ENV 320 – Tropospheric Chemistry

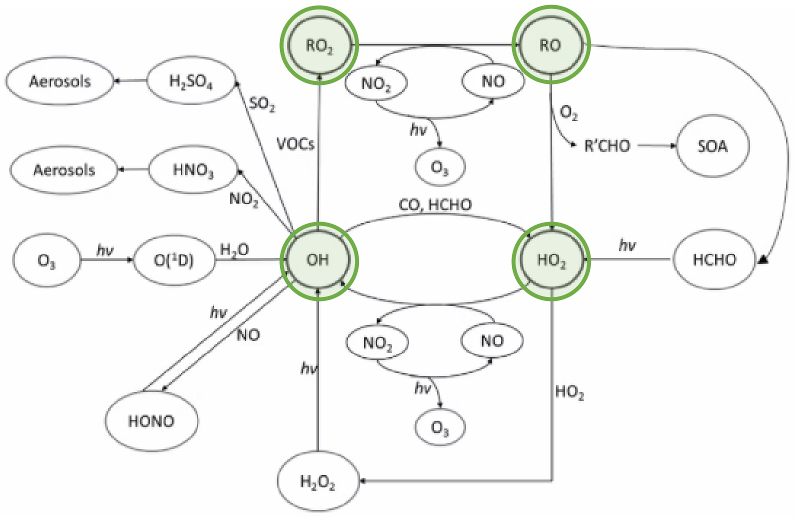
Exercise session

02.05.2025

Where does ozone come from in the urban atmosphere ?

0	✕	It is directly emitted by cars and industrial sources.
0	✓	From reactions involving VOCs and NOx through photochemical reactions.
0	✕	It comes from trees and other natural sources emitting ozone.
0	✕	It is produced by the combustion of fossil fuels.

Which species are radicals ?



0 ✕
H_2SO_4, HNO_3

0 ✕
HONO, H_2O_2, HCHO

0 ✓
HO_2, OH, RO_2, RO

0 ✕
O_3, $O(^1D)$

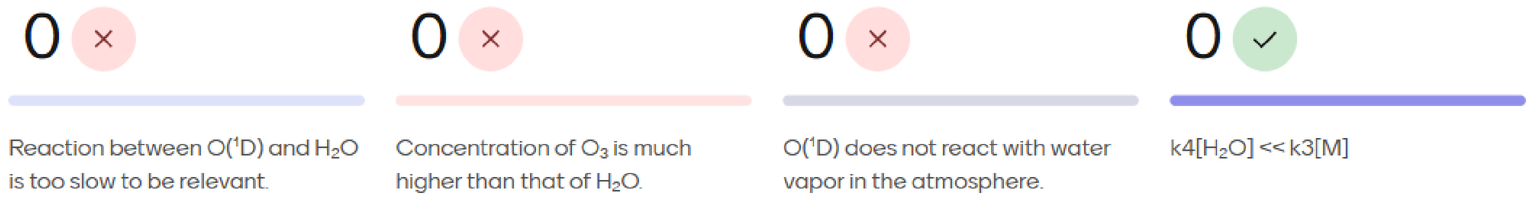
Why can k4[H2O] often be neglected in the steady-state equation for $[O(^1D)]$?

$$[O(^1D)] = \frac{j_{O_3 \rightarrow O(^1D)}[O_3]}{k_3[M] + k_4[H_2O]}$$

The reaction is actually **fast** and a key source of OH in the atmosphere.

While $[O_3]$ matters for $O(^1D)$ production, the **neglect of k_4[H2O]** relates to **loss**, not ozone concentration.

$O(^1D)$ **does** react with H_2O, producing 2 OH radicals.



Reaction between $O(^1D)$ and H_2O is too slow to be relevant.

Concentration of O_3 is much higher than that of H_2O.

$O(^1D)$ does not react with water vapor in the atmosphere.

$k4[H_2O] << k3[M]$

Formation rate of $O(^1D)$

Remember stratospheric chemistry lecture: excited state of oxygen

Ozone is at the origin!

Production of $O(^1D)$: P

$$O_3 + h\nu \xrightarrow{1b} O_2 + O(^1D)$$

«*j*» is used for photolysis rate = k_1

$$j_{O_3 \rightarrow O(^1D)}[O_3] = (k_3[M] + k_4[H_2O])[O(^1D)]$$

Losses of $O(^1D)$: L

$$O(^1D) + M \xrightarrow{3} O + M$$

M is N_2 or O_2, quenching to ground state, and $O + O_2 \rightarrow O_3$; null cycle

$$O(^1D) + H_2O \xrightarrow{4} 2\,OH$$

Fast loss of $O(^1D)$

→ pseudo steady state

→ P=L

$$\rightarrow \frac{d[O(^1D)]}{dt} \approx 0$$

$$[O(^1D)] = \frac{j_{O_3 \rightarrow O(^1D)}[O_3]}{k_3[M] + k_4[H_2O]}$$

EXERCISE :

Calculate rates of production for various relative humidities.

Formation rate of $O(^1D)$

Consider the following:

- At 298 K, for the atmospheric mixture M = N_2/O_2 (>99%):

$$k_3\left(M = \frac{N_2}{O_2}\right) = 2.9 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1}$$

$$k_4 \qquad 2.2 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

- The first-order photolysis rate coefficient of O_3 → $O(^1D)$:

$$j_{O_3 \rightarrow O(1D)} = 6 \times 10^{-5}\ s^{-1}$$

- Considering mixing ratios, and considering the N_2/O_2 mixture (M) is ~100% of the dry atmosphere, we have:
  $[O_3] = \xi_{O_3}[M]$, and $[H_2O] = \xi_{H_2O}[M]$

- So:

$$\boxed{[\mathrm{O}(^1\mathrm{D})] = \frac{j_{\mathrm{O_3 \rightarrow O(^1D)}}\xi_{\mathrm{O_3}}[\mathrm{M}]}{k_3[\mathrm{M}] + k_4\xi_{\mathrm{H_2O}}[\mathrm{M}]} = \boxed{\frac{j_{\mathrm{O_3 \rightarrow O(^1D)}}\xi_{\mathrm{O_3}}}{k_3 + k_4\xi_{\mathrm{H_2O}}}}}$$

$$\boxed{[\mathrm{O}(^1\mathrm{D})] = \frac{j_{\mathrm{O_3 \rightarrow O(^1D)}}[\mathrm{O_3}]}{k_3[\mathrm{M}] + k_4[\mathrm{H_2O}]}}$$

- At midlatitudes at the surface at noon, we assume: $\xi_{O_3} \approx 50$ ppb = 50×10^{-9}

- For ξ_{H_2O} we need the relative humidity.

$$\xi_{H_2O} = RH \times \xi_{H_2O,\,sat}$$

$$\xi_{H_2O,\,sat} = 20.1\,\frac{g}{kg}\quad at\ 298\ K$$

EXERCISE :

Calculate rates of $O(^1D)$ production for relative humidities of 20%, 50% and 90%.

Formation rate of $O(^1D)$

$$[O(^1D)] = \frac{j_{O_3 \rightarrow O(^1D)} \xi_{O_3} [M]}{k_3 [M] + k_4 \xi_{H_2O} [M]}$$

$$= \frac{j_{O_3 \rightarrow O(^1D)} \xi_{O_3}}{k_3 + k_4 \xi_{H_2O}}$$

- At RH 20%: $\xi_{H_2O} = 0.2 \times 0.021 = 0.0042$

$$[O(1D)] = \frac{6 \times 10^{-5} \times 50 \times 10^{-9}}{(2.9 \times 10^{-11}) + (2.2 \times 10^{-10} \times 0.0042)} = 0.1003\ \frac{molecule}{cm^3}$$

- At RH 50%: $\xi_{H_2O} = 0.5 \times 0.021 = 0.0105$

$$[O(1D)] = \frac{6 \times 10^{-5} \times 50 \times 10^{-9}}{(2.9 \times 10^{-11}) + (2.2 \times 10^{-10} \times 0.0105)} = 0.0958\ \frac{molecule}{cm^3}$$

- At RH 90%: $\xi_{H_2O} = 0.9 \times 0.021 = 0.0189$

$$[O(1D)] = \frac{6 \times 10^{-5} \times 50 \times 10^{-9}}{(2.9 \times 10^{-11}) + (2.2 \times 10^{-10} \times 0.0189)} = 0.0905\ \frac{molecule}{cm^3}$$

Small changes with RH because $k_4 \xi_{H_2O} << k_3$ at the denominator

Things are different when considering the production of OH

Formation rate of OH radical

$$O(^1D) + H_2O \xrightarrow{4} 2\,OH$$

$$\boxed{P_{OH} = 2k_4[O(^1D)][H_2O]}$$

Replace [O(^{1}D)] with
(from previous slide)

$$[O(^1D)] = \frac{\boxed{j_{O_3\to O(^1D)}[O_3]}}{k_3[M] + \cancel{k_4[H_2O]}}$$

$$\boxed{P_{OH} = \frac{2\,j_{O_3\to O(^1D)}k_4}{k_3}\frac{[H_2O]}{[M]}[O_3]}$$

Now we have a direct dependence on [H_2O] (and hence RH)

$$\begin{aligned}\epsilon_{OH} &= \frac{\boxed{2\,k_4[O(^1D)][H_2O]}}{\boxed{j_{O_3\to O(^1D)}[O_3]}} \\ &= \frac{2k_4[O(^1D)][H_2O]}{(k_3[M] + k_4[H_2O])[O(^1D)]} \\ &= \frac{2\,k_4[H_2O]}{k_3[M] + k_4[H_2O]} \\ &\cong \frac{2\,k_4[H_2O]}{k_3[M]} = \frac{2k_4\xi_{H_2O}}{k_3}\end{aligned}$$

Ratio of **OH produced from O(^{1}D)** to **O(^{1}D) produced**

RH(%)	10	25	50	80
ϵ_{OH}	0.047	0.12	0.23	0.38

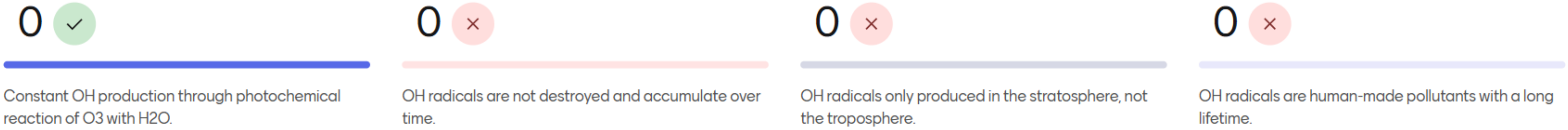
At 80% RH, nearly 40 % of the O(^{1}D) formed leads to OH radicals.

Why are there always enough OH radicals in the troposphere ?

OH radicals are **constantly destroyed** in reactions but are **rapidly recycled** in photochemical cycles.

OH radicals are primarily produced in the **troposphere**, especially from ozone photolysis and reactions with water vapor.

OH radicals are **not human-made pollutants** and have a **short lifetime**, reacting quickly with other compounds.



0 ✓

Constant OH production through photochemical reaction of O3 with H2O.

0 ✗

OH radicals are not destroyed and accumulate over time.

0 ✗

OH radicals only produced in the stratosphere, not the troposphere.

0 ✗

OH radicals are human-made pollutants with a long lifetime.

What is the average concentration of OH radicals in the atmosphere ?

0 ✗	0 ✓	0 ✗	0 ✗
10^-6 molecules/cm3	10^6 molecules/cm3	10^-4 molecules/cm3	10^24 molecules/cm3

Which reaction is **not** an OH sink ?

OH **formation**

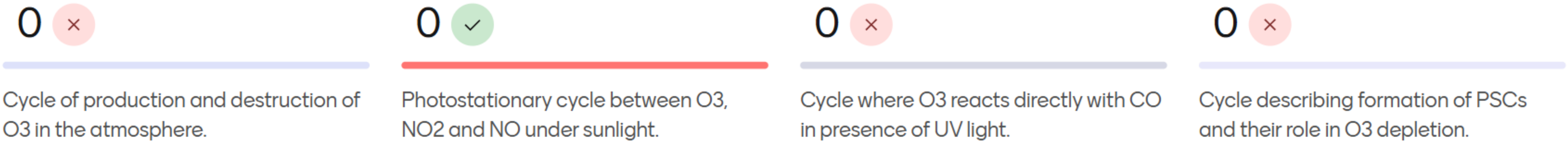
- 0 ✗ Reaction with VOCs
- 0 ✗ OH + NO --> HONO
- 0 ✓ HO2 + NO --> OH + NO2
- 0 ✗ OH + NO2 --> HNO3
- 0 ✗ OH + CO + O2 --> HO2 + CO2

What is the Leighton Cycle ?

This describes the **Chapman cycle**.

This describes a different atmospheric process. The Leighton cycle involves **NO_2** and ozone, not **CO**.

This describes the **processes** related to **ozone depletion in the polar regions**, specifically in winter, but is not related to the Leighton cycle, which focuses on **OH** radical formation.



0 ✗

Cycle of production and destruction of O3 in the atmosphere.

0 ✓

Photostationary cycle between O3, NO2 and NO under sunlight.

0 ✗

Cycle where O3 reacts directly with CO in presence of UV light.

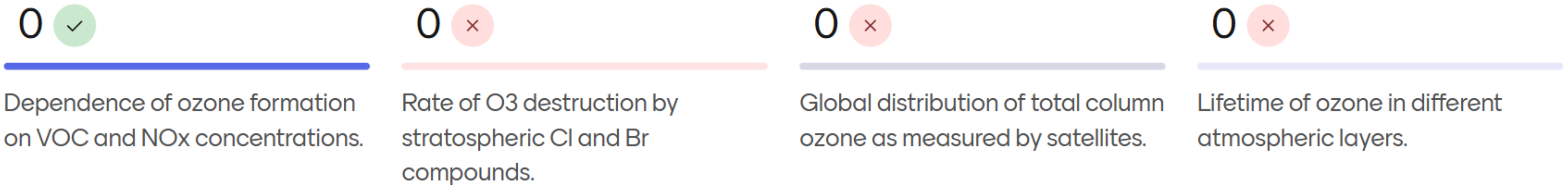
0 ✗

Cycle describing formation of PSCs and their role in O3 depletion.

What does the ozone isopleth plot show ?

Refers to **stratospheric ozone depletion**, not **tropospheric ozone formation.**

Ozone mapping



0 ✓	0 ✗	0 ✗	0 ✗
Dependence of ozone formation on VOC and NOx concentrations.	Rate of O3 destruction by stratospheric Cl and Br compounds.	Global distribution of total column ozone as measured by satellites.	Lifetime of ozone in different atmospheric layers.

The most important oxidants are :

0 ×

Day: O_3 ; Night: NO_3

0 ✓

Day: OH ; Night: NO_3

0 ×

Day: NO_x ; Night: NO_3

0 ×

Day: OH ; Night: NO_2

CH_4 oxidation

$$CH_4 + OH \xrightarrow{1} CH_3 + H_2O \qquad \text{(R1)}$$

CH_3… methyl radical, reacts instantaneously

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$$

CH_3O_2… methyl peroxy radical, reacts instantaneously

$$CH_4 + OH \xrightarrow[O_2]{1} CH_3O_2 + H_2O$$

Remember the CO + OH reaction, analogy.

Methane has a lifetime of approx 9 years against OH. Because of its high concentration (~1920 ppb) it has an important effect on tropospheric chemistry in the remote atmosphere.

In exercises, calculate the lifetime of CH_4.

CH_4 oxidation

$CH_4 + OH \xrightarrow{1} CH_3 + H_2O$ (R1)

CH_3… methyl radical, reacts instantaneously

Rate coefficient for R1 : $k_1 = 2.45 \cdot 10^{-12} \cdot e^{(-1775/T)}$ cm^3 $molecule^{-1}$ s^{-1}

T = 273 K

[OH] = 10^6 molecules cm^{-3}

Lifetime of CH_4 against OH :

$$\frac{d[CH_4]}{dt} = -k[CH_4][OH]$$

$$\frac{d[CH_4]}{dt} = -k_{eff}[CH_4] \quad \text{with} \quad k_{eff} = k[OH]$$

Pseudo-first order because [OH] assumed constant on the timescale of methane decay

$$\tau = \frac{1}{k_{eff}} = \frac{1}{k[OH]} = \frac{1}{2.45 \cdot 10^{-12} \cdot e^{\left(-\frac{1775}{273}\right)} \cdot 10^6} = 271984064.3\, s = \mathbf{8.6\ years}$$

Methane has a lifetime of approx 9 years against OH. Because of its high concentration (~1920 ppb) it has an important effect on tropospheric chemistry in the remote atmosphere.

Is there an annual cycle in the global ozone distribution ?

- O_3 generally **low** throughout the year over the **tropical oceans**.
- Over **middle latitudes** : **seasonal variations** with pronounced **spring maximum**.
  - March – May for Northern hemisphere (NH)
  - September – November for Southern hemisphere (SH)
- Over **industrialized regions** of NH : high O_3 concentrations during summer
  - Industrial areas emit large amounts of **NOx** and **VOCs** = chemical ingredients for O_3 formation.
  - **Longer days** and **stronger sunlight** in **summer** increase photolysis rates.

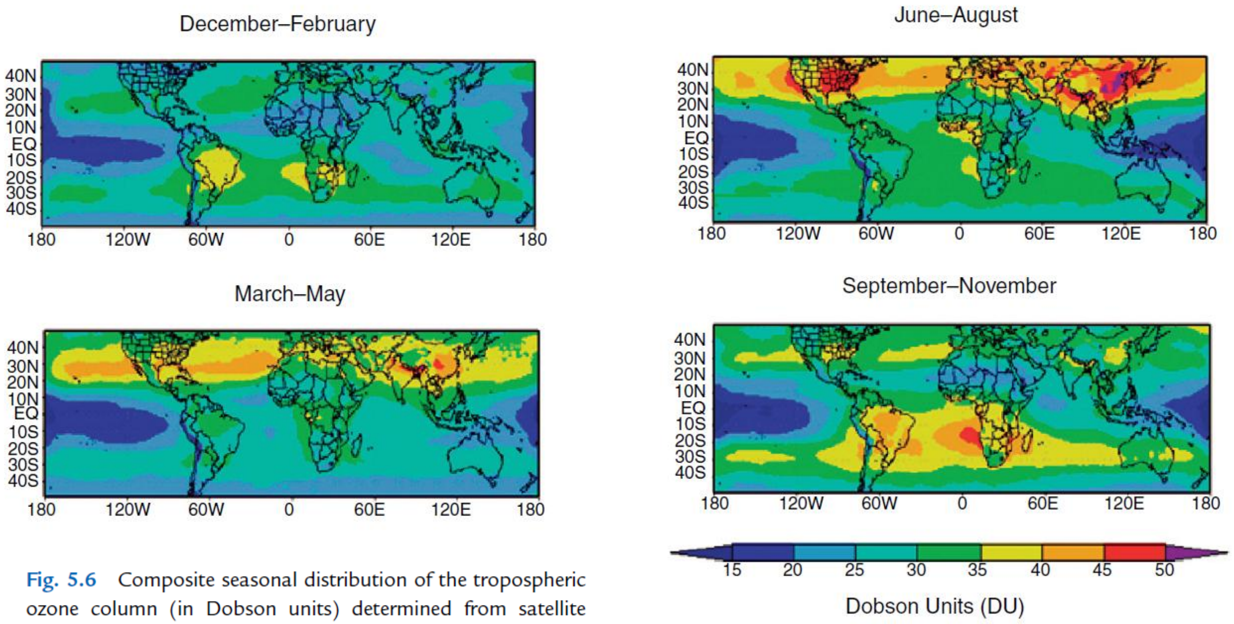


Fig. 5.6 Composite seasonal distribution of the tropospheric ozone column (in Dobson units) determined from satellite measurements from 1979 to 2000. [From *Atmos. Chem. Phys.* **3**, 895 (2003).]

Wallace and Hobbs, 2006

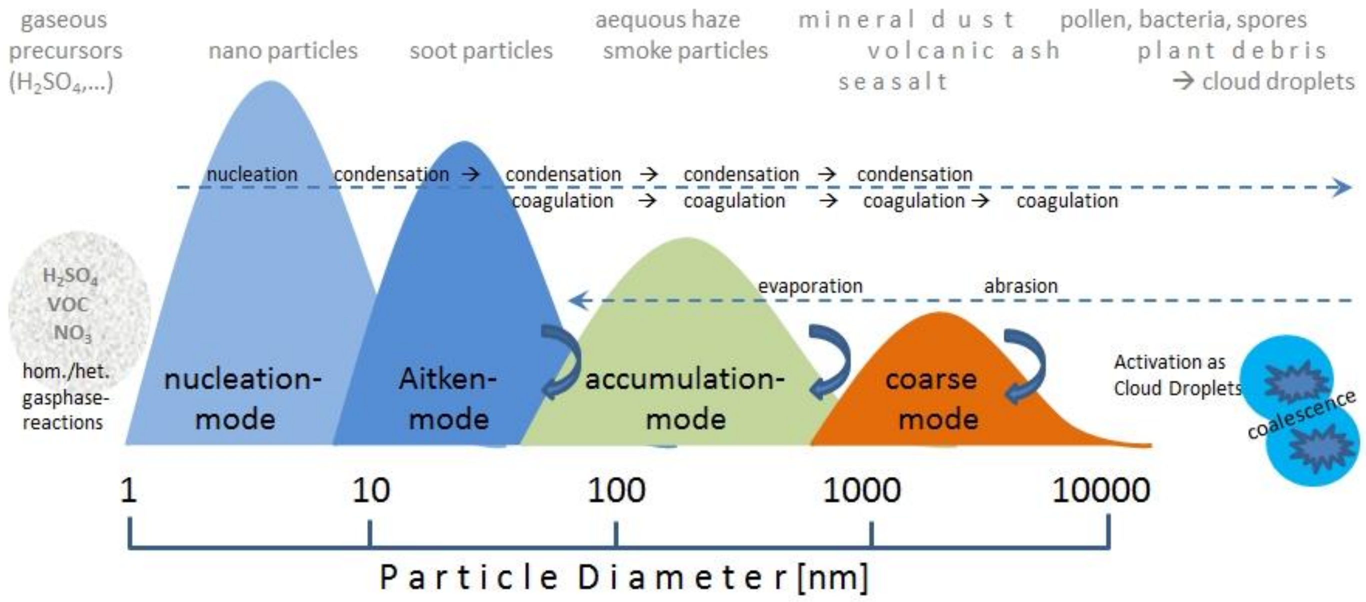
0 ✓

Yes

0 ×

No

What is the size range of aerosols ?



0 ✕

10 - 1000 nm

0 ✕

10 - 1000 µm

0 ✓

1 - 10000 nm

0 ✕

1 - 100 nm

https://www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/aerosol/cont_nav/particle_size_distribution_node.html

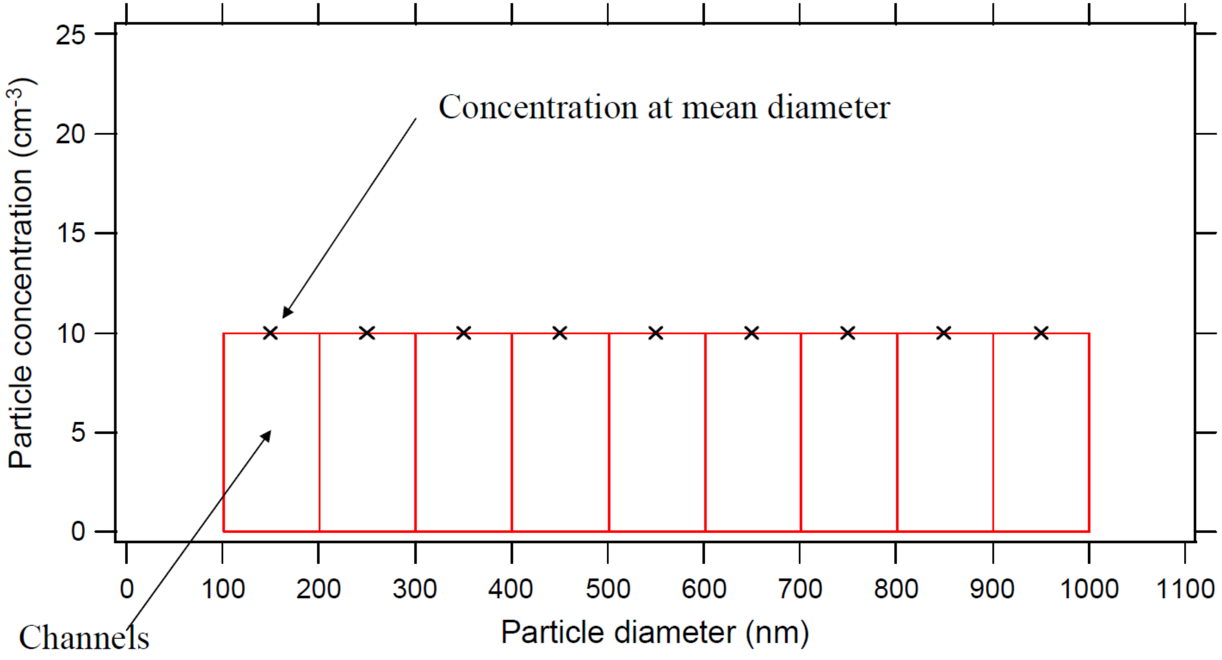
How is the total particle number of atmospheric aerosols typically expressed ?

The **Knudsen number** describes flow regimes, not particle number distributions.

0 ✗	0 ✗	0 ✓	0 ✗
By the mass concentration in micrograms per cubic meter (µg/m^3).	As the surface area per unit volume.	As number distribution per logarithmic diameter interval (dN/dlogDp).	By the Knudsen number.

Derivation of the size distribution

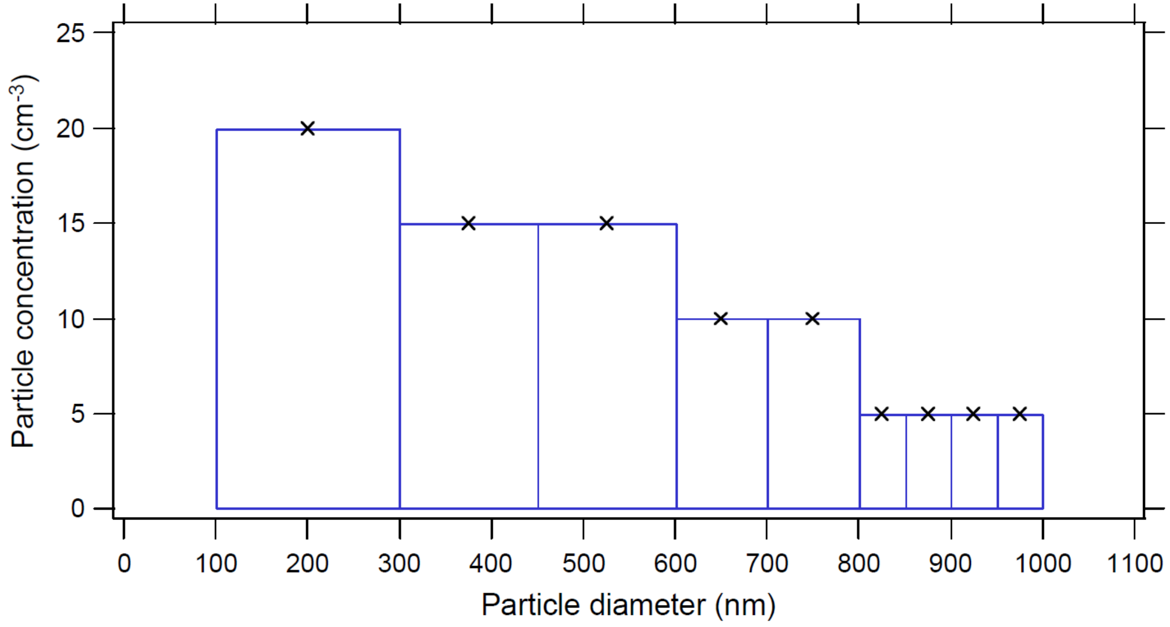
Example 1:
9 size classes (instrumental channels) with a width of **100 nm**, with **10 particles cm^{-3}** per channel. We consider the measured concentration (dN) in each channel.



Example 2:
We now use a different measurement instrument with **different channel widths**.

→ The shape of the size distribution changes, while the aerosol population is exactly the same.

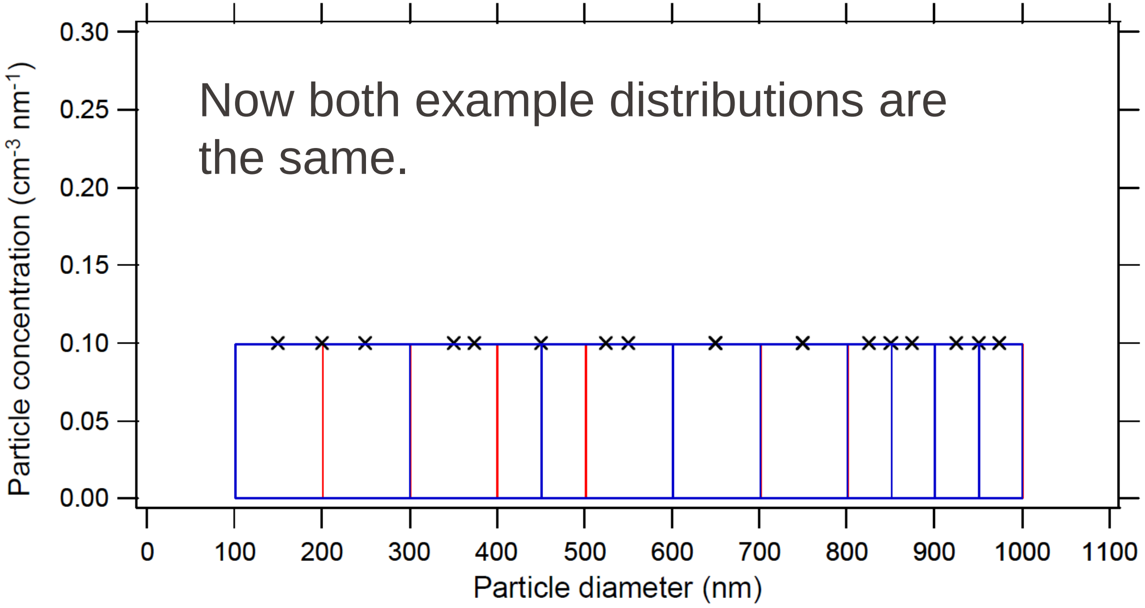
→ This is **problematic**.



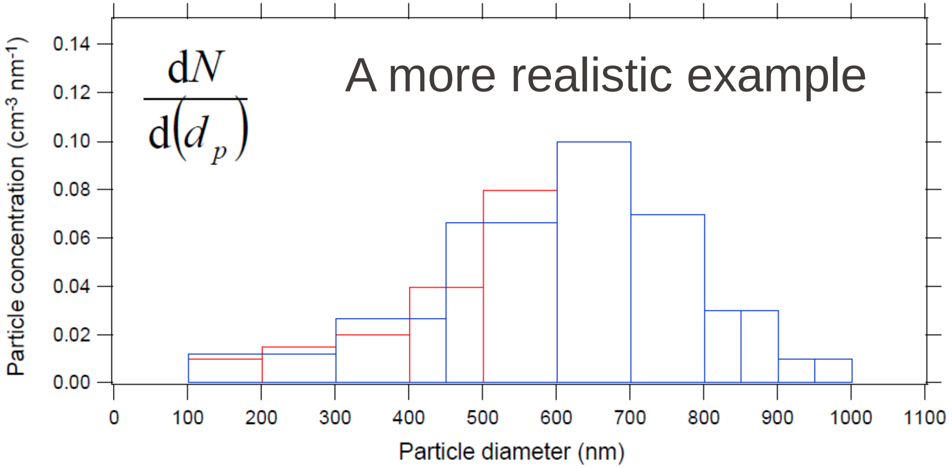
Derivation of the size distribution

To avoid this problematic effect, we divide the measured concentrations by the width of the channel (**normalization**).

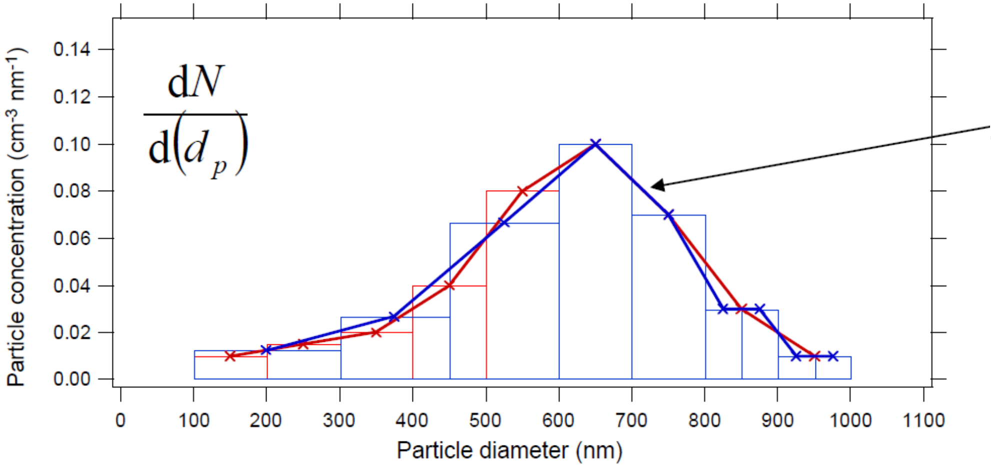
$$\frac{dN}{d_p^{(n+1)} - d_p^{(n)}} := \frac{dN}{d(d_p)}$$



Now both example distributions are the same.



A more realistic example



Nearly the same despite different channels

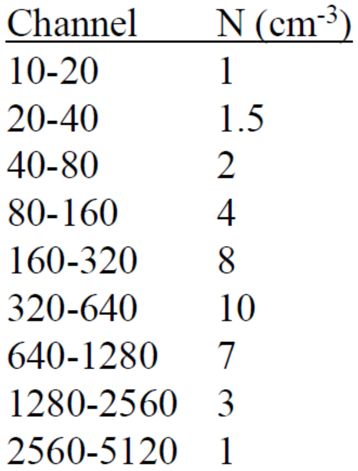
Derivation of the size distribution

In the atmosphere the **size range of aerosol particles** ranges over **several orders of magnitude**, we therefore use a **logarithmic scale** for the diameter axis.
(Note, also the size channels of measurement systems are selected to be roughly logarithmic.)

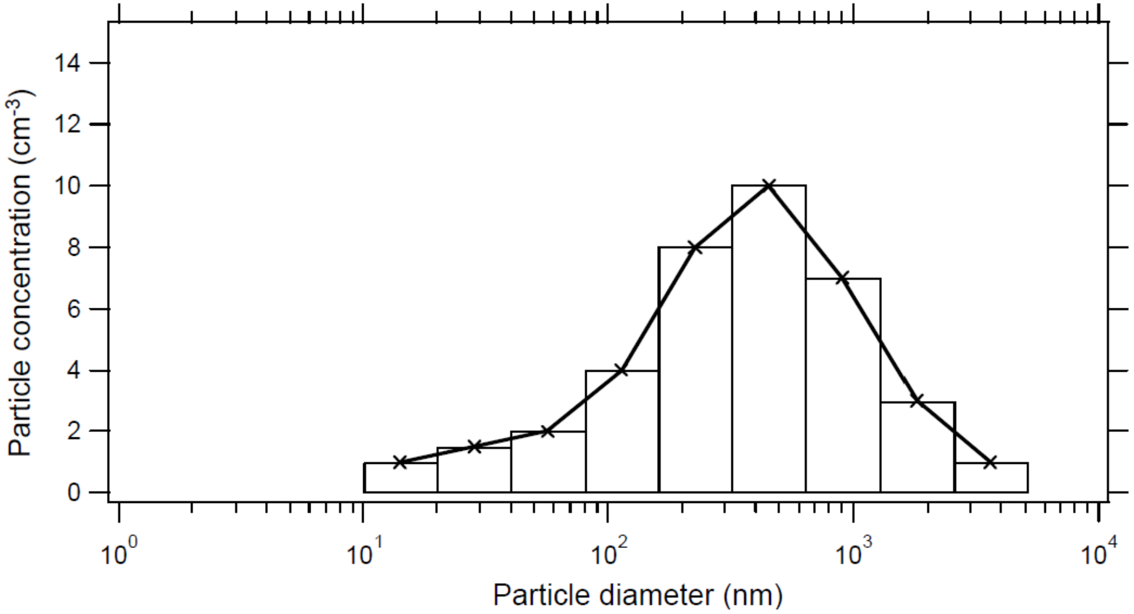
$$\frac{dN}{dlogd_p} = \frac{dN}{\log\left(\frac{d_p^{u.b.}}{d_0}\right) - \log\left(\frac{d_p^{l.b.}}{d_0}\right)} = \frac{dN}{\log\left(\frac{d_p^{u.b.}}{d_p^{l.b}}\right)}$$

log a – log b = log(a/b)

An even more realistic example:



Channel	N (cm^{-3})
10-20	1
20-40	1.5
40-80	2
80-160	4
160-320	8
320-640	10
640-1280	7
1280-2560	3
2560-5120	1



u.b. upper bound of size channel
l.b. lower bound

d_0 is needed because we cannot use the logarithm for a dimension (only for a number)