GE510 Physical Principles of the Envt

Atmospheric chemistry and non-CO2 greenhouse gases

What you need to know about each of these chemicals

1. CH4 methane
2. O3   ozone
3. N2O nitrous oxide
4. Halocarbons

Reactive gases (influence GHGs):

5. OH-   Hydroxyl radical
6. Nox   Nitrogen oxides (“knox”)
7. CO   Carbon monoxide

An example of complexity of interactions among these chemicals in the troposphere:

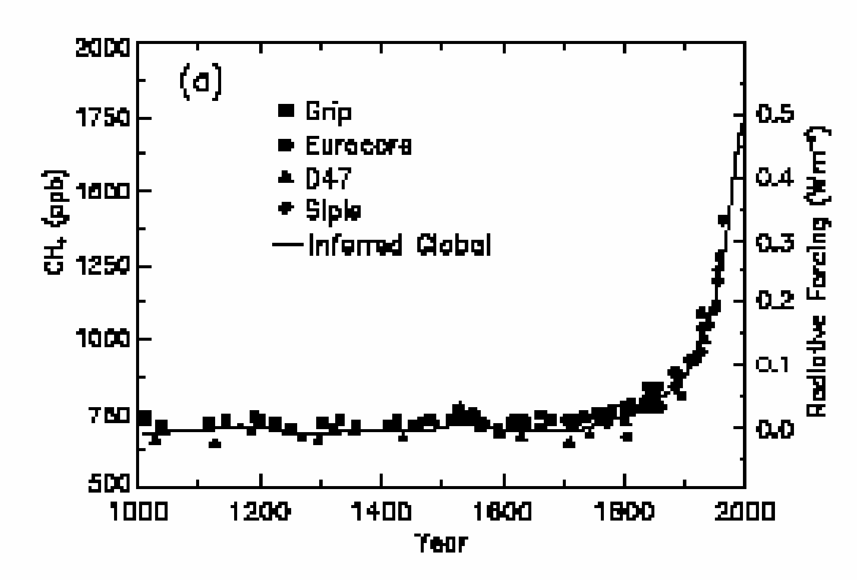
Nox (humans) promotes O_3 formation
O_3 promotes OH formation
OH consumes CH_4 and CO but promotes CO_2
CO promotes O_3 formation

5 of the 7 chemicals we discuss here are involved in spatially/temporally variable atmospheric reactions.

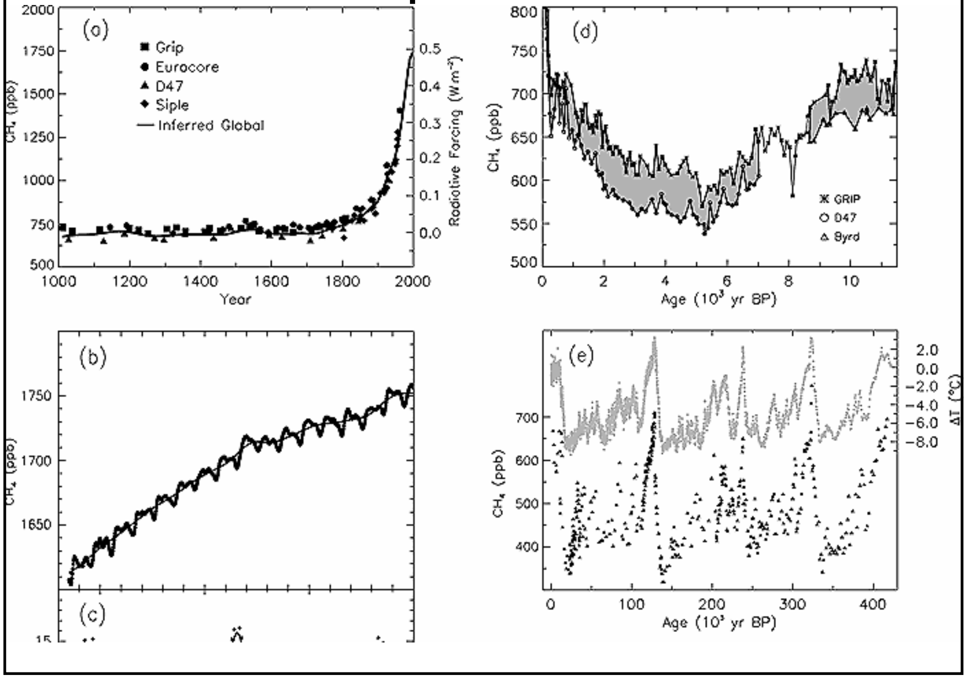
Methane (CH_4)

- **Production: wetlands, rice, ruminants, fossil fuels, plants?**
- **Anaerobic envts: in aerobic envts, usually CO_2 is metabolic end product, but no O_2 around in wetlands etc. CH_4 becomes the 'waste' product but it is high quality waste, energetically.**
- **Molecule for molecule, 23X more GWP than CO_2**
- **~ 9 yr mean residence time (pretty well mixed)**
- **About 1.8 ppm, more than doubled from 1750**
- **Consumed largely by OH^-, but not so readily…**
  $CH_4 + OH^- \rightarrow CH_3 + H_2O$

CH4 increase is well-resolved globally



Modern CH4 rise is unprecedented



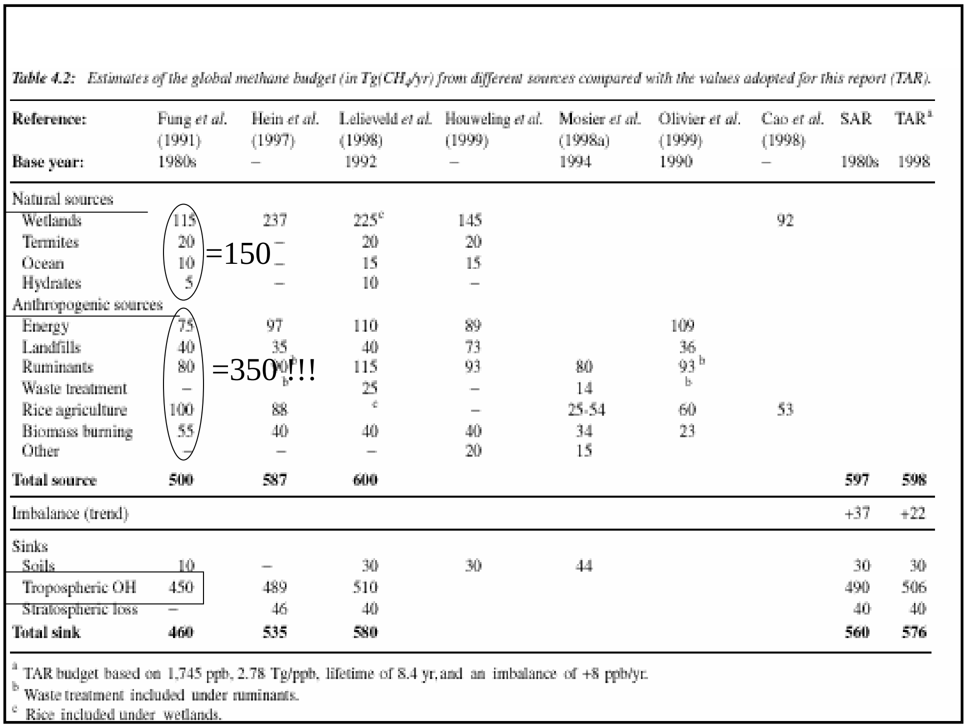


Table 4.2: Estimates of the global methane budget (in Tg(CH$_4$/yr) from different sources compared with the values adopted for this report (TAR).

Reference:	Fung *et al.* (1991)	Hein *et al.* (1997)	Lelieveld *et al.* (1998)	Houweling *et al.* (1999)	Mosier *et al.* (1998a)	Olivier *et al.* (1999)	Cao *et al.* (1998)	SAR	TAR[a]
Base year:	1980s	–	1992	–	1994	1990	–	1980s	1998
Natural sources									
Wetlands	115	237	225[c]	145			92		
Termites	20	–	20	20					
Ocean	10	–	15	15					
Hydrates	5	–	10	–					
Anthropogenic sources									
Energy	75	97	110	89		109			
Landfills	40	35	40	73		36			
Ruminants	80	90[b]	115	93	80	93[b]			
Waste treatment	–	[b]	25	–	14	[b]			
Rice agriculture	100	88	[c]	–	25-54	60	53		
Biomass burning	55	40	40	40	34	23			
Other	–	–	–	20	15				
Total source	**500**	**587**	**600**					**597**	**598**
Imbalance (trend)								+37	+22
Sinks									
Soils	10	–	30	30	44			30	30
Tropospheric OH	450	489	510					490	506
Stratospheric loss	–	46	40					40	40
Total sink	**460**	**535**	**580**					**560**	**576**

[a] TAR budget based on 1,745 ppb, 2.78 Tg/ppb, lifetime of 8.4 yr, and an imbalance of +8 ppb/yr.

[b] Waste treatment included under ruminants.

[c] Rice included under wetlands.

=150

=350 !!!

Tropospheric Ozone (O3)

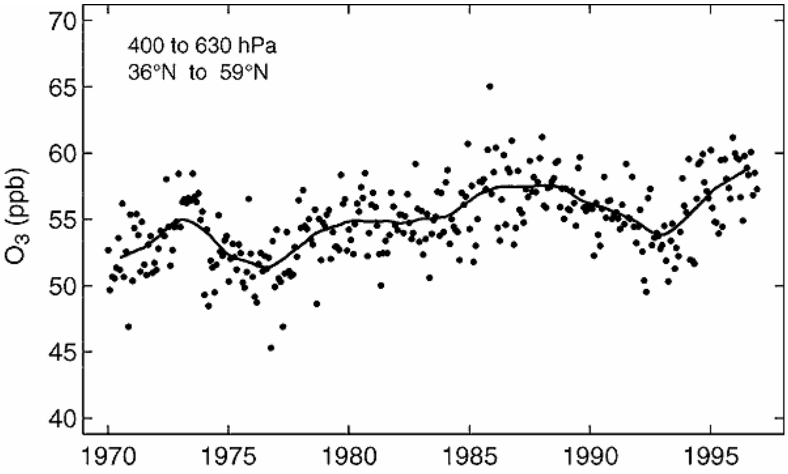
- **Mean residence time: weeks! Highly variable spatially**

- **Direct greenhouse gas, but hard to quantify GWP**

- **Bad in troposphere, good in stratosphere**

- **No ice core data, too reactive, hard to get a handle on past levels. Some data suggest Europe has 3X ozone today compared to late 1800s. Uncertain trends over last few decades…**

Ozone highly variable



WGI: Figure 4.8: Mid-tropospheric O3 abundance (ppb) in northern mid-latitudes (36°N-59°N) for the years 1970 to 1996.

Tropospheric Ozone (O3)

•Production: NOX pollution (cars, factories, biomass burning) –

NO2 + uv -> NO + O
O + O2 -> O3

Note: uv is UltraViolet light – increases in troposphere with stratospheric ozone depletion!

also, CO pollution –
CO + 2O2 -> CO2 + O3

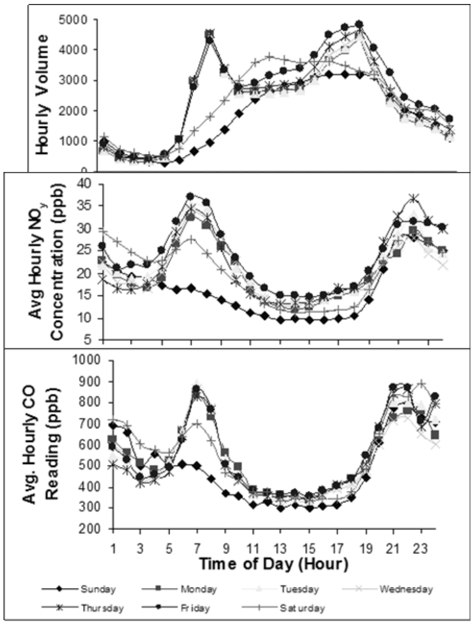
and NOX + uV + volatile organic hydrocarbons…

Consumption: largely by uv light, producing OH -

O3 + H2O + uv -> O2 + 2OH-

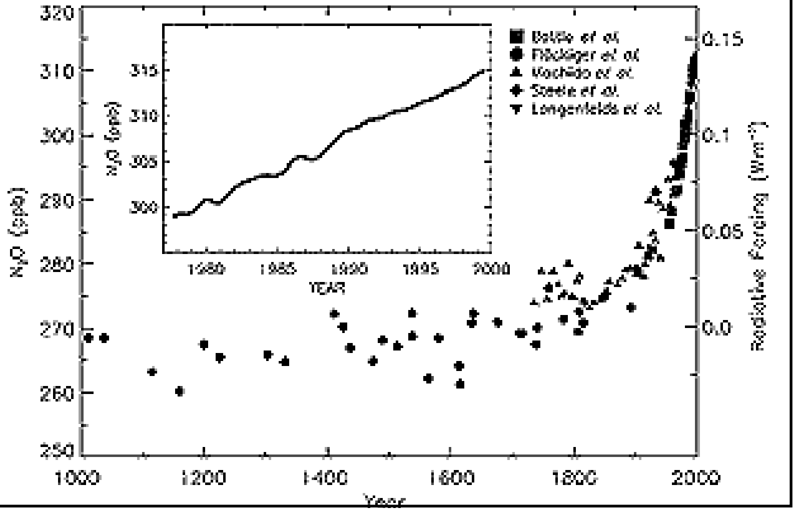
Traffic in Charlotte, NC

Perry & Owens 2001 (unpublished)



Nitrous oxide (N2O): no laughing matter

- **Long residence time, inert in troposphere (120 yrs)**
- **GWP: 300!**
- **Rising due to humans:**



- **Rising due to humans:**

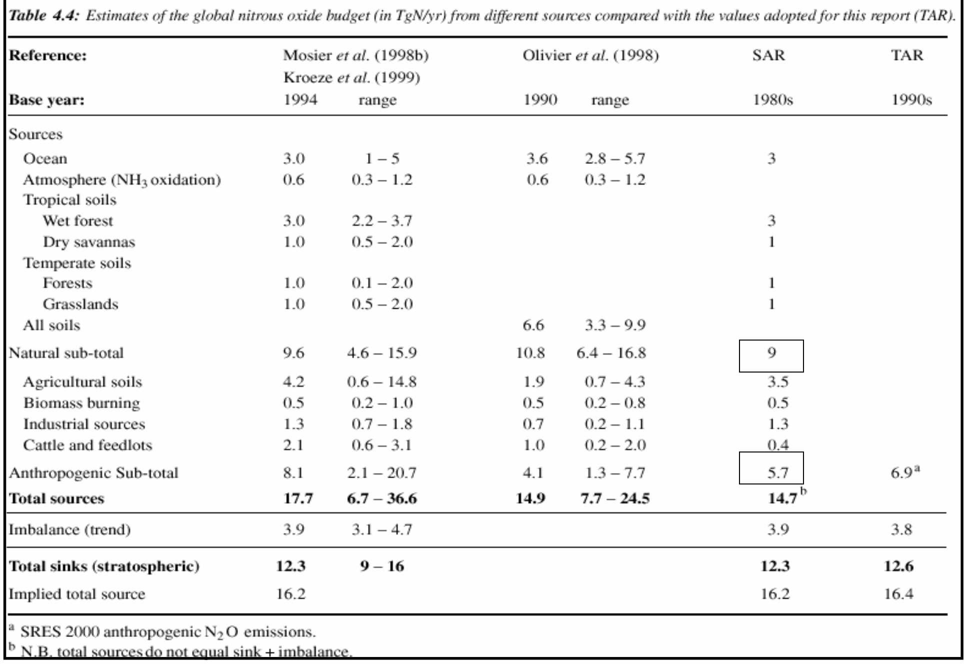


Table 4.4: Estimates of the global nitrous oxide budget (in TgN/yr) from different sources compared with the values adopted for this report (TAR).

Reference:	Mosier *et al.* (1998b) Kroeze *et al.* (1999)		Olivier *et al.* (1998)		SAR	TAR
Base year:	1994	range	1990	range	1980s	1990s
Sources						
Ocean	3.0	1 – 5	3.6	2.8 – 5.7	3	
Atmosphere (NH_3 oxidation)	0.6	0.3 – 1.2	0.6	0.3 – 1.2		
Tropical soils						
Wet forest	3.0	2.2 – 3.7			3	
Dry savannas	1.0	0.5 – 2.0			1	
Temperate soils						
Forests	1.0	0.1 – 2.0			1	
Grasslands	1.0	0.5 – 2.0			1	
All soils			6.6	3.3 – 9.9		
Natural sub-total	9.6	4.6 – 15.9	10.8	6.4 – 16.8	9	
Agricultural soils	4.2	0.6 – 14.8	1.9	0.7 – 4.3	3.5	
Biomass burning	0.5	0.2 – 1.0	0.5	0.2 – 0.8	0.5	
Industrial sources	1.3	0.7 – 1.8	0.7	0.2 – 1.1	1.3	
Cattle and feedlots	2.1	0.6 – 3.1	1.0	0.2 – 2.0	0.4	
Anthropogenic Sub-total	8.1	2.1 – 20.7	4.1	1.3 – 7.7	5.7	6.9[a]
Total sources	**17.7**	**6.7 – 36.6**	**14.9**	**7.7 – 24.5**	**14.7**[b]	
Imbalance (trend)	3.9	3.1 – 4.7			3.9	3.8
Total sinks (stratospheric)	**12.3**	**9 – 16**			**12.3**	**12.6**
Implied total source	16.2				16.2	16.4

[a] SRES 2000 anthropogenic N_2O emissions.

[b] N.B. total sources do not equal sink + imbalance.

Nitrous oxide (N2O):

- **Production: mostly soils, but lots due to human disturbance of soils (agriculture, N deposition)**

- **Consumption: not reactive in troposphere, breaks up in stratosphere due to UV light (photolysis)**

An aside:

60% of N deposition on land surfaces is by humans!

Soils return this ultimately in the forms of N2 and N2O

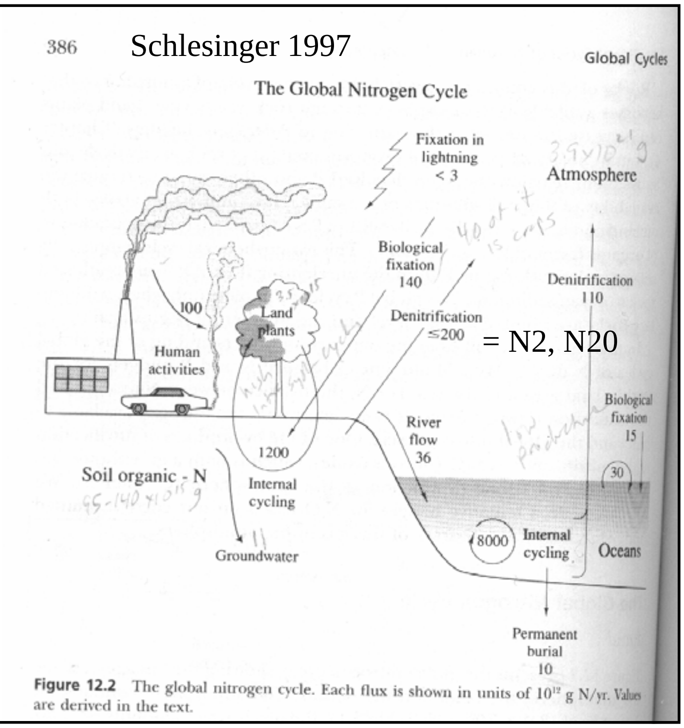


Figure 12.2 The global nitrogen cycle. Each flux is shown in units of 10^{12} g N/yr. Values are derived in the text.

Getting N2 into other forms costs a lot of energy.

Bacteria use plant energy to do this.

Humans use fossil fuels and short cut this natural process (Haber process, cars, factories)

N2O results…

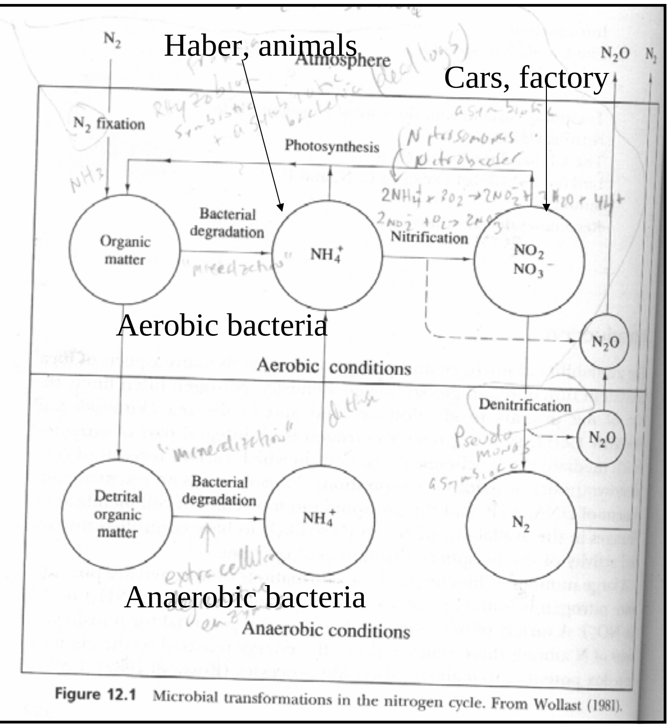
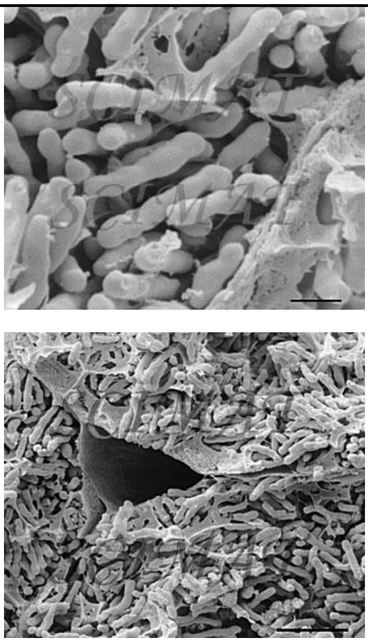


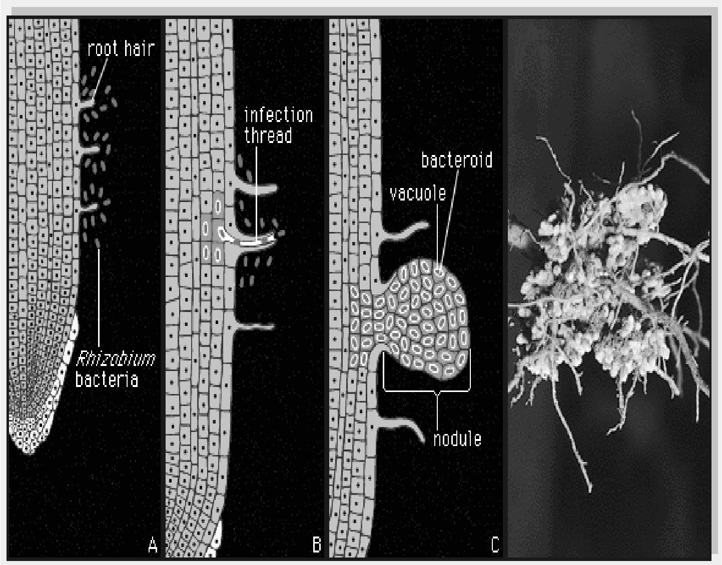
Figure 12.1 Microbial transformations in the nitrogen cycle. From Wollast (1981).

Soybean
Root
nodules



Bar = 5 um

bar = 1 um



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Hydroxyl radical (OH-)

- Key controller of other GHG’s (CH4, CO2) and other atmospheric pollutants (HNO3, HSO3) in troposphere

- Mean residence time: seconds! Highly spatially variable, not certain if there is any global trend

- Production in troposphere: mostly photochemical (ozone hole!)

  $O_3 + uv \rightarrow O + O_2$

  $O + H_2O \rightarrow 2OH^-$

- Consumption:

  $CH_4 + OH \rightarrow CH_3 + H_2O$

  $CO + OH \rightarrow H + CO_2$

  $NO_2 + OH \rightarrow HNO_3$

  $SO_2 + OH \rightarrow HSO_3$

- CO competes with CH4 for consumption of OH…

A few words about chemical reactions:

Speed of reactions vs. direction of reactions

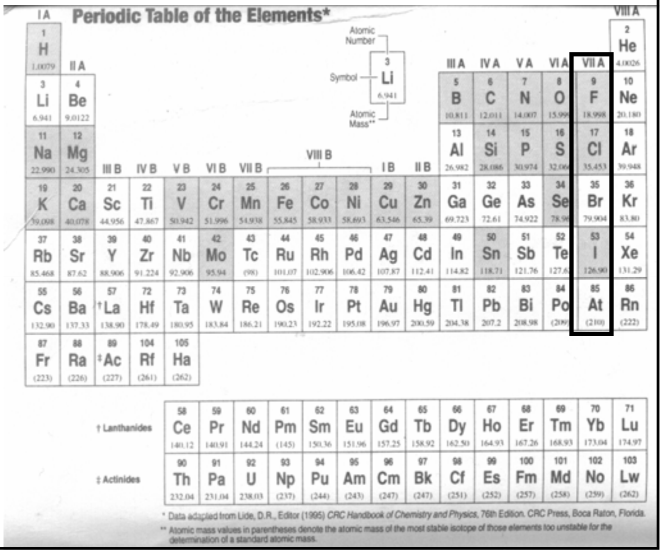
$CH_4 + OH \rightarrow CH_3 + H_2O$

Vs. $CO + 2OH \rightarrow H_2O + CO_2$ (faster rxn)

Halocarbons (‘halogen-carbons’)

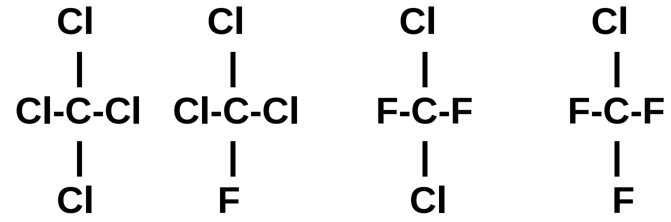
- **Halogens (flourine, chlorine, bromine, etc.). Alone, these are very reactive elements (why?)**

Unpaired electrons and the octet rule



Halocarbons (‘halogen-carbons’)

- **When combined with carbon, they become extremely stable Some examples:**



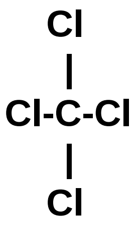
$$\begin{array}{cccc} \mathrm{Cl} & \mathrm{Cl} & \mathrm{Cl} & \mathrm{Cl} \\ | & | & | & | \\ \mathrm{Cl\text{-}C\text{-}Cl} & \mathrm{Cl\text{-}C\text{-}Cl} & \mathrm{F\text{-}C\text{-}F} & \mathrm{F\text{-}C\text{-}F} \\ | & | & | & | \\ \mathrm{Cl} & \mathrm{F} & \mathrm{Cl} & \mathrm{F} \end{array}$$

carbon tetrachloride **CFC-11** **CFC-12** **CFC-13**

(carbon as legos vs. halogens as superglue)

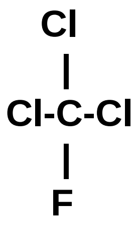
Halocarbons (‘halogen-carbons’)

•Nomenclature



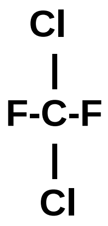
$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}C{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$

carbon tetrachloride



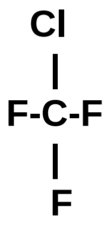
$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}C{-}Cl}\\ |\\ \mathrm{F}\end{array}$$

CFC-11



$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{F{-}C{-}F}\\ |\\ \mathrm{Cl}\end{array}$$

CFC-12



$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{F{-}C{-}F}\\ |\\ \mathrm{F}\end{array}$$

CFC-13

90 + X = C + H + F
e.g. 90 + (CFC)13 = 103 = 1 carbon, 0 hydrogen, 3 flourine
e.g. 90 + (HFC)23 = 113 = 1 carbon, 1 hydrogen, 3 flourine
e.g. 90 + (CFC)113 = 203 = 2 carbon, 0 hydrogen, 3 flourine

Halocarbons (‘halogen-carbons’)

•Hydroflourocarbons are generally less stable than CFC’s (see lifetimes in Table 4.1)

•This is good for the ozone layer, not so good for applications like refrigeration etc.

•Most halocarbons are very strong greenhouse gases

•The key benefit of HFC’s are that they don’t contain chlorine.

•Why is this lack of chlorine so important for the ozone layer? We need to look at a bit of chemistry in the stratosphere…

CFC's and the ozone hole: the role of Cl

•Cl participates in a *Catalytic Reaction Cycle*, which has the crucial property of regenerating the original catalytic agent (Cl) to facilitate further stratospheric ozone destruction.

•Here's a generalized ozone destruction reaction:

Cl• + O3 -> ClO• + O2
O3 + hv -> O• + O2
O• + ClO• -> Cl• + O2

Net: 2O3 -> 3O2

Where X• and XO• are highly reactive chemicals ("•" indicates a 'free' (unpaired) electron that is highly unstable)
Bottom line: Cl helps destroy O3 and is regenerated to do it again!

CFC's and the ozone hole: the role of Cl

A question: how do we get Cl• from CFC's?

UV light in the stratosphere is strong enough, and abundant enough, to break up CFC's

An example with CFC-11:

$CFCl_3$ + uV (<260nm) + O2 -> CO2 + F• + 3Cl•

A single CFC molecule can release 3 (or even up to 4, with CCl4) Cl's!!

Note we also have F• released – why isn't it important? It is quicky consumed to form HF, and slow to regenerate.

An interesting, and important, aside:

Here again is the ozone destruction by Cl:

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
$O_3 + h\nu \rightarrow O\bullet + O_2$
$\underline{O\bullet + ClO\bullet \rightarrow Cl\bullet + O_2}$
Net: $2O_3 \rightarrow 3O_2$

It turns out that we can plug in $NO\bullet$ or $NO_2\bullet$ as well:

$NO\bullet + O_3 \rightarrow NO_2\bullet + O_2$
$O_3 + h\nu \rightarrow O\bullet + O_2$
$\underline{O\bullet + NO_2\bullet \rightarrow NO\bullet + O_2}$
Net: $2O_3 \rightarrow 3O_2$

But where does the $NO\bullet$ or $NO_2\bullet$ in the stratosphere come from?

Largely from N_2O (nitrous oxide)!!
Example:

$N_2O + O\bullet \rightarrow 2NO$

Thus, by increasing nitrous oxide emissions, humans still impact stratospheric ozone. The montreal protocol doesn’t cover N_2O.

In fact, the initial studies of stratospheric ozone depletion focused on N_2O (Crutzen) before Molina/Rowland considered Cl.

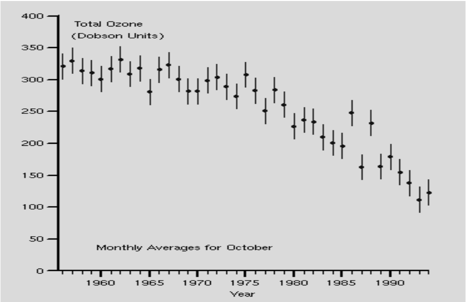
Further thoughts on the ozone hole:

•It occurs largely over antarctica and to a lesser degree, the arctic (see Farman paper). Why?

Answer: Cold temperatures and large seasonality in light
We'll explain why those factors matter later…

Why we usually hear about the ozone hole over antarctica. (and in the antarctic spring)

1. **Cold temperatures mean ice clouds**
2. **Ice cloud particles provide focal surfaces for ozone depleting chemical reactions to occur ('heterogeneous reactions').**
3. **Polar night allows ozone depleting chemicals to build up on cloud ice particles, polar day allows light to release and react these ozone depleting chemicals.**



Strat. Ozone depletion occurs in the polar spring over antarctica, moreso the farther south one goes.

Empirical findings of Farman et al. validated the predictions of Molina and Rowland

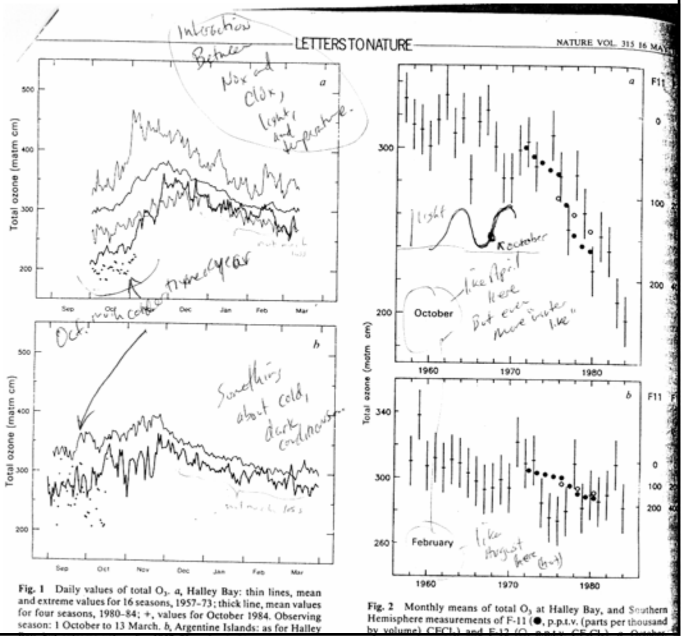

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Fig. 1 Daily values of total O_3. *a*, Halley Bay: thin lines, mean and extreme values for 16 seasons, 1957–73; thick line, mean values for four seasons, 1980–84; +, values for October 1984. Observing season: 1 October to 13 March. *b*, Argentine Islands: as for Halley

Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. (parts per thousand

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Argentine Islands

Halley Bay

Halley Bay

Key steps in stratospheric ozone depletion:

1. **Winter buildup of ozone destoying 'reservoir' molecules: a latent atmospheric 'poison':**

Everywhere in stratosphere, a natural feedback on ozone depletion is locking up of N and Cl catalysts:

HO• + NO_2 +M -> HNO_3 + M (nitric acid)
ClO• + NO_2 + M -> $ClONO_2$ + M (chlorine nitrate)

M is a mediator molecule that absorbs excess rxn energy.

But these products are temporary and can photodissociate back to the initial reactants:
HNO_3 + hv (<330nm) -> HO + NO_2
$ClONO_2$ + hv (<450nm) -> ClO + NO_2
But in polar winter, no light for this process, so the reactants build up

---

Key steps in stratospheric ozone depletion:

2. **Chemical breakup of reservoir molecules is enhanced with freezing stratospheric temperatures:**

$ClONO_2$ + HCl -> Cl_2 + HNO_3
(here HCl is a harmless reservoir molecules with renders Cl harmless to ozone).

The Cl_2 can photodissociate to form damaging Cl:
Cl_2 + hv (<450nm) -> 2Cl•

However, in the gas phase, the reaction at the top of this page is so slow as to be negligible. Must be another way to release Cl• In stratospheric ice clouds, the reaction occurs very fast – both $ClONO_2$ and HCl attach readily to ice crystals.

Summary:

The timing of seasonal ozone loss found by Farman et al. makes sense with this mechanism.

ClONO2 builds up over the long winter because there is little light for dissociating it.

In spring, temperatures still cold, but light increases, allowing for dissociation of Cl2 into Cl, and rapid depletion of ozone.

Question: why not as strong over the arctic?

Some concluding thoughts:

"*The issues of ozone depletion and climate change are inter-connected; hence, so are the Montreal and Kyoto Protocols.* Changes in ozone affect the earth's climate, and changes in climate and meteorological conditions affect the ozone layer…

Hence, decisions taken (or not taken) under one Protocol have an impact on the aims of the other Protocol. For example, decisions made under the Kyoto Protocol with respect to methane, nitrous oxide, and carbon dioxide will affect the rate of recovery of ozone, while decisions regarding controlling HFC's may affect decisions regarding the ability to phase out ozone-depleting substances.

WMO Scientific Assessement of Ozone depletion: 1998