Methane and Nitrous Oxide AOSC 680

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Class Web Sites:

http://www2.atmos.umd.edu/~rjs/class/fall2024 https://umd.instructure.com/courses/1367293

Goals :

• CH₄

- sources and sinks
- lifetime
- human influences (mighty complicated!)

1

 $\cdot N_2O$

sources and sinks

- human influence
- connection to stratospheric O₃

Note:

1 Gt (gigaton) = 10^9 tons, which also equals 10^{15} grams

1 Mt (megaton) = 10^6 tons, which also equals 10^{12} grams, or 1 Tg (Terra gram)

Lecture 6 17 September 2024

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CH₄ is the most reduced form of carbon

Decreasing oxidation number (reduction reactions)

-4	0	+2	+4
CH₄	CH ₂ O	CO	CO ₂
Methane	Formaldehyde	Carbon Monoxide	Carbon dioxide

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons: added to an element (negative #) or removed from an element (positive #)



C in CO₂: has donated two electrons to each oxygen atom, completing the L shell of electrons & resulting in an electron configuration analogous to helium. This molecule is extremely stable.

CH₄ is the most reduced form of carbon

Decreasing oxidation number (reduction reactions)

-4	0	+2	+4
CH₄	CH ₂ O	CO	CO ₂
Methane	Formaldehyde	Carbon Monoxide	Carbon dioxide

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:

added to an element (negative #) or removed from an element (positive #)



C in CH₄: has received an electron from each H atom. All electrons are paired and hence this compound is relatively stable

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Background



- SSP: Share Socioeconomic Pathways (SSPs) Number represents ∆RF of climate (W m⁻²) at the end of this century
- GHG mixing ratio time series for CO₂, CH₄, N₂O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups

Figure from McBride et al., 2021: <u>https://esd.copernicus.org/articles/12/545/2021</u> See also Riahi et al., 2017 <u>https://www.sciencedirect.com/science/article/pii/S0959378016300681</u> for an overview of the SSPs

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AT6, Q1:

According to Table 3.2 of Chemistry in Context, what was pre-industrial atmospheric abundance of CH_4 **and** is this consistent with Figure 3.7 of the Houghton reading?

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Table 3.2	Examples of Greenhouse Gases				
Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
carbon dioxide CO_2	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH_4	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl ₂ F ₂	0	0.56 ppb	102	Liquid coolants, foams	8100

*A single value for the atmospheric lifetime of CO₂ is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.



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as well as Fig 1.2 from Paris Climate Agreement: Beacon of Hope also shown in Lecture 2



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AT6, Q2:

What is the approximate current atmospheric abundance of CH₄?

NOAA Earth System Research Laboratory (Boulder, Co) is "go to" place for information regarding GHGs

Latest data indicate CH_4 is over 1900 ppb and rising and also that CH_4 was about 1760 ppb in late-1990s and about 1.84 ppm in mid-2017.



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AT6, Q3:

What are the values given for:

a) enhanced greenhouse effect caused by a molecule of CH_4 relative to that of a molecule of CO_2 given on pg 47 of Houghton

b) the GWP for CH₄ given in Table 3.2 of Chemistry in Context

c) the GWP for CH₄ over 20-year time horizon used on page 26 of Paris Climate Agreement: Beacon of Hope

The ~ 10 year atmospheric lifetime for CH₄ has important policy implications. This is best illustrated by comparing the human release of CH_4 to that of CO_2 . Throughout the world, humans presently release about 335 Tg of CH₄ and 39 Gt of CO_2 per year. Since 1000 Tg = 1 Gt, these sources are 0.335 Gt of CH_4 and 39 Gt of CO_2 per year: i.e., the mass of CO_2 released to the atmosphere each year by human society is about 116 times more than the mass of CH₄. The impact on climate is entirely dependent on the time scale of interest. Nearly all of the CH₄ released to the atmosphere in year 2015 will be gone by the end of this century. The *CO*₂-equivalent</sub> emission of CH₄, found by multiplying the current release by the GWP for CH₄ for a 100-year time horizon, is 28×0.335 Gt of CH₄ or 9.4 Gt per year. If our concern is global warming over the next century, then we would conclude the human release of CO₂ in year 2015 was about four times more harmful for climate $(39 \div 9.4 = 4.1)$ than the release of CH₄. However, if our concern is the next two decades, we must consider the GWP of CH₄ over a 20-year time horizon. In this case, the CO₂equivalent emission of CH_4 is 84 \times 0.335 Gt or 28.1 Gt per year, and we would conclude the present human release of CH₄ is nearly as harmful for climate (28.1 versus 39) as the release of CO₂.

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What are the values given for:

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b) the GWP for CH₄ given in Table 3.2 of Chemistry in Context

c) the GWP for CH₄ over 20-year time horizon used on page 26 of Paris Climate Agreement: Beacon of Hope

Table 1.1 Paris, Beacon of Hope

Global Warming Potentials							
GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)			
100 Year Time	100 Year Time Horizon						
CH ₄	21	23	25	28			
N ₂ O	310	296	298	265			
20 Year Time Horizon							
CH ₄	56	62	72	84			
N ₂ O	280	275	289	264			

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AT6, Q3:

What are the values given for:

a) enhanced greenhouse effect caused by a molecule of CH₄ relative to that of CO₂ given on pg 47 of Houghton

b) the GWP for CH₄ given in Table 3.2 of *Chemistry in Context*

c) the GWP for CH₄ over 20-year time horizon used on page 26 of *Paris Climate Agreement: Beacon of Hope*

Although the concentration of methane in the atmosphere is much less than that of carbon dioxide (only ~1800 ppb in 2011 compared with about 400 ppm for carbon dioxide), its greenhouse effect is far from negligible. That is because the enhanced greenhouse effect caused by a molecule of methane is about <u>eight times</u> that of a molecule of carbon dioxide.⁹ Page 47, Houghton

Endnote 9, Houghton:

The ratio of the enhanced greenhouse effect of a molecule of methane compared to a molecule of carbon dioxide is known as its global warming potential (GWP) ... The figure of about 8 given here for the GWP of methane is for a time horizon of 100 years. The GWP is also often expressed as the ratio of the effect for unit mass of each gas in which case the GWP for methane (whose molecular mass is 0.36 of that of carbon dioxide) becomes about 23 for the 100-year time horizon. About 75% of the contribution of methane to the greenhouse effect is because of its direct effect on the outgoing thermal radiation. The other 25% arises because of its influence on the overall chemistry of the atmosphere. Increased methane eventually results in small increases in water vapour in the upper atmosphere, in tropospheric ozone and in carbon dioxide, all of which in turn add to the greenhouse effect. For more information see IPCC WGI 2013, Chapter 8, p. 700.

Footnote 8, Paris, Beacon of Hope:

Some textbooks and reports provide GWP values on a per molecule basis, rather than a per mass basis. A molecule of CO_2 with atomic mass of 44 weighs 2.75 times a molecule of CH_4 (atomic mass of 16). Using the IPCC (2013) value for the GWP of CH4 on a 100 year time horizon, without consideration of carbon cycle feedback, scientists would state CH_4 is 28 times more potent than CO_2 on a per mass basis and, at the same time, is 10.2 (28 ÷ 2.75) times more potent than CO_2 on a per molecule basis.

Scientific utility of quantifying the human and natural sources of CH₄



lf:

Production of CH₄ = Loss of CH₄ <u>and</u> if the loss involves a chemical reaction of CH₄ with a Gas, then Production of CH₄ = k [CH₄] [Gas], where k is the rate of a chemical reaction and [] denotes abundance Assuming k and [Gas] are constant over time, we can write: Production^{Preindustrial} = k [CH₄]^{Preindustrial} [Gas] & Production^{Present} = k [CH₄]^{Present} [Gas]

which can be re-arranged to yield:

k [Gas] = Production^{Preindustrial} / [CH₄]^{Preindustrial} & k [Gas] = Production^{Present} / [CH₄]^{Present}

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Scientific utility of quantifying the human and natural sources of CH₄

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If:

k [Gas] = Production<sup>Preindustrial</sup> / [CH<sub>4</sub>]<sup>Preindustrial</sup> & k [Gas] = Production<sup>Present</sup> / [CH<sub>4</sub>]<sup>Present</sup>

Then:

Production<sup>Preindustrial</sup> / [CH<sub>4</sub>]<sup>Preindustrial</sup> = Production<sup>Present</sup> / [CH<sub>4</sub>]<sup>Present</sup>

Or:

[CH<sub>4</sub>]<sup>Preindustrial</sup> / [CH<sub>4</sub>]<sup>Present</sup> = Production<sup>Preindustrial</sup> / Production<sup>Total</sup>

Or:

[CH<sub>4</sub>]<sup>Preindustrial</sup> / [CH<sub>4</sub>]<sup>Present</sup> = Source<sup>Preindustrial</sup> / Source<sup>Present</sup>
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From prior slide:

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[CH<sub>4</sub>]<sup>Preindustrial</sup> / [CH<sub>4</sub>]<sup>Present</sup> = Source<sup>Preindustrial</sup> / Source<sup>Present</sup>
```

Presumably:

Source^{Preindustrial} = Source^{Present} – Source^{Human} (i.e., presumably "nature" has not changed)

If so, then top equation can be written as:

$$[CH_4]^{Preindustrial} / [CH_4]^{Present} = (Source^{Present} - Source^{Human}) / Source^{Present}$$
$$= 1 - Source^{Human} / Source^{Present} = 1 - (335 \text{ Tg yr}^{-1}) / (553 \text{ Tg yr}^{-1})$$
$$= 1 - 0.61 = 0.39$$

AT6, Q1:

According to Table 3.2 of Chemistry in Context what was pre-industrial atmospheric abundance of CH_4 ? \Rightarrow 700 ppb

AT6, Q2:

Atmospheric abundance of CH_4 in 2005 from slide 7 \Rightarrow 1770 ppb

ppb / ppb = !!!

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CH₄ is in fact lost by reaction with OH, the hydroxyl radical

$CH_4 + OH \rightarrow H_2O + CH_3$

$$\frac{dCH_4}{dt} = Production - Loss = Production - k^{CH4 + OH} [CH_4] [OH]$$

Rate constant (speed at which CH_4 reactions with OH):

 $k^{\text{CH4+OH}} = 1.85 \times 10^{-20} \times \text{T}^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

which is obtained from analysis of laboratory measurements

Bimolecular Gas Phase Reactions

$\mathsf{OH} + \mathsf{CH}_4 \to \mathsf{CH}_3 + \mathsf{H}_2\mathsf{O}$

Rate constant recommended by IUPAC

 $k^{\text{OH+CH4}} = 1.85 \times 10^{-20} \times \text{T}^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$



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CH₄ is in fact lost by reaction with OH, the hydroxyl radical

$CH_4 + OH \rightarrow H_2O + CH_3$

$$\frac{dCH_4}{dt} = Production - Loss = Production - k^{CH4+OH} [CH_4] [OH]$$

Arrhenius Expression for rate constant: i.e., speed at which CH₄ reactions with OH:

$$k^{\text{CH4+OH}} = 1.85 \times 10^{-12} \times \text{T}^{2.82} e^{-987/T} \text{ cm}^3 \text{ sec}^{-1}$$

which is obtained from analysis of laboratory measurements

Lifetime of
$$CH_4 = \frac{Abundance}{Loss} = \frac{[CH_4]}{k^{CH4 + OH}[OH][CH_4]} = \frac{1}{k^{CH4 + OH}[OH]}$$

Commonly T = 272 K and [OH] = 1×10^6 molec cm⁻³ are used, yielding:

Lifetime of CH₄ =
$$\frac{1}{k^{\text{CH4} + \text{OH}} [\text{OH}]} = \frac{1}{3.60 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}}$$

= 2.77×10⁸ sec = yr

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 CH_3CCI_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known



https://www.eshinoda.gov/esd/assessments/ozone/2016/report/enapter1_2016020he/issessment.put

Methyl chloroform (1,1,1-trichloroethane) is an excellent solvent and one of the least toxic of the chlorinated hydrocarbons. Prior to the Montreal Protocol, it was widely used for cleaning metal parts and circuit boards, as an aerosol propellant, and as a solvent for inks, paints, and adhesives. It was also the standard cleaner for photographic film (movie/slide/negatives, etc.). Methyl chloroform was also used as a thinner in correction fluid products such as Liquid Paper.

Montreal Protocol banned the use of methyl chloroform and it was rapidly phased out, throughout the world.

See <u>http://en.wikipedia.org/wiki/1,1,1-Trichloroethane</u>

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 CH_3CCI_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

 $CH_3CCI_3 + OH \rightarrow CH_2CCI_3 + H_2O$



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 CH_3CCI_3 (methyl chloroform) is lost by reaction with OH & its atmospheric abundance / industrial production are well known

 $CH_3CCI_3 + OH \rightarrow CH_2CCI_3 + H_2O$

 $\frac{dCH_{3}CCl_{3}}{k} = Production - k^{CH3CCl_{3} + OH} [CH_{3}CCl_{3}] [OH]$



The global average OH concentration, $9.4 \pm 1.3 \times 10^5$ molec cm⁻³, for observations obtained from 1978 to 2000, does not vary statistically from that derived by us earlier for the 1978 to 1994 period $9.7 \pm 1.3 \times 10^5$ molec cm⁻³

Prinn et al., Science, 2001

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Houghton & Chemistry in Context give a Lifetime for CH₄ of 12 Years What's up with the 12 year lifetime?

Lifetime of CH₄ =
$$\frac{1}{k^{\text{CH4} + \text{OH}} [\text{OH}]} = \frac{1}{3.59 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}}$$

= 2.79×10⁸ sec = 8.8 yr

10 Taking into account the loss processes due to reaction with OH in the troposphere, chemical reactions and soil loss lead to a lifetime of about ten years. However, the effective lifetime of methane against a perturbation in concentration in the atmosphere (the number quoted here) is complex because it depends on the methane concentration. This is because the concentration of the radical OH (interaction with which is the main cause of methane destruction), due to chemical feedbacks, is itself dependent on the methane concentration (see IPCC WGI 2013, Chapter 8, p. 714).

Endnote #10, Chapter 3, Houghton

Understanding the observed time series of CH₄ is a "hot ticket item" in modern atmospheric chemistry



<u>https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4</u> See also <u>https://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html</u>

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Atmospheric CH₄ and Energy from Gas, Rice, Cattle Trends



Fracking

Monthly dry shale gas production





Note: We derived these shale gas estimates from Enverus state administrative data. Data are through December 2023. We updated the factors we use to convert gross natural gas to dry natural gas based on the latest *Natural Gas Annual* data. This update affected historical production volumes from some formations. PA=Pennsylvania, WV=West Virginia, OH=Ohio, NY=New York, TX=Texas, NM=New Mexico, LA=Louisiana, OK=Oklahoma, ND=North Dakota, MT=Montana, CO=Colorado, WY=Wyoming, AR=Arkansas

https://www.eia.gov/energyexplained/natural-gas/where-our-natural-gas-comes-from.php

Combustion of CH₄ yields ~70% more energy, per CO₂ released to the atmosphere, than combustion of coal

Break even point for "climate", natural gas versus coal, is leakage of: 2.3% of CH4 for GWP over a 20-yr time horizon 6.9% of CH4 for GWP over a 100-yr time horizon

Footnote #35, Chapter 4, Paris Beacon of Hope

These papers offer conflicting views on the cause of the recent rise in CH₄

• Kirschke et al., Nature Geoscience, 2013:

-

Methane is an important greenhouse gas, responsible for about 20% of the warming induced by longlived greenhouse gases since pre-industrial times. By reacting with hydroxyl radicals, methane reduces the oxidizing capacity of the atmosphere and generates ozone in the troposphere. Although most sources and sinks of methane have been identified, their relative contributions to atmospheric methane levels are highly uncertain. As such, the factors responsible for the observed stabilization of atmospheric methane levels in the early 2000s, and the renewed rise after 2006, remain unclear. Here, we construct decadal budgets for methane sources and sinks between 1980 and 2010, using a combination of atmospheric measurements and results from chemical transport models, ecosystem models, climate chemistry models and inventories of anthropogenic emissions. The resultant budgets suggest that data-driven approaches and ecosystem models overestimate total natural emissions. We build three contrasting emission scenarios — which differ in fossil fuel and microbial emissions — to explain the decadal variability in atmospheric methane levels detected, here and in previous studies, since 1985. Although uncertainties in emission trends do not allow definitive conclusions to be drawn, we show that the observed stabilization of methane levels between 1999 and 2006 can potentially be explained by decreasing-to-stable fossil fuel emissions, combined with stable-to-increasing microbial emissions. We show that a rise in natural wetland emissions and fossil fuel emissions probably accounts for the renewed increase in global methane levels after 2006, although the relative contribution of these two sources remains uncertain.

These papers offer conflicting views on the cause of the recent rise in CH₄

• Schaefer *et al., Science*, 2016 :

Between 1999 and 2006, a plateau interrupted the otherwise continuous increase of atmospheric methane concentration $[CH_4]$ since preindustrial times. Causes could be sink variability or a temporary reduction in industrial or climate-sensitive sources. We reconstructed the global history of $[CH_4]$ and its stable carbon isotopes from ice cores, archived air, and a global network of monitoring stations. A box-model analysis suggests that diminishing thermogenic emissions, probably from the fossil-fuel industry, and/or variations in the hydroxyl CH_4 sink caused the $[CH_4]$ plateau. Thermogenic emissions did not resume to cause the renewed $[CH_4]$ rise after 2006, which contradicts emission inventories. **Post-2006 source increases are predominantly biogenic, outside the Arctic, and arguably more consistent with agriculture than wetlands.** If so, mitigating CH_4 emissions must be balanced with the need for food production.

• Worden et al., Nature Communications, 2017:

Several viable but conflicting explanations have been proposed to explain the recent ~8 ppb per year increase in atmospheric methane after 2006, equivalent to net emissions increase of ~25 Tg CH₄ per year. A concurrent increase in atmospheric ethane implicates a fossil source; a concurrent decrease in the heavy isotope content of methane points toward a biogenic source, while other studies propose a decrease in the chemical sink (OH). Here we show that biomass burning emissions of methane decreased by 3.7 (±1.4) Tg CH₄ per year from the 2001–2007 to the 2008–2014 time periods using satellite measurements of CO and CH₄, nearly twice the decrease expected from prior estimates. After updating both the total and isotopic budgets for atmospheric methane with these revised biomass burning emissions (and assuming no change to the chemical sink), we find that fossil fuels contribute between 12–19 Tg CH₄ per year to the recent atmospheric methane increase, thus reconciling the isotopic- and ethane-based results.

See also https://insideclimatenews.org/news/10032016/mysterious-global-methane-rise-asian-agriculture-or-us-fracking

These papers offer conflicting views on the cause of the recent rise in CH₄

• Wolf et al., Carbon Balance and Management, 2017:

Livestock play an important role in carbon cycling through consumption of biomass and emissions of methane. Recent research suggests that existing bottom-up inventories of livestock methane emissions in the US, such as those made using 2006 IPCC Tier 1 livestock emissions factors, are too low. This may be due to outdated information used to develop these emissions factors. ...

Using the new emissions factors, we estimate global livestock emissions of 119.1 ± 18.2 Tg methane in 2011; this quantity is 11% greater than that obtained using the IPCC 2006 emissions factors, encompassing an 8.4% increase in enteric fermentation methane, a 36.7% increase in manure management methane, and notable variability among regions and sources. ...

Our results suggest that livestock methane emissions, while not the dominant overall source of global methane emissions, may be a major contributor to the observed annual emissions increases over the 2000s to 2010s. Differences at regional and local scales may help distinguish livestock methane emissions from those of other sectors in future top-down studies. The revised estimates allow improved reconciliation of top-down and bottom-up estimates of methane emissions, will facilitate the development and evaluation of Earth system models, and provide consistent regional and global Tier 1 estimates for environmental assessments.

Time for Another YouTube Video



https://www.youtube.com/watch?v=MnRFUSGz ZM

These papers offer conflicting views on the cause of the recent rise in CH₄

- Tollefson *et al., Nature,* 2022:
 - Tropical wetlands such as those pictured (Brazil)
 major source of CH₄ emissions
 - Isotopic signature seems to indicate most of the rise in the emissions of CH₄ are [recent] biological in origin, rather than extraction of fossil fuels [ancient biological]





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Wetter-gets-Wetter, Dry-gets-Drier (WWDD) Paradigm



Projected changes in annual maximum daily precipitation at (a) 1.5°C, (b) 2°C warming compared to the 1851-1900 baseline.

Results are based on simulations from the CMIP6 multi6 model ensemble under the SSP1-1.9, SSP1-2.6, SSP2-4.5, SSP3-7.0, and SSP5-8.5 scenarios. The numbers on the top right indicate the number of simulations included. Uncertainty is represented as follows: no overlay indicates regions with high model agreement, where \geq 80% of models 9 agree on sign of change; diagonal lines indicate regions with low model agreement, where < 80% of models agree on sign of change

https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC AR6 WGI Chapter 11.pdf

See also <u>https://www.preventionweb.net/news/explainer-what-new-ipcc-report-says-about-extreme-weather-and-climate-change</u> Hadley Cell Circulation: <u>http://www.windows2universe.org/vocals/images/HadleyCell_small.jpg</u>

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Nitrous Oxide: N₂O

Table 3.2	Examples of Greenhouse Gases				
Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

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N₂O Time Series



http://www.esrl.noaa.gov/gmd/hats/combined/N2O.html

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Nitrous Oxide: N₂O

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nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310

Davidson and Kanter, ERL, 2014:



https://iopscience.iop.org/article/10.1088/1748-9326/9/10/105012/meta

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Table 6.9, IPCC 2013

Sources and Sinks of N_2O

SECTION 2 (N ₂ O) All units for N ₂ O	1	
	AR5 (2006/2011)	
Anthropogenic sources		
Fossil fuel combustion and industrial processes	0.7 (0.2–1.8) ^a	T
Agriculture	4.1 (1.7–4.8) ^b	
Biomass and biofuel burning	0.7(0.2–1.0) ^a	
Human excreta	0.2 (0.1–0.3) ^a	
Rivers, estuaries, coastal zones	0.6 (0.1–2.9) ^c	
Atmospheric deposition on land	0.4 (0.3–0.9) ^d	
Atmospheric deposition on ocean	0.2 (0.1–0.4) ^e	
Surface sink	-0.01 (01) ^f	
Total anthropogenic sources	6.9 (2.7–11.1)	
Natural sources ^a		
Soils under natural vegetation	6.6 (3.3–9.0)	
Oceans	3.8(1.8–9.4)	
Lightning	_	
Atmospheric chemistry	0.6 (0.3–1.2)	
Total natural sources	11.0 (5.4–19.6)	
Total natural + anthropogenic sources	17.9 (8.1–30.7)	
Stratospheric sink	14.3 (4.3–27.2) ^g	
Observed growth rate	3.61 (3.5–3.8) ^h	
Global top-down (year 2011) ⁱ	1	
Burden (Tg N)	1553	T
Atmospheric Loss	11.9±0.9	
Atmospheric Increase	4.0±0.5	Prior slide:
Total Source	15.8±1.0	16.3 (Total)
Natural Source	9.1±1.0	11.0 (Natural
Anthropogenic Source	6.7±1.3	5.3 (Human)

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The Nitrogen Cycle

Haber-Bosch: $N_2(gas) + 3 H_2(gas) \rightarrow 2 NH_3(gas)$ Led to large scale, economical production of ammonia based fertilizer



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The Nitrogen Cycle

The reactive forms of nitrogen in this cycle continuously change chemical forms. Thus, the ammonia that starts out as fertilizer may end up as NO, in turn increasing the acidity of the atmosphere. Or the NO may end up as N_2O , a GHG that is currently rising.



Chapter 6, Chemistry in Context

N₂O and NO_y

Loss of N₂O occurs mainly in the stratosphere due to: photolysis – main sink reaction with electronically excited O(¹D) – minor sink



Fig. 11. Diurnally averaged loss rate for N_2O (10^2 molecules cm⁻³ s⁻¹) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N_2O by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

The minor sink for N₂O loss has a path that results in "fixed nitrogen":

 $N_2O + O(^1D) \rightarrow NO + NO$

Fixed nitrogen (NO_v) is crucial to stratospheric chemistry

Oxides of nitrogen catalyze loss of stratospheric O_3 & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.

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N₂O and Stratospheric Ozone



Difference of stratospheric O_3 in the 2090s for a computer simulation run using N₂O from RCP 8.5 minus that of a simulation using N₂O from RCP 2.6

Rising N₂O leads to:

a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO₂ mediated loss cycles.

b) speeds up the rate of OH+NO₂+M→HNO₃ & CIO+NO₂+M→ CINO₃+M in the lowermost stratosphere, leading to slower ozone loss by these cycles & less O₃ where these cycles dominate total loss of O₃

Computer models project stratospheric column O₃ will decline as N₂O rises

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