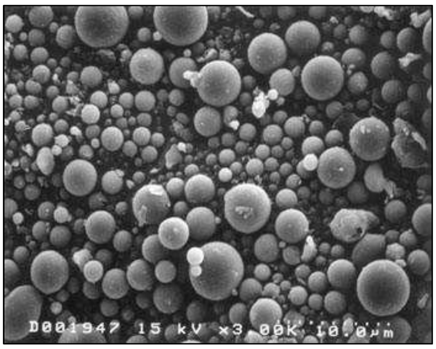
"Tuliptree leaf with ozone damage" by M. Długosz licensed under CC BY-SA 4.0

A security agent with an anti-pollution mask in Hong Kong by Odessa3 licensed under Public Domain

2.5. ATMOSPHERIC AEROSOL

In addition to gases, the atmosphere contains a mixture of small (0.001-100 µm) liquid and solid particles that are suspended in the air. These particles are referred to as **aerosols** or **Particulate Matter (PM)**. They be grouped into two broad classifications:

- **Primary aerosols**, emitted directly from sources
- **Secondary aerosols**, formed in the atmosphere by chemical or physical reactions.



Photomicrograph of fly ash by United States Department of Transportation licensed under Public Domain

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Sources of atmospheric aerosol

- **Natural sources** include volcanic eruptions, soil-dust, sea-spray uplift, natural biomass burning fires and biological material release.
- **Anthropogenic sources** include fugitive dust emissions (dust from road paving + building construction and demolition), fossil-fuel combustion, anthropogenic biomass burning and industrial emissions.

Chemical composition of atmospheric aerosol

PM's composition is highly variable and directly associated with the characteristics of the surrounding gas. It includes inorganic ions and elements, elemental carbon, organic compounds and crustal substances. The organic fraction is particularly difficult to characterize, since it often contains thousands of organic compounds.

Contribution of different natural and anthropogenic sources to the global amount of Particulate Matter (PM)

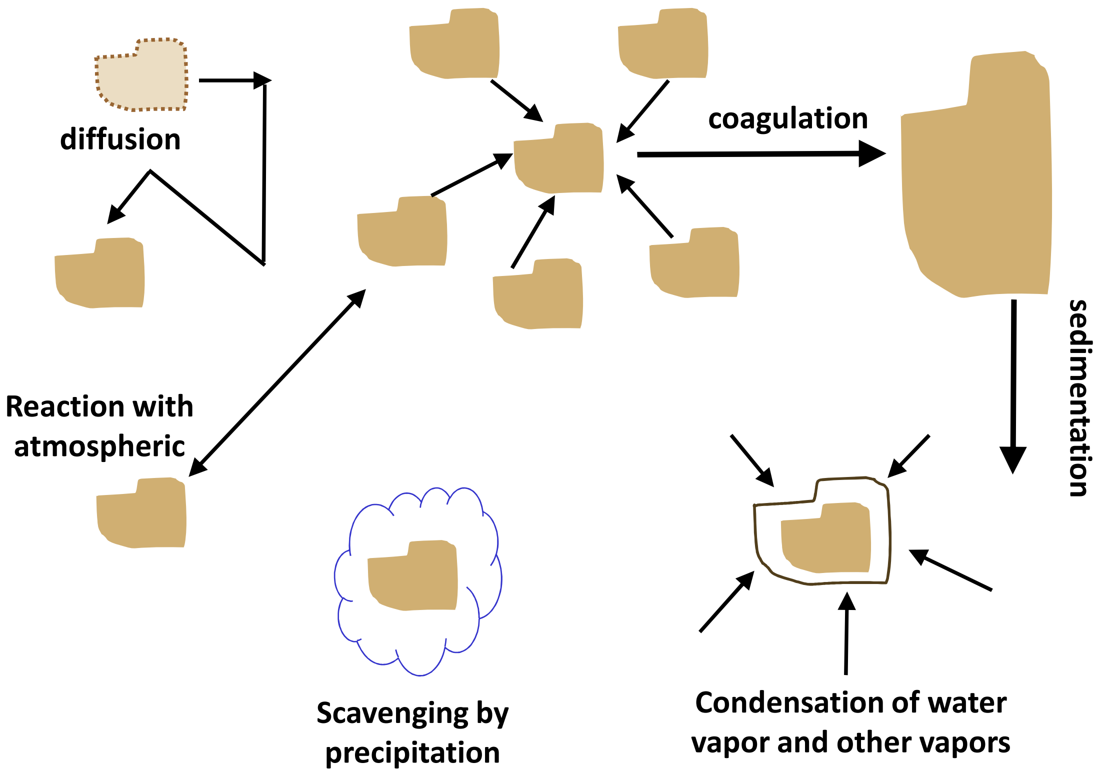
	Annual production or emission ($Tg \cdot y^{-1}$)	
	Range	**Probable estimation**
Natural		
Wind erosion	1000 – 3000	1500
Marine aerosol	1000 - 10000	1300
Volcanoes	4 – 10000	30
Primary biological particles	26 – 80	50
Forest fires	3 – 150	20
Secondary inorganic particles	100 – 260	180
Secondary organic particles	40 – 200	160
Anthropogenic		
Direct emissions	50 – 160	120
Secondary inorganic particles	260 – 460	330
Secondary organic particles	5 – 25	10

Smoke from a wildfire by Nerval licensed under Public Domain

Processes atmospheric aerosol undergoes in the atmosphere

Next figures illustrates the primary processes involved in introducing mass into each size range and the removal mechanisms.

Small colloidal particles are subject to **diffusion** processes. Some particles serve as nuclei upon which **vapors condense**. Some particles **react chemically** with atmospheric gases or vapors to form different compounds. When two particles collide in the air, they tend to adhere to each other, thereby forming progressively larger and larger particles by **coagulation**. The larger the particle becomes, the greater its weight and the greater its likelihood of falling to the ground: **sedimentation** (**dry deposition**). Washout of particles by rain or other forms of precipitation (snowflakes, hail, mist, fog…) is a common form of agglomeration and sedimentation (**wet deposition**).



Effects of atmospheric aerosol

- They can travel long distances and serve as vehicles on which pollutants are able to reach water bodies and soils.
- They are hazardous for human health, as they are small enough to be absorbed deeply into lungs and cause health problems.
- They are also a major contributor to reduced visibility.

"Hong Kong haze comparission" by Tokyoahead licensed under CC BY 3.0

Size/distribution of atmospheric aerosol

PM can be divided into **three modes**: nucleation mode, accumulation mode and large mode. A mode is a region of the size spectrum in which distinct peaks in concentration occur.

- **Aitken nuclei** are those that are smaller than 0.1 µm in diameter. They are also known as **Cloud Condensation Nuclei** (CCN) as they can become activated to form to cloud or fog droplets in the presence of supersaturation of water vapor. They are mainly produced when hot gases become supersaturated, condensate and coagulate. PM in this size range have a short lifetime of the order of minutes, as they increase in size by coagulation. That is why this mode is also known as **nucleation mode**.

- **Accumulation mode** consists of particles with a diameter between 0.1 and 2.5 µm. These particles have significant but small settling velocities; therefore, they can be suspended in the air for long periods of time and travel long distances. They tend to form from the condensation of *low volatility* gases and coagulation of CCN.

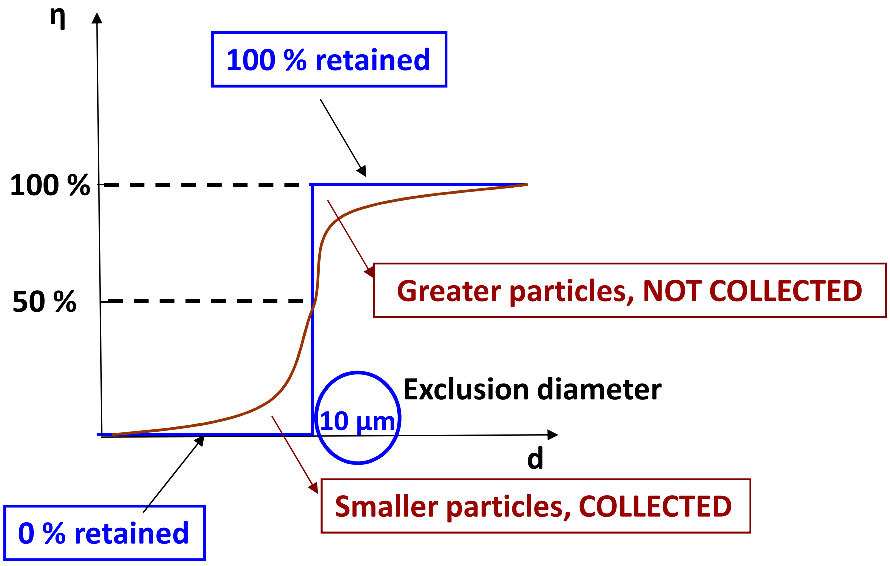
Particles in the nucleation and accumulation modes together are **fine particles.**

- **Large aerosol particles**, usually 2.5 to 10 µm in diameter, originate from windblown dust, sea salt and other debris in the atmosphere as well as from mechanical processes, grinding, pulverization, and so on. Coarse mode particles are heavy enough to sediment out rapidly. They are removed from the atmosphere within hours. However, this mode can predominate near its sources.

Air quality standards which regulate the total suspended particulates classify the particles according to their size based on the 50% cut-off point. The measurements are taken by **specific sampling instruments** with inlets using **size exclusion mechanisms** to segregate the mass of each size fraction. Then, the mass of particles falling into two size categories is measured: $PM_{2.5}$ and PM_{10}.

Air quality monitoring station by Bidgee licensed under CC BY 3.0

Theoretical and real efficiencies for a sampling device calibrated for PM_{10}



PM_{10} refers to “particulate matter which passes through a size-selective inlet as defined in the reference method for the sampling and measurement of PM_{10}, EN 12341, with a 50 % efficiency cut-off at 10 µm **aerodynamic diameter**” *Directive 2008/50/EC on ambient air quality and cleaner air for Europe*

$PM_{2.5}$ refers to “particulate matter which passes through a size-selective inlet as defined in the reference method for the sampling and measurement of $PM_{2.5}$, EN 14907, with a 50 % efficiency cut-off at 2.5 µm **aerodynamic diameter**” *Directive 2008/50/EC on ambient air quality and cleaner air for Europe*

Since most particles are not spherical, the particle size is often described using an **equivalent diameter**. The equivalent diameter is the diameter of a sphere that has the same fluid properties as the particle under consideration.

Assuming spherical particles with a diameter ≈ 1 µm **Stokes' Law** can be applied:

$$Vt = \frac{g\, d^2\, (\rho_p - \rho_g\,)}{18\mu}$$

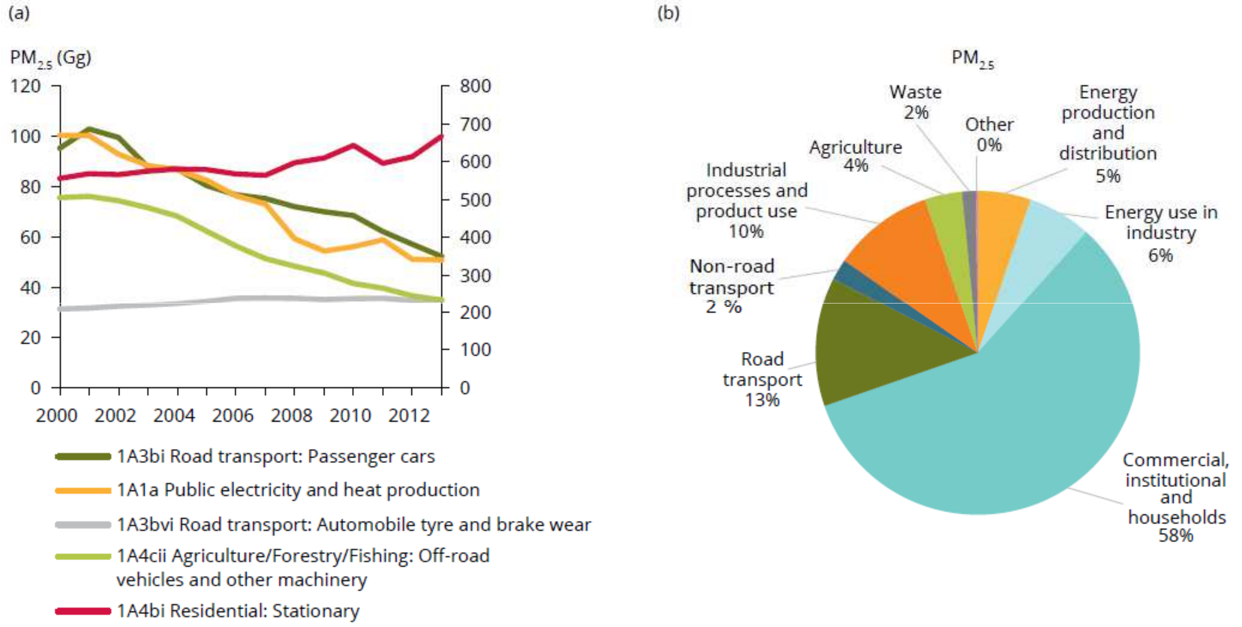
Where: v_t = terminal or settling velocity [L·T^{-1}]
d= diameter of the particles [L]
g = acceleration of gravity [L·T^{-2}]
ρ_p = density of the particles [M·L^{-3}]
ρ_g = air density [M·L^{-3}]
μ = air viscosity [M·L^{-1}·T^{-1}]

From previous equation, the effective diameter for an irregular particle is derived: Stokes' diameter.

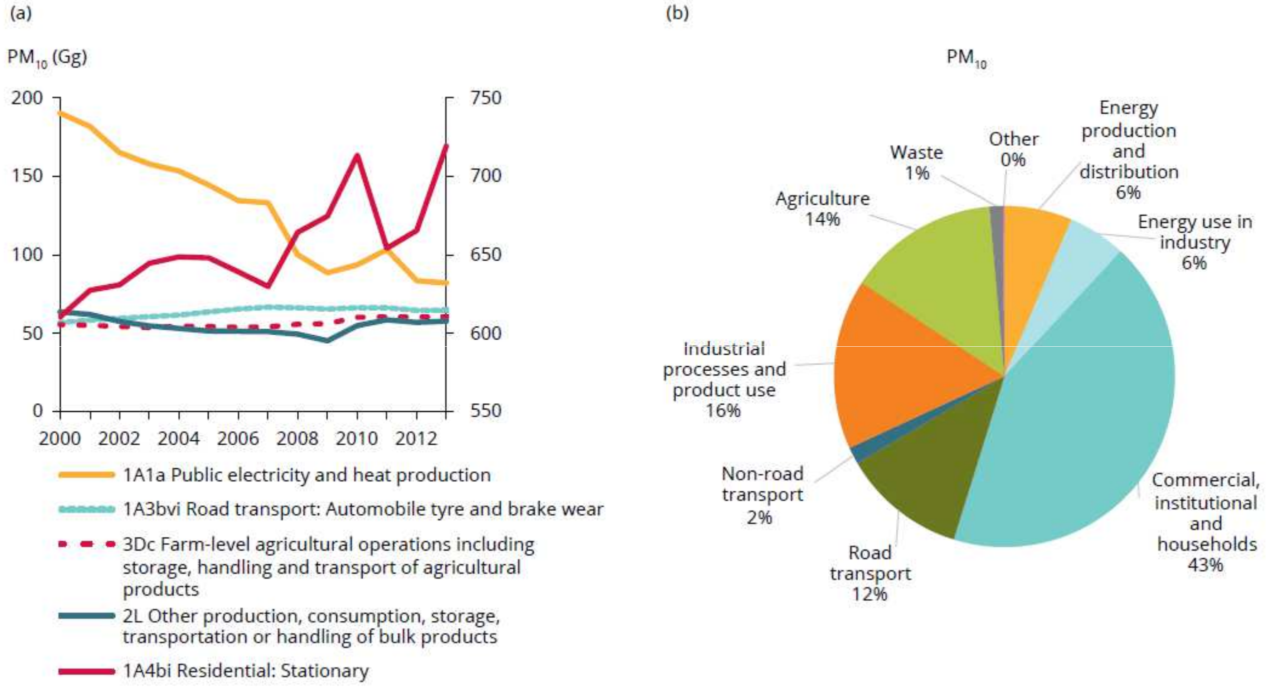
Stokes' diameter is the diameter of a sphere with the same density and settling velocity as the particle

Deviations: 1) PM < 1 µm as settling particles "slip between" air molecules and 2) PM >10 µm because they settle rapidly and generate turbulence as they fall Thus, Stokes' Law is only applicable between 1-10 µm.

Since the density of a particle is often not known an arbitrary density of 1 g·cm^{-3} is conventionally assigned to ρ_p; when this is done, the diameter is called the **aerodynamic diameter**.



PM$_{2.5}$ emissions in the EU-28: (a) trend in PM2.5 emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013



PM$_{10}$ emissions in the EU-28: (a) trend in PM10 emissions from the five most important key categories, 1990–2013; (b) share of emissions by sector group, 2013