IEooc_Background2_Exercise1: Global Warming Potential (GWP) calculations

Sample solution (*) See accompanying Excel file for additional calculations)

Goal: *Understand and replicate central calculations of the atmospheric physics of greenhouse gases (GHG) and the global warming potential to compare the impact of different GHG on global warming.*

Hint: *The numeric values in this exercise were taken from the 4th IPCC Assessment Report (AR), where enough documentation is provided to reproduce the final GWP results. Numbers from the newly released 6th AR are also provided in the sample solution, but without calculation details.*

Task 1: CO_2 content of the atmosphere: With a given average CO_2-volume concentration of the atmosphere of 410 ppm: (1 ppm = 1 part per million)

(a) How much is that in %?
(b) How much volume of CO_2 is contained in a cubic meter (m^3) of air?
(c) How large is the mass share of CO_2 in the atmosphere (for dry air), both in % and in ppm, under the assumption that both CO_2 and air can be described as an ideal gas?

Answer*:

(a) One percent is one over a hundred. 100% are 100 over a hundred, which is also 1 million of a million (ppm). 1 % is then 1 Million / 100 = 10000 of a million (ppm). 410 ppm are then 410/10000 % = 0.041%, or 0.41 per mille (one over a thousand).
(b) One percent of a cubic meter (1000 liter) are 10 liter, and 0.041 of that are 0.41 liter.
(c) There are different ways to arrive at this result:

The average molar mass of air, M_L = 28.96 g/mol.
(https://de.wikipedia.org/wiki/Mittlere_molare_Masse)

Intuitive approach: If a certain share of a given volume of air has a higher molar mass than the average (44.01 instead of 28.96 g/mole), its mass share is higher by a factor of 44.01/28.96.

Exact calculation: The value we are looking for can be written as weighted average, with x (the share in the total number of particles as weighting factor):

M_L = 28.96 g/mole = x · 44.1 g/mole + (1-x) ·Y g/mol.

For any given and constant pressure and temperature (ideal gas assumption!), the volume is proportional to the number of particles, and hence the particle share identical to the volume share! We can insert for x: 0.041%:

It follows (Excel!): Y = (28.96 g/mole - x · 44.1 g/mole)/(1-x) = 28.954 g/mole. The average molar mass of air without the CO_2 included.

Now, we look at this equation again, for 1 mole of particles. We only look at the masses and ignore the 1 mole now:

m_L (for 1 mole) = 28.96 g = x · 44.1 g + (1-x) ·28.9538 g.

For the MASS-share of CO_2 in this total mass y, we obtain:

$$y = \frac{44.1 \cdot x}{28.96} = \frac{44.1}{28.96} \cdot x$$

The mass share is hence exactly the volume share scaled with the ratio of the two molar masses!

A value of **y = 623 ppm** follows (Excel!). The volume share of CO_2 in air is about 410 ppm, mass share about 623 ppm.

Task 2: specific radiative forcing: To determine the global warming potential of a kg of individual substances, the concentration-specific atmospheric radiative forcing a_{a_i} of a greenhouse gas must be converted to a mass-based one, a_{m_i}. The concentration-specific atmospheric radiative forcing a_{a_i} of a greenhouse gas is given as the contribution to total radiative forcing of the atmosphere (in W/m²) of a billionth of volume share of this gas in the atmosphere (1 part per billion (10^9) = 1 ppb):

$$[a_{a_i}] = W \cdot m^{-2} \cdot ppb^{-1}$$

$$[a_{m_i}] = W \cdot m^{-2} \cdot kg^{-1} \quad (1)$$

For example, a_{a_CH4} was determined to be $(5.7 \pm 1.4) \cdot 10^{-4}$ W/m²/ppb (see Table 7.15 in Chapter 7, Part I of the 6th IPCC Assessment Report).

Use a_{a_i} to determine the quantity a_{m_i}, which is the mass-based atmospheric radiative forcing (per kg of gas *i*), using relevant ancillary quantities such as the molar mass and the total mass of the atmosphere. Write down your result as an equation!

Answer:

If we know how many kilogram of gas i correspond to 1 ppb (volume) of the Earth's atmosphere, we can scale from ppb to kg.

The answer to that question is actually already given by task 1c: Here, we showed that the mass share y_i of gas i equals to M_i/(28.96 g/mole) * x_i, where M_i is the molar mass of i and x_i the volume share of i in the atmosphere.

Here, the volume share x_i equals 1 ppb (that is 10^{-9}), and hence, the mass share is

$$y_i = M_i/(28.96\ g/mole) * 10^{-9}$$

Multiplication of y_i with the total mass of the atmosphere M_{atm} (=5.15E18 kg, see https://de.wikipedia.org/wiki/Erdatmosph%C3%A4re) yields the mass (in kg) of gas i, which are contained in 1 ppb (volume) in the atmosphere.

Division by that number results in the specific radiative forcing per kg:

$$a_{m_i} = \frac{a_{a_i}}{M_{atm} \cdot \frac{M_i}{28.96 g / mol} \cdot 10^{-9}} = 10^9 \cdot \frac{a_{a_i}}{M_{atm}} \cdot \frac{28.96 g / mol}{M_i} \quad (2)$$

For carbon dioxide, for example, follows (Excel!) from a_{a_CO2} = 1.37E-5 $Wm^{-2}ppb^{-1}$:

a_{m_CO2} = 1.75E-15 $Wm^{-2}kg^{-1}$.

Task 3: Atmospheric decay of methane: The following relationship holds for the time decay of any given quantity of methane in the atmosphere:

$$R_{CH4}(t) = e^{-\frac{t}{\tau_{CH4}}} \quad (3)$$

Here, $R_{CH4}(t)$ denotes the share of the original amount of methane, emitted at time $t = 0$, which is still present at time t. τ_{CH4} is a constant.

For methane: τ_{CH4} = 12.4 yr (11.8±1.8 yr according to the 2022 update in chapter 7 of part I of the 6th IPCC Assessment report)

(a) How large is the remaining share of the original methane emissions after the time τ_{CH4} has passed?
(b) After which time is half (50%) of the original amount left (so-called half-life?) For the case of an exponential decay, write down your result as equation! (The result holds for all exponential decays, including radioactive decay or the decomposition of toxic substances in landfills.)
(c) Plot the function $R_{CH4}(t)$! (0-100 years)
(d) How large is, according to the above equation, the average lifetime of the CH_4 emitted to the atmosphere?

Source: Numbers and equations from: "Anthropogenic and Natural Radiative Forcing", Table 8.A.1 in part I of the 5th IPCC Assessment report, and from: "Anthropogenic and Natural Radiative Forcing, Supplementary Material", Section 8.SM.11.1: Equations for the Global Warming Potential of part I of the 5th IPCC Assessment report.

Answer:

(a) For t = τ_{CH4}, we have: $R_{CH4}(t) = e^{-1} = 1/e = 0.368 = 36.8\%$.
(b) This is the mathematical condition for the so-called half life $t_{1/2}$, for which by definition holds:

$$0.5 = e^{-\frac{t_{1/2}}{\tau_{CH4}}} \quad (4)$$

This equation can be resolved directly for $t_{1/2}$, which yields:

$$\ln(0.5) = -\ln(2) = \frac{t_{1/2}}{\tau_{CH4}} \rightarrow t_{1/2} = \ln(2) \cdot \tau_{CH4} \quad (5)$$

For methane, that leads to $t_{1/2}$ = 8.6 years.
This relationship holds for all exponential decay processes, including radioactive decay or the decomposition of toxic substances in landfills.
(c) See Excel, sheet „Task 3-4-5", column F, as well as Fig. 1:

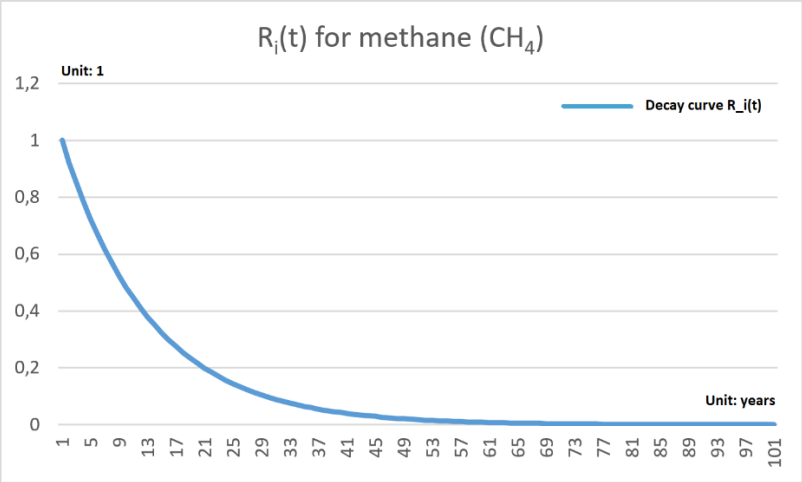

Figure 1: $R_{CH4}(t)$: Atmospheric decay of methane.

As expected, the figure shows a strong exponential decline over time, with a half life of about 9 years.

Hint: A graphical representation of data always needs to have:

- A title or, when inserted into a text, a caption.
- A legend
- Units for the x and y axes
- Small changes and annotations can quickly be done/inserted by taking a screenshot of the raw plot and editing the plot using MS Paint or so. That is sufficient for term papers and reports.

Figure 1 above was exported from Excel via screenshot and edited with Paint (Windows), which is quick to do.

(d) Aus dieser Perspektive kann man die mittlere Lebensdauer definieren als die (hypothetische) Zeit, nach der alle Anteile gleichzeitig verschwinden. Diese Lebensdauer ist in Abb. 2 eingezeichnet und wird ermittelt, indem man die Flächen unter beiden Kurven gleichsetzt. Dies folgt aus dem „Links-rechts-Ansatz“ der Lebensdauern der einzelnen Anteile. Im Falle der mittleren Lebensdauer ist für alle Anteile nach T_quer der Aufenthalt in der Atmosphäre zu Ende.
The average lifetime of methane (or any other gas) can be determined via Fig. 1. Here we take advantage of the fact that this figure can be read from two directions:
The usual reading direction of such a plot is from bottom to top: We assign a fraction (remaining fraction in the atmosphere) to each time point.
However, we can also read the figure from left to right: Each given fraction between 0 and 1 is assigned a lifetime. It's like a race. The fractions at the very top disappear first, the fractions at the very bottom last the longest.

From this perspective, the average lifetime can be defined as the (hypothetical) time after which all shares disappear simultaneously (at exactly the average lifetime). This lifetime is plotted in Fig. 2 and is determined by equating the areas under both the blue and the black curves. This follows from the "left-right approach" of the lifetimes of the individual shares. In the case of the mean lifetime, residence in the atmosphere is over for all components after T_bar.

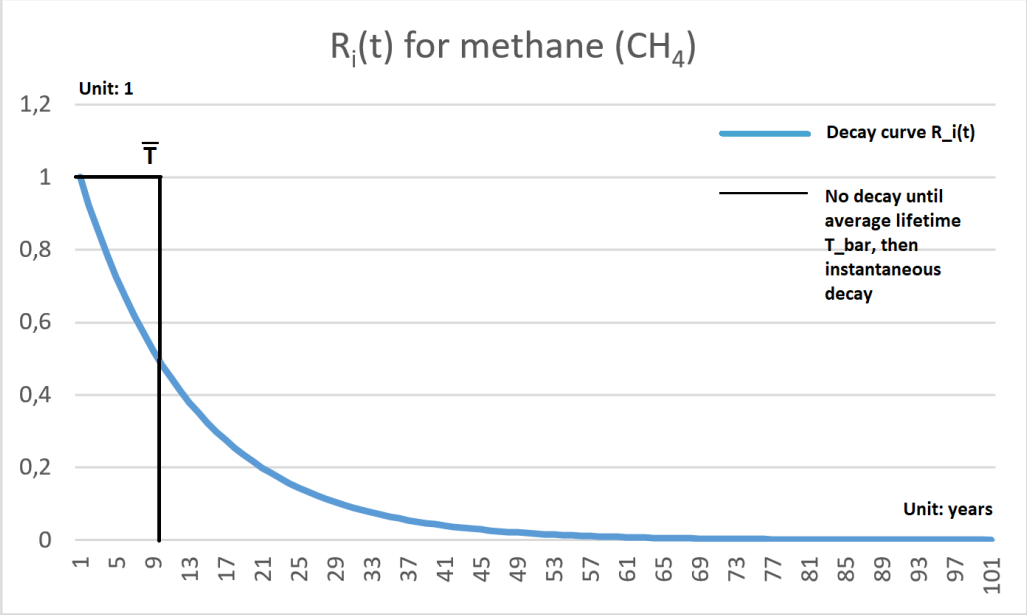

Figure 2: $R_{CH4}(t)$: Atmospheric decay of methane, with average lifetime shown. The area under the blue curve equals the area under the black curve.

Therefore the following equation holds:

$$\bar{T}_{CH4} = \int_0^{\infty} R_{CH4}(t)\, dt = \int_0^{\infty} e^{-\frac{t}{\tau_{CH4}}}\, dt = \tau_{CH4} \cdot \left(-e^{-\frac{t}{\tau_{CH4}}} \right) \Big|_0^{\infty} = \tau_{CH4} \cdot \big((-0) - (-1) \big) = \tau_{CH4}$$

(6)

Which means:

For the exponential decay, the average lifetime equals the decay constant τ_i.

For methane: T_bar_CH4 = τ_{CH4} = 12,4 years.

Task 4: Atmospheric decay of carbon dioxide: The following relation holds for the decay of a given amount (set here to 100%) of carbon dioxide (CO_2) in the atmosphere:

$$R_{CO2}(t) = a_0 + \sum_{i=1}^{3} a_i \cdot e^{-\frac{t}{\tau_i}} \quad (7)$$

Here, $R_{CO2}(t)$ denotes the share of the original amount of the gas at time $t = 0$, which is still present in the atmosphere at time t. The values of the different parameters are given in Table 1:

Table 1: Numerical values for the parameters in the equation for R_{CO2} above. **Sources**: Numbers and equations from: "Anthropogenic and Natural Radiative Forcing", Table 8.A.1 in part I of the 5th IPCC Assessment report as well as: "Anthropogenic and Natural Radiative Forcing, Supplementary Material", Section 8.SM.11.1: Equations for the Global Warming Potential of part I of the 5th IPCC Assessment report.

Variable/Order	0	1	2	3
a	0.2173	0.2240	0.2824	0.2763
τ	---	394.4	36.54	4.304

(a) How large is the share of the original amount of CO_2 after 10/20/50/100/200/500/1000/many, many years?
(b) After how many years has the share of the remaining CO_2 in the atmosphere fallen down to 50%? Here, an approximate answer, based on the numerically obtained values for the different future years, is sufficient to determine the year around which $R_{CO2}(t)$ is about 0.5.
(c) How large is (by the equation above) the average lifetime of CO_2 emitted to the atmosphere?
(d) Plot the function $R_{CO2}(t)$!

Answer*:

(a) See Excel workbook for this exercise, sheet „Task 3-4-5", column E, and Table 2 below:

Table 2: Remaining share of the originally emitted amount of CO_2 after a given time span. $R_{CO2}(t=0) = 1$.

Time (Years)	10	20	50	100	200	500	1000	Infinite
Share R_{CO2}	0.68	0.60	0.49	0.41	0.35	0.28	0.24	0.2173

The fraction of the emitted CO_2 that remains in the atmosphere declines relatively fast, down to about 50% after only 50 years. The dissipated share of the emitted CO_2 is absorbed by the oceans or by vegetation.

(b) See Excel work boot for this exercise, sheet „Task 3-4-5“, column E, and Figure 3 below. Here, one can see that after $t_{1/2}$ **= 45 years**, the atmospheric fraction of the originally emitted CO_2 has declined to just below 50%. The half life of CO_2 in the atmosphere hence is about 45 years.

(c) Here, we proceed exactly as in the above task for methane. Due to the 'baseline', i.e., the approx. 21.73% of the CO_2, which still remains in the atmosphere in the long-term equilibrium, about a fifth of the initial quantity has an infinite life span according to this model. Therefore, the area under the blue curve in Fig. 3 is infinitely large. How long the other 80% remains in the atmosphere is irrelevant: **The average lifetime of CO_2 in the atmosphere is infinite.** (According to the 'standard model' of the global carbon cycle). In general, the half-life of a substance does not equal its mean lifetime!

(d) See Excel work boot for this exercise, sheet „Task 3-4-5“, column E, and Figure 3 below:

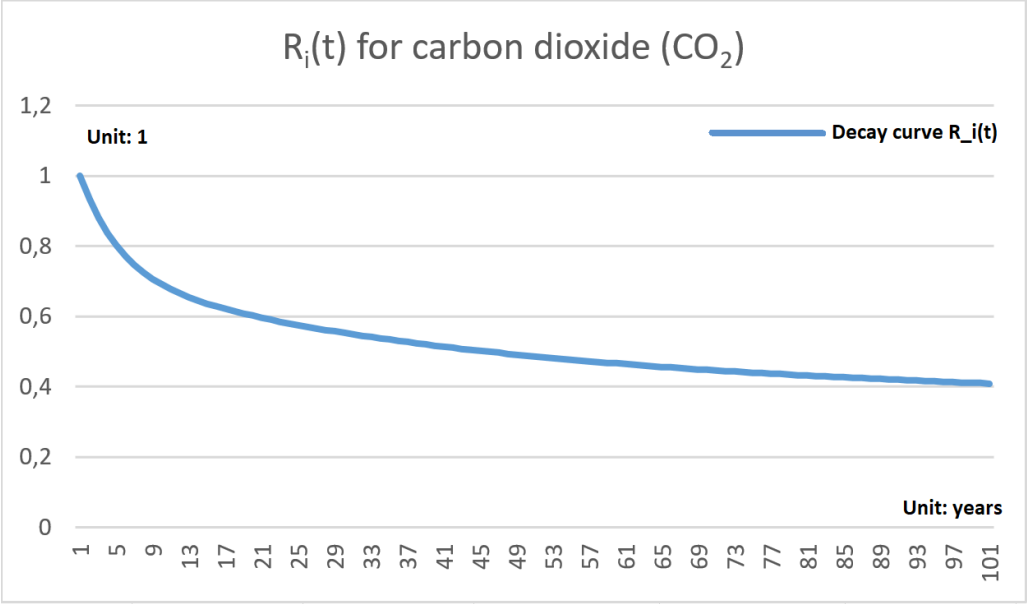

Figure 3: $R_{CO2}(t)$: Atmospheric decay of carbon dioxide. The curve converges against a baseline of about 0.22.

As expected, the figure shows at first a strong (exponential) decay of the curve over time, these are the contributions of the 'fast terms' with lifetimes of 4.3 and 36.5 years (table 1 and task 3d). After a few decades, the decay curve converges against a 'slow base', which decays only very slowly (lifetime of 394 years) and a constant baseline of 21.7%.

Task 5: Global warming potential of methane for different time horizons.

Determine the global warming potential of methane for a time horizon of 20 years and for 100 years! Use the results of the above tasks and note (see info below)* that the specific radiative forcing for methane is increased by an additional factor of 1.65!

To solve this task, the above equations for R_i can be integrated analytically, or the R_i values of the individual years can be integrated numerically in Excel.

Data:

- Decay curves of the different GHG: see tasks 3 and 4.
- Specific radiative forcing of the different gases:

CO_2:	1.75435E-15	$Wm^{-2}kg^{-1}$	See AR5 WG I, 8.SM.11.3 'Updates of Metric Values'
CH_4:	1.27991E-13	$Wm^{-2}kg^{-1}$	See AR5 WG I Ch 8, Table 8.A.1
N_2O:	3.84645E-13	$Wm^{-2}kg^{-1}$	See AR5 WG I Ch 8, Table 8.A.1

- Correction factor c_i for each gas to consider secondary (like decomposition effects on ozone and stratospheric water vapor)*

CO_2	1
CH_4	1.65
N_2O	1

*) See the following quotation from section 7.6.1.3 from part I of the 6th AR: "The effect of a compound on climate is not limited to its direct radiative forcing. Compounds can perturb the carbon cycle affecting atmospheric CO_2 concentrations. Chemical reactions from emitted compounds can produce or destroy other greenhouse gases or aerosols."

Answer*:

For the numeric solution, the $R_i(t)$-curves are integrated in a first step ($\int_0^t R_i(\tau)d\tau$), to determine the ‚cumulative share' which is the integral of the share over time. Here, one simply adds the different functional values from year 0 to year *t*, which is sufficient because the width of the bar for each year is 1. (See the Excel workbook for this exercise, sheet „Task 3-4-5", columns I and J. and Figure 4 below.)

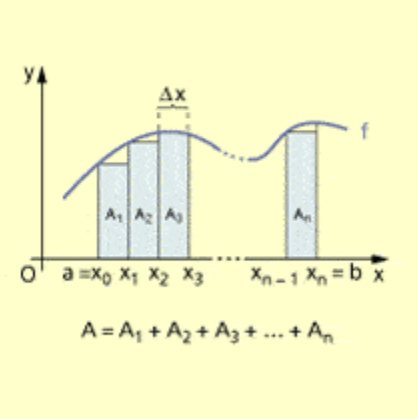

Figure 4: Numerical integration of a function. The numerical value of the integral is the sum of the different area segments, which are the product of the function's value at each x value, times the distance between the different x values. Source: https://www.lernhelfer.de/schuelerlexikon/mathematik-abitur/artikel/numerische-integration

With the values for the integral underneath the decay curve (see Excel) and the above-listed values for a_{m_i} and the correction factors for the GWP (Table 3 and Excel, sheet „Task 3-4-5", columns U-X):

$$GWP_i(T) = \frac{a_{m_i} \cdot c_i \cdot \int_0^T R_i(t)dt}{a_{m_CO2} \cdot \int_0^T R_{CO2}(t)dt} \quad (8)$$

Table 3: Numerical determination of the global warming potential. The value for CO_2 is determined to check the calculation, the one for N_2O is provided as additional result.

Global warming potential,	**numerical**		
	CO_2	**CH_4**	**N_2O**
20 years time horizon	1	84,2792869	282,106006
100 years time horizon	1	29,2697659	284,133575

These values are not the final results, as they require proper rounding! One can see that the GWP for CH_4 declines rather quickly with the time horizon of the analysis, and that the GWP of N_2O even increases with time, as it decays slower than CO_2 is dissipated from the atmosphere.

For the analytical solution, one integrates the curves for $R_i(t)$ not numerically, by summing up the values, but one determines the integral as a function, based on the functional relationships for $R_i(t)$.

We have here:

$$R_i(t) = e^{-\frac{t}{\tau_i}} \rightarrow \int_0^T R_i(t)dt = -\tau_i \cdot e^{-\frac{t}{\tau_i}} \Big|_0^T = \tau_i \cdot \left(1 - e^{-\frac{T}{\tau_i}}\right) \quad (9)$$

This relationship holds for all gases with exponential decay, including CH_4 und N_2O. Using equation 9, the definite integral can be calculated with Excel or another computational tool.

The decay curve of CO_2 can also be integrated simply by summing up the integrals of the individual terms in the decay curve function. This is because the integral is a linear operator, hence, the order of sum and integral can be swapped. It follows:

$$R_{CO2}(t) = a_0 + \sum_{i=1}^{3} a_i \cdot e^{-\frac{t}{\tau_i}} \rightarrow$$

$$\int_0^T R_{CO2}(t) = a_0 \cdot T - \sum_{i=1}^{3} \tau_i \cdot a_i \cdot e^{-\frac{t}{\tau_i}} \Big|_0^T$$

$$\int_0^T R_{CO2}(t) = a_0 \cdot T + \sum_{i=1}^{3} \tau_i \cdot a_i \cdot \left(1 - e^{-\frac{T}{\tau_i}}\right) \quad (10)$$

The values for this integral can now be calculated and directly inserted into the definition equation of the GWP above.

The results are shown in Table 4:

Table 4: Analytical values for the global warming potential (GWP) of different greenhouse gases and different time horizons. The value for CO_2 is determined to check the calculation, the one for N_2O is provided as additional result.

Integrals over R_i			
	CO_2	**CH_4**	**N_2O**
20 years horizon	14.24167994	9.9285791	18.4345338
100 years horizon	52.35538857	12.3961002	68.0502016

GWP	**CO_2**	**CH_4**	**N_2O**
20 years horizon	1	83.9212835	283.801814
100 years horizon	1	28.5016451	284.978607

These values are not the final results, as they require proper rounding!

These values are very similar to the numerical ones, but not equal. The reason for this deviation is that the approximation of the true area by bars with a width of 1 year under the curve (see Fig. 4) is not exact.

Since for these gases, the GWP calculation is analytically possible without great difficulties, we give preference to this solution path and state that:

The GWP of methane over a time horizon of 20 years is about 84.

The GWP of methane over a time horizon of 100 years is about 28.5.

Note **Check Table 7.15 in chapter 7 of part I of the 6th IPCC Assessment Report for updates and uncertainty ranges!**

Global warming potential, AR 6 update, with uncertainty ranges				
	CO_2 (by def.)	**CH_4 (fossil)**	**CH_4 (non-fossil)**	**N_2O**
20 years	1	82.5 ± 25.8	80.8 ± 25.8	273 ± 118
100 years	1	29.8 ± 11	27.2 ± 11	273 ± 130

Atmospheric lifetime				
	CO_2	**CH_4 (fossil)**	**CH_4 (non-fossil)**	**N_2O**
years	multiple	11.8 ± 1.8	11.8 ± 1.8	109 ± 10