Dear Dr. Detlev Helmig,

First of all, I thank you very much for your willingness to participate in the upcoming IPCC Expert Meeting on SLCF in Geneva on 28-31 May. I would like to request you, on behalf of the scientific steering committee for this meeting, to deliver a presentation at the meeting, **on impacts of atmospheric chemistry on the lifetimes of SLCF (VOC, ozone, NOX, etc)**. We expect it to be for 15 minutes including short Q&A for 2-3 minutes and to be delivered on Day 1. Could you kindly accept our request? We would very much appreciate your cooperation.

Best regards, Kiyoto Tanabe Co-Chair,

IPCC Task Force on National Greenhouse Gas Inventories

# Impacts of atmospheric chemistry on the lifetimes of SLCF

Detlev Helmig[1], Andrea Pozzer[2]

[1]Institute of Arctic and Alpine Research, University of Colorado, Boulder, USA;
[2] Max Planck Institute for Chemistry, Mainz, Germany

**GAW research on reactive gases**

**What are reactive gases?**

The reactive gases as a group are very diverse and include surface ozone (O3), carbon monoxide (CO), volatile organic compounds (VOCs), oxidised nitrogen compounds (NOx, NOy), and sulphur dioxide (SO2). All of these compounds play a major role in the chemistry of the atmosphere and as such are heavily involved in inter-relations between atmospheric chemistry and climate, either through control of ozone and the oxidising capacity of the atmosphere, or through the formation of aerosols. The global measurement base for most of them is entirely unsatisfactory, the only exceptions being surface ozone and carbon monoxide.

Scientific Advisory Group for Reactive Gases advises on implementation of the GAW Programme for this group of gases.

Recommendations on the measurements and their quality assurance are given in respective Measurement Guidelines.

Data on reactive gases can be found at the WMO/GAW World Data Centre for Greenhouse Gases (WDCGG).

GAW observations of reactive gases collected in near-real time are used for model validation in the MACC project.

**Surface ozone**

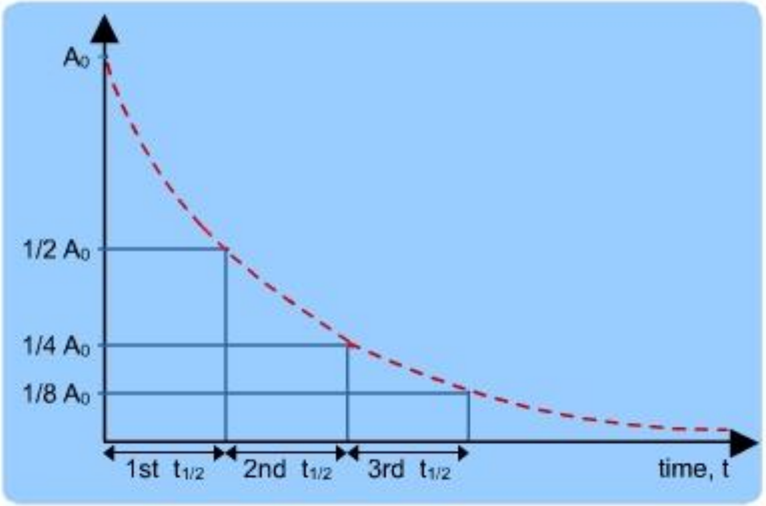
Surface ozone observations in GAW (movie)

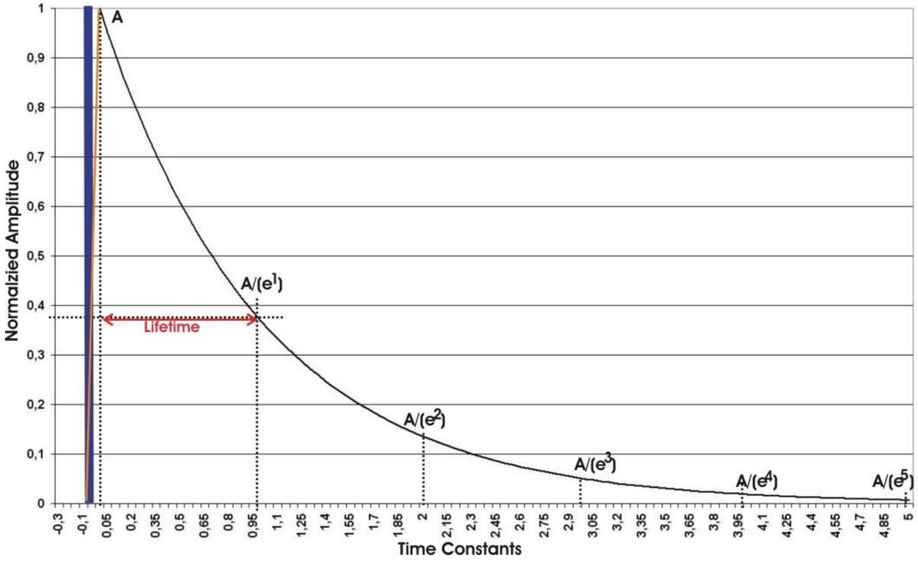
WMO-GAW Scientific Advisory Group for Reactive Gases

- Aerosols
    - Black Carbon
    - Organic Carbon
    - PM2.5
- Precursors (ozone precursors and aerosol precursors
    - NOx
    - CO
    - NMVOC (including BVOC)
    - $SO_2$
    - $NH_3$

# “Lifetime”

Natural lifetime: “lifetime” = time for concentration of species to fall to 1/e (36%) of starting value





# “Lifetime”

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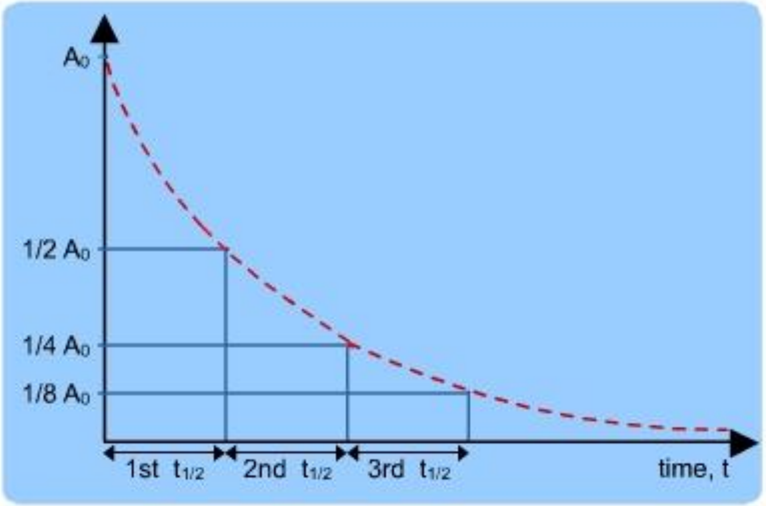
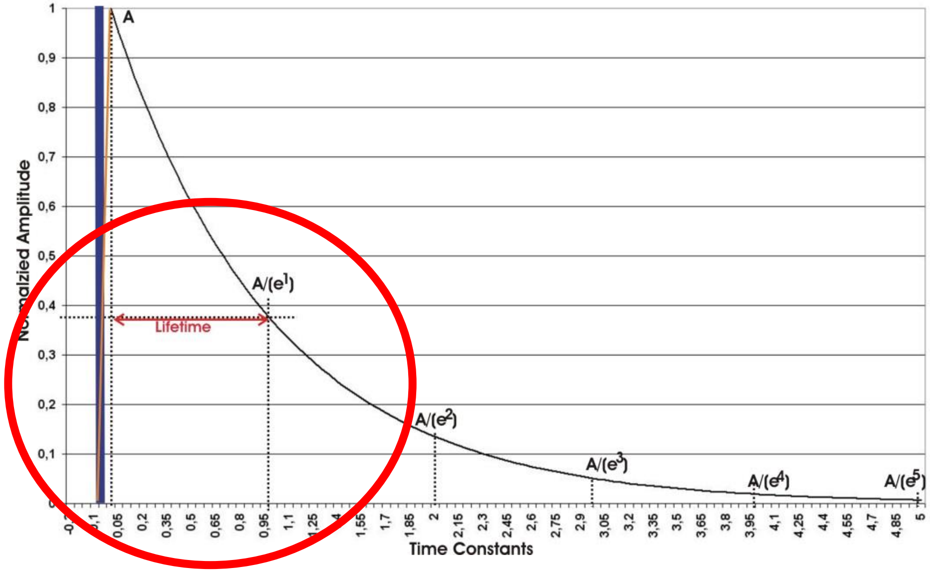
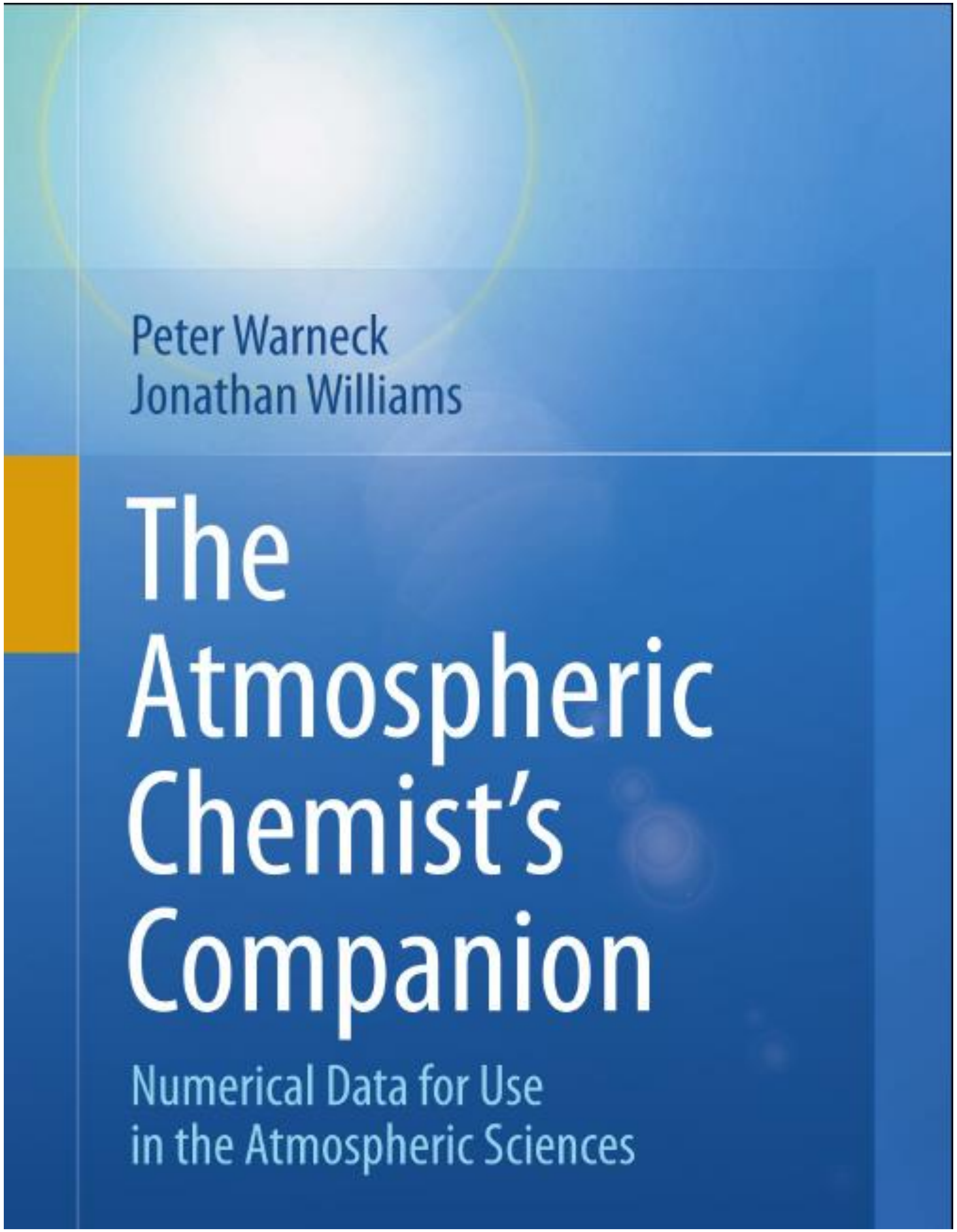




Dr. Peter Warneck
Max Planck Institute for Chemistry
Mainz
Germany

Dr. Jonathan Williams
Max Planck Institute for Chemistry
Mainz
Germany



Peter Warneck
Jonathan Williams

The Atmospheric Chemist's Companion

Numerical Data for Use in the Atmospheric Sciences

Published 2012, Springer

**Table 4.1** Overview on important trace gases in the troposphere: approximate residence times, molar mixing ratios, global distribution, sources and sinks[a]

| Trace gas | Distribution | |
|---|---|---|
| Residence time | Abundance[b] | Major sources and sinks ($Tg\ a^{-1}$)[c] |
| Carbon monoxide, CO (2 m) | 150 ppb (NH)<br>50 ppb (SH) | Anthropogenic (+450), biomass burning (+700) $CH_4$ oxidation (+600), oxidation natural VOC (+800), reaction with OH (−2,000), stratosphere (−100), uptake by soils (−300) |
| Ozone, $O_3$ (2 m) | 15–50 ppb<br>Equator < poles | Influx from stratosphere (+600), photochemical production (+4,000), photochemical loss (−3,700), dry deposition (−800) |
| Nitrogen oxides, $NO_x$ (2 days) | 30 ppt (M)<br>0.3–5 ppb (C) | Fossil fuel-derived (+21), biomass burning (+8), emission from soils (+7), lightning (+5), loss occurs by oxidation of $NO_2$ to $HNO_3$ |
| Nitric acid, $HNO_3$ (6 days) | 70 ppt (M)<br>0.1–2 ppb (C)<br>50–130 ppt (FT) | Oxidation of $NO_2$ (+43), dry deposition (−16), attachment to aerosol particles followed by wet deposition (−27) |
| Ammonia, $NH_3$ (~3 days) | 50–90 ppt (M)<br>5 ppb (C) | Domestic animals (+22), emissions from oceans (+7), vegetation (+6), use of fertilizer (+6), dry deposition (−15), conversion to $NH_4^+$ aerosol followed by wet deposition (−30) |
| Sulfur dioxide, $SO_2$ (4 days) | 20–90 ppt (M)<br>0.1–2 ppb (C) | Fossil fuel-derived (+150), volcanoes (+16), oxidation of DMS (+40), dry deposition (−75), Conversion to $SO_4^{2-}$ and wet deposition (−120) |

**Table 4.1** (continued)

| Trace gas | Distribution | |
|---|---|---|
| Residence time | Abundance[b] | Major sources and sinks (Tg $a^{-1}$)[c] |
| Ethane, $C_2H_6$<br>(60 days) | 1.3 ppb (M, NH)<br>0.4 ppb (M, SH) | Biomass burning (+7), natural gas loss (+6), the major sink is reaction with OH |
| Propane, $C_3H_8$<br>(12 days) | 1 ppb (M, NH)<br>0.2 ppb (M, SH) | Anthropogenic sources (+23), the major sink is reaction with OH |
| Benzene, $C_6H_6$<br>(10 days) | 0.3 ppb (C)<br><0.1 (FT) | Industrial + fossil fuel (+1.5), Biofuel (+2)<br>Biomass burning (+2.7), major sink is OH |
| Toluene, $C_7H_8$<br>(2 days) | 0.6 ppb (C)<br><0.05 (FT) | Industrial + fossil fuel (+4.7), Biofuel (+1.1)<br>Biomass burning (+1.8), major sink is OH |
| Isoprene, $C_5H_8$<br>(0.2 day) | 0.2–5 ppb (C) | Emissions from deciduous trees (+570), the major sink is reaction with OH |
| Terpenes, $C_{10}H_{16}$<br>(0.4 day) | 0.03–2 ppb (C) | Emissions from coniferous and deciduous trees (+140), sinks are reactions with OH and $O_3$ |

## Major Sinks of Atmospheric Reactive Trace Gases

| **$NO_x$** | **CO** | **NMVOC** | **$SO_2$** | **$NH_3$** | **$O_3$** |
|---|---|---|---|---|---|
| OH | OH | OH | OH | dry dep. | photolysis |
| dry dep. | soils | ozone | dry dep. | aerosol | chemical rxn |
| wet dep. | | Cl | wet dep. | wet dep. | dry dep. (non-stomatal) |
| aerosol | | $NO_3$ | | | |
| | | photolysis | | | dry dep. (stomates) |
| | | aerosol | | | |
| | | | | | OH |

**Table 4.7** Modeled global budgets of tropospheric ozone (Tg $a^{-1}$)[a]

| Influx from stratosphere | Chemical production[b] | Chemical loss[b] | Dry deposition | Global burden (Tg) | Residence time (days) | Model[c] |
|---|---|---|---|---|---|---|
| 570 | 3,310 | 3,170 | 710 | 350 | 33 | TM3 (1) |
| 470 | 4,900 | 4,300 | 1,070 | 320 | 22 | GEOS-Chem (2) |
| 593 | 4,895 | 4,498 | 990 | 322 | 21 | CHASER (3) |
| 340 | 5,260 | 4,750 | 860 | 360 | 23 | MOZART-2 (4) |
| 540 | 4,560 | 4,750 | 860 | 290 | 19 | MATCH-MPIC(5) |
| 523 | 4,486 | 3,918 | 1,090 | 296 | 22 | LMDz-INCA (6) |
| 395 | 4,980 | 4,420 | 950 | 273 | 19 | STOCHEM (7) |
| 520 | 4,090 | 3,850 | 760 | 283 | 22 | FRSGC/UCI (8) |
| 715 | 4,436 | 3,890 | 1,261 | 303 | 21 | LMDz-INCA (9) |
| 770 ± 400 | 3,420 ± 770 | 3,470 ± 520 | 770 ± 180 | 300 ± 30 | 24 ± 2 | 11 models (10) |
| 520 ± 200 | 5,060 ± 570 | 4,560 ± 720 | 1,010 ± 220 | 340 ± 40 | 22 ± 2 | 25 models (11) |

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D7, PAGES 8931–8980, APRIL 16, 2000

# Three-dimensional climatological distribution of tropospheric OH: Update and evaluation

C. M. Spivakovsky,[1] J. A. Logan,[1] S. A. Montzka,[2] Y. J. Balkanski,[1,3]
M. Foreman-Fowler,[1,4] D. B. A. Jones,[1] L. W. Horowitz,[1,5] A. C. Fusco,[1]
C. A. M. Brenninkmeijer,[6] M. J. Prather,[7] S. C. Wofsy,[1] and M. B. McElroy[1]

**Primary OH source:**

$O_3$ + hv -> $O(^1D)$ + $O_2$
$O(^1D)$ + $H_2O$ -> 2 OH

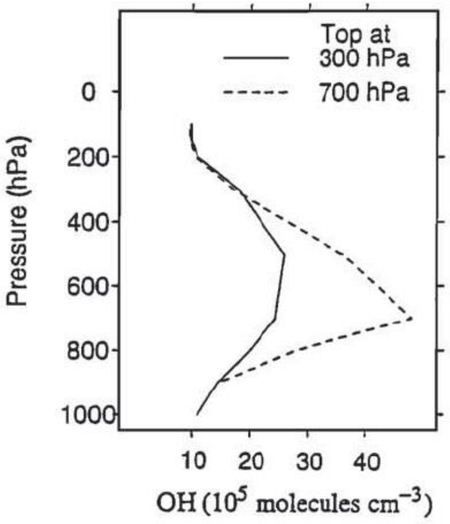


**Figure 4.** Vertical profiles of OH ($10^5$ molecules cm$^{-3}$) averaged over 24 hours at the equator for the cloud with optical depth 5 extending to 700 hPa (dashed line) and to 300 hPa (solid line). The optical depth of the cloud is distributed uniformly with altitude from the cloud top to 900 hPa.

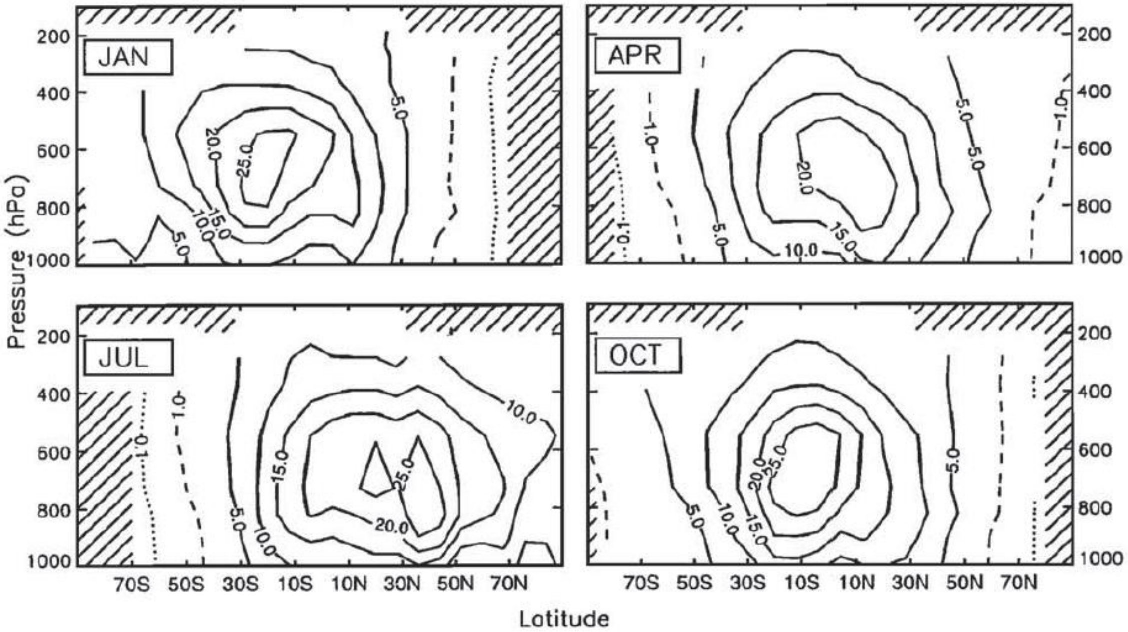
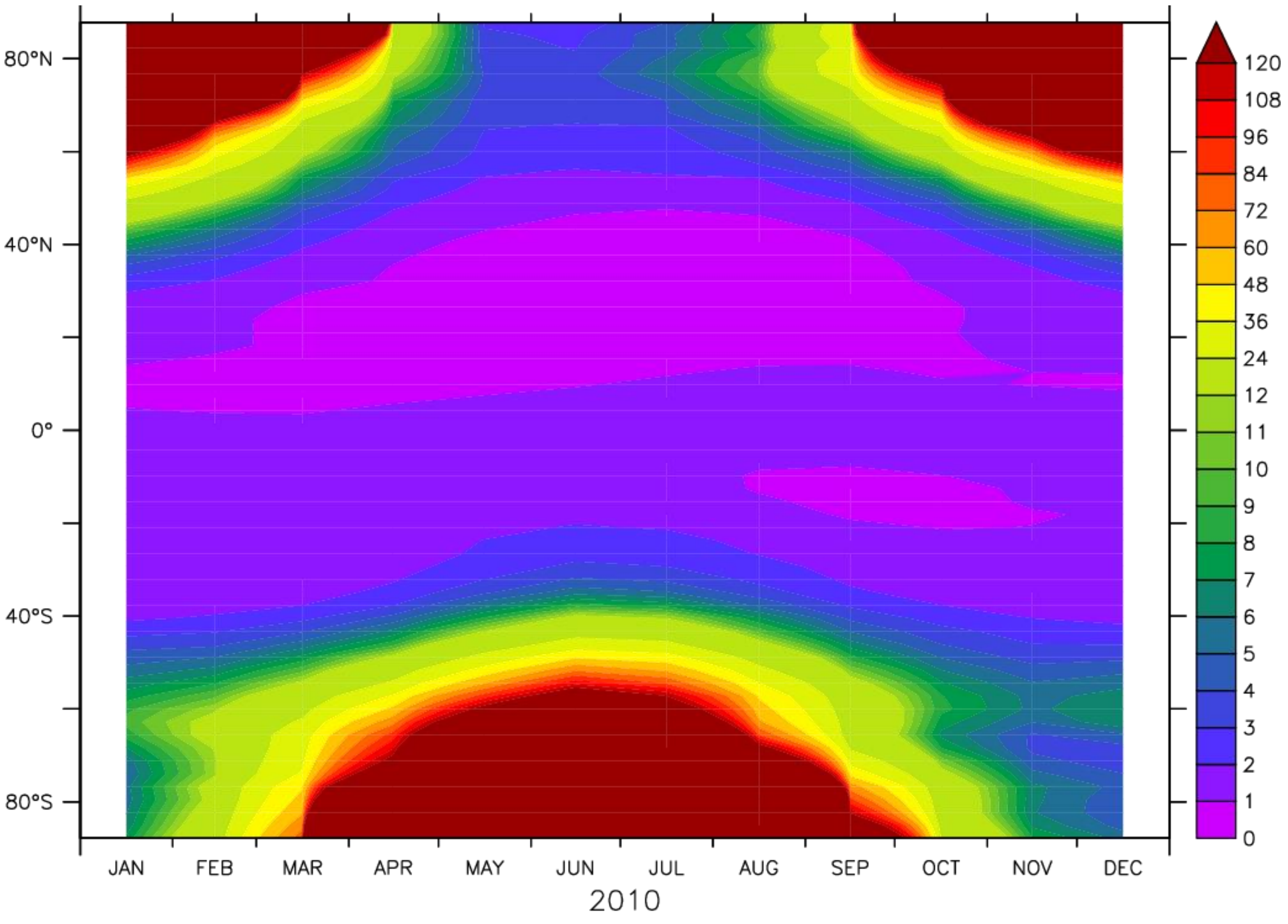


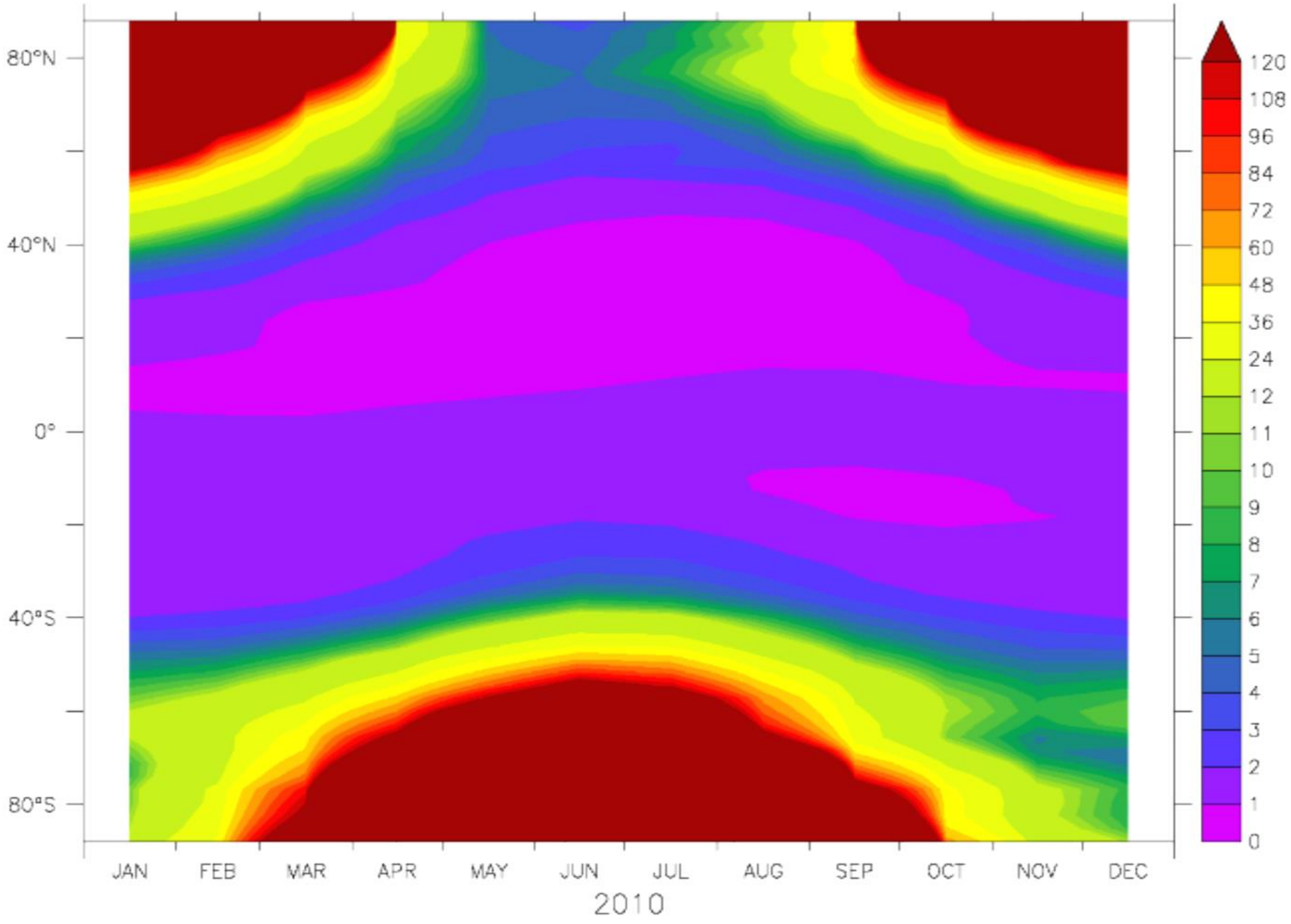
**Figure 6.** Zonally and monthly averaged concentrations of OH ($10^5$ molecules cm$^{-3}$) for January, April, July and October, including night hours. Contours are given for 0.1 (dotted lines), 1 (dashed lines), and for values from 5 to 30, with increments of 5 (solid lines).

# Global and seasonal lifetime of carbon monoxide



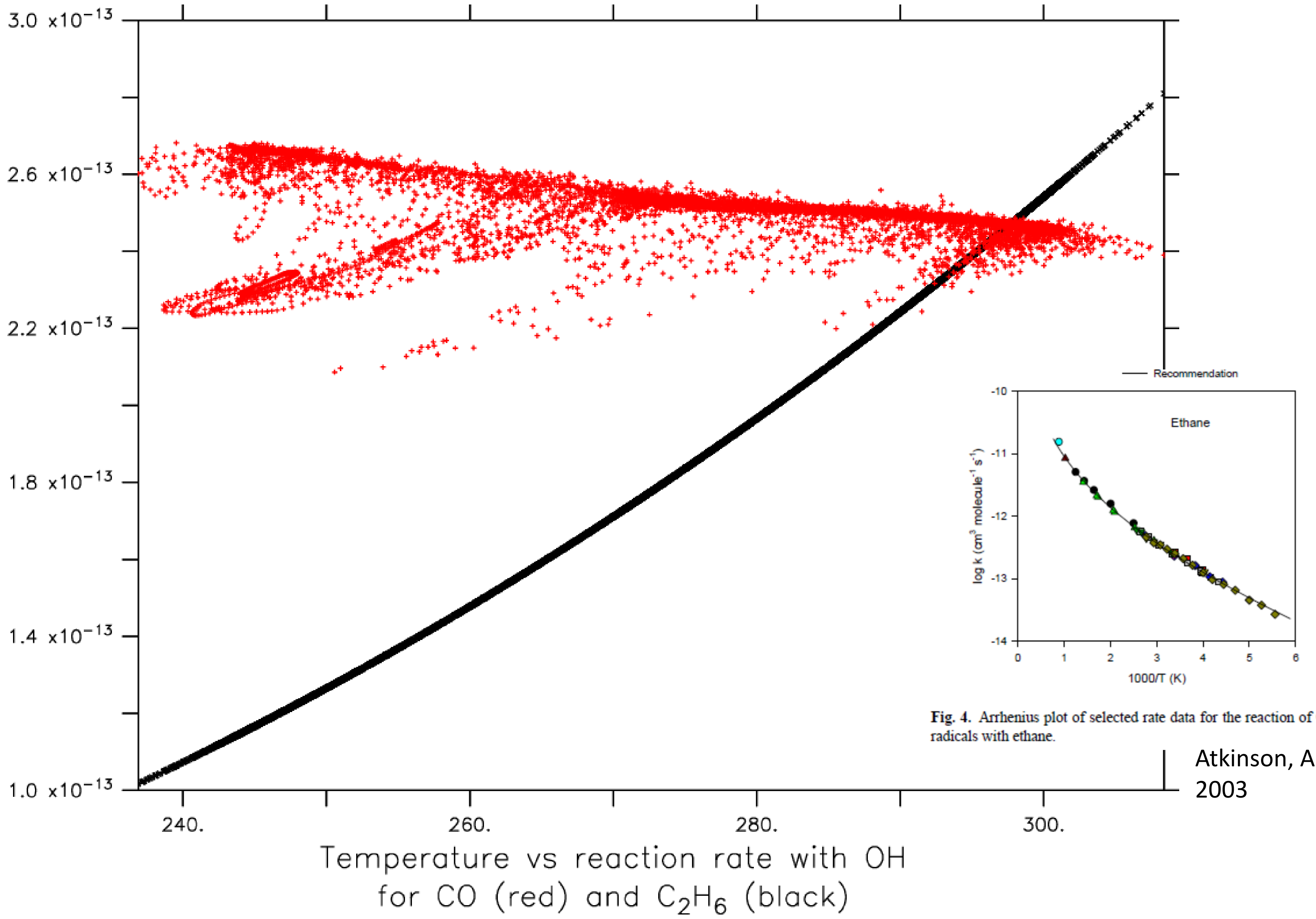
CO lifetime at the surface (months)

# Global and seasonal lifetime of ethane



$C_2H_6$ lifetime at the surface (months)

# Lifetime as a function of temperature

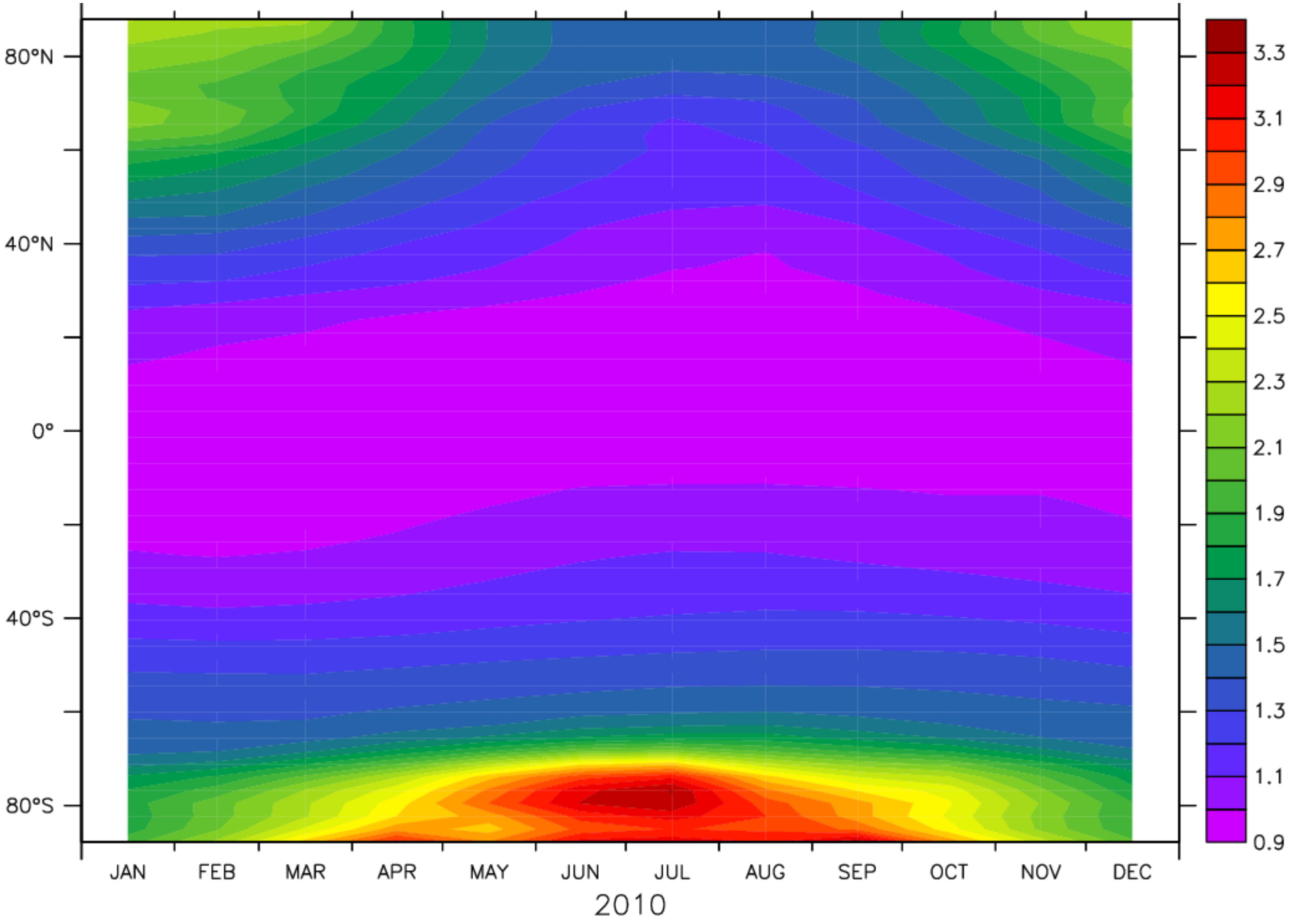


Temperature vs reaction rate with OH for CO (red) and $C_2H_6$ (black)

**Fig. 4.** Arrhenius plot of selected rate data for the reaction of OH radicals with ethane.

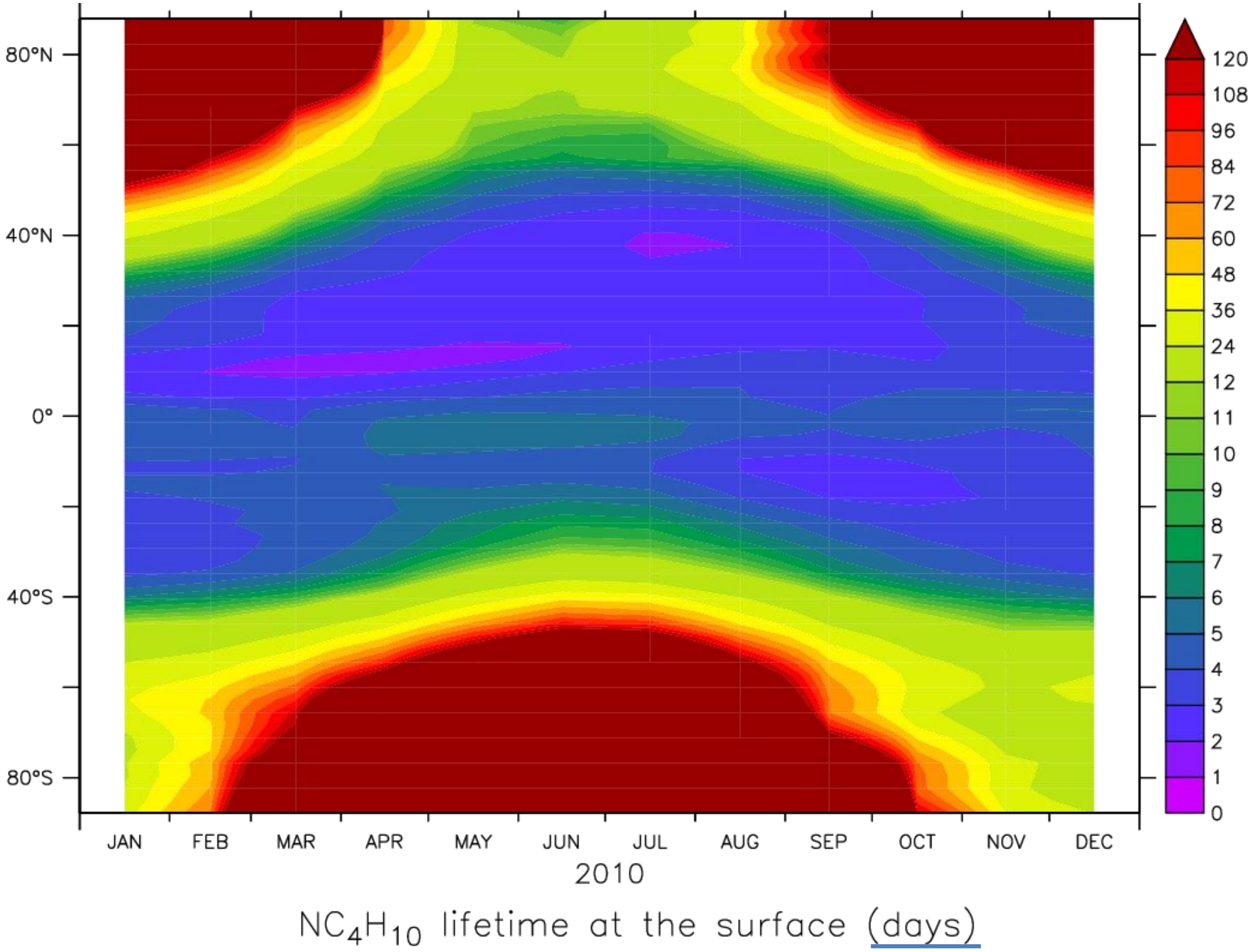
Atkinson, ACP, 2003

# Lifetime as a function of temperature



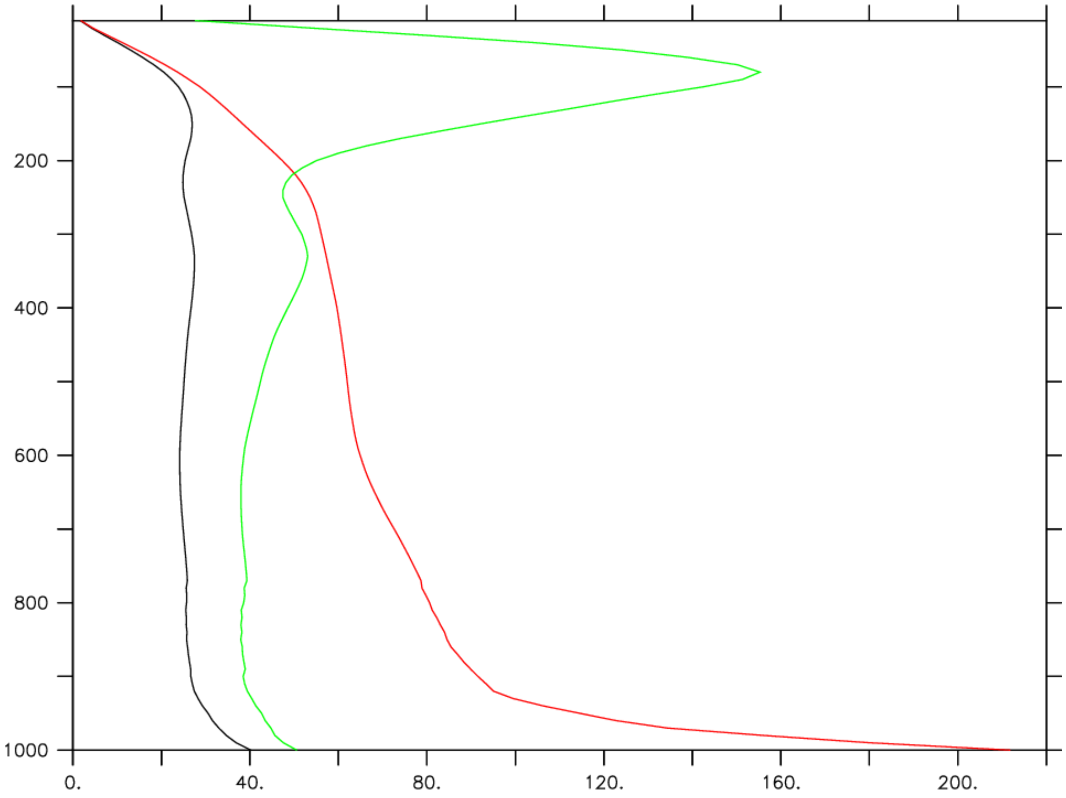
ratio of $C_2H_6$/CO lifetime at the surface

# Global and seasonal lifetime of n-butane



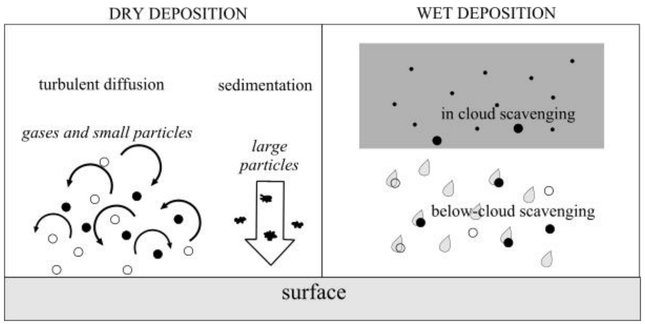
# Lifetime dependence on elevation

$CH_3COCH_3$ lifetime in days at 50N in August

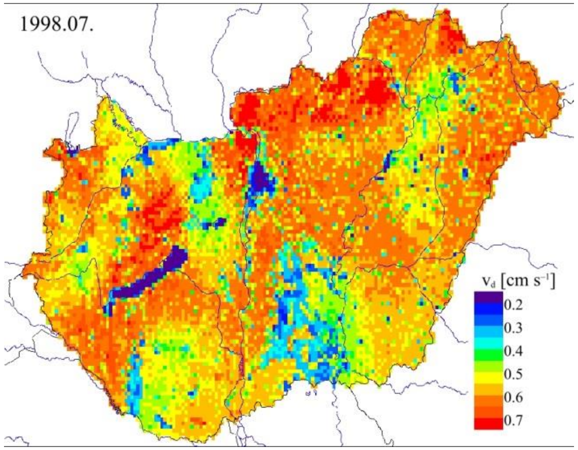


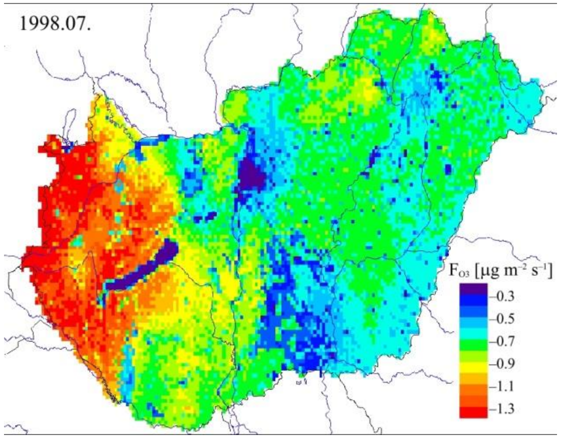
black: total, green: OH, red: photolysis

# Ozone Dry Deposition



Flux = -$v_d$ x Concentration



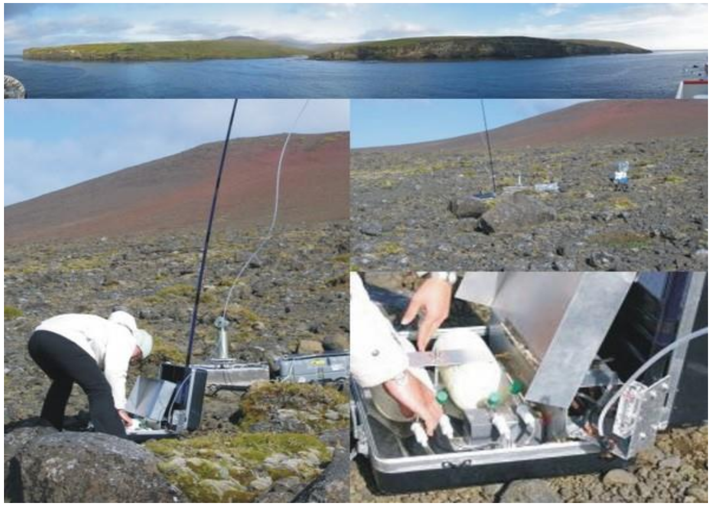


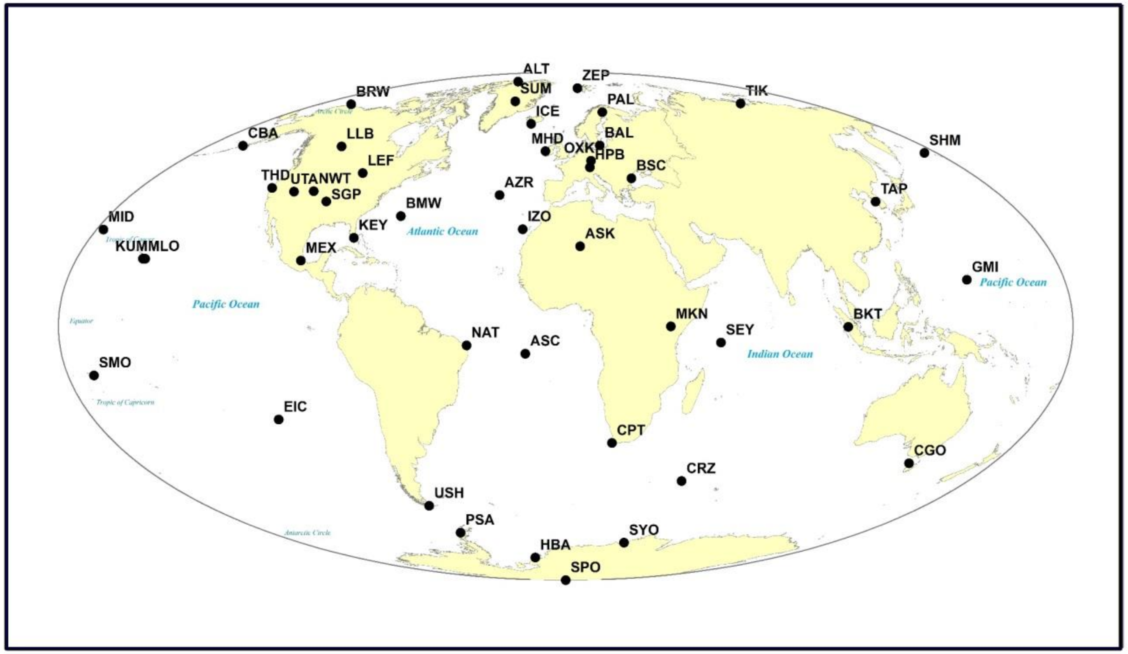
http://elte.prompt.hu/sites/default/files/tananyagok/AtmosphericChemistry/

## Ozone Deposition Velocity ($v_d$; cm/s)

| 4 | 2 | 1 | 0.1 | 0.01 |
|---|---|---|---|---|
| Tropical Forests | Vegetated Land | Agricultural Fields | Soil | Snow/Ice/Water |

# Reflection of VOC lifetimes in a global data set



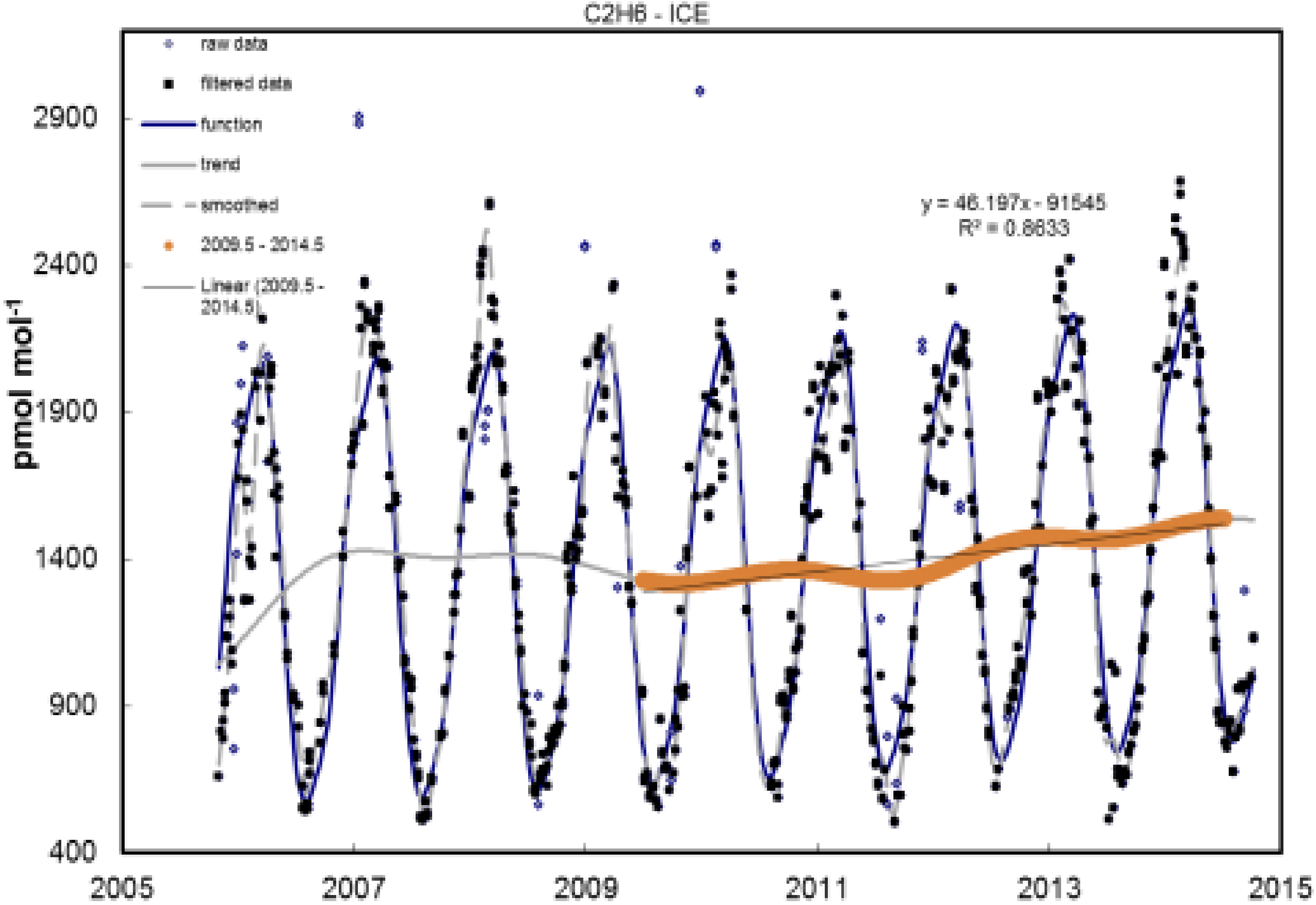


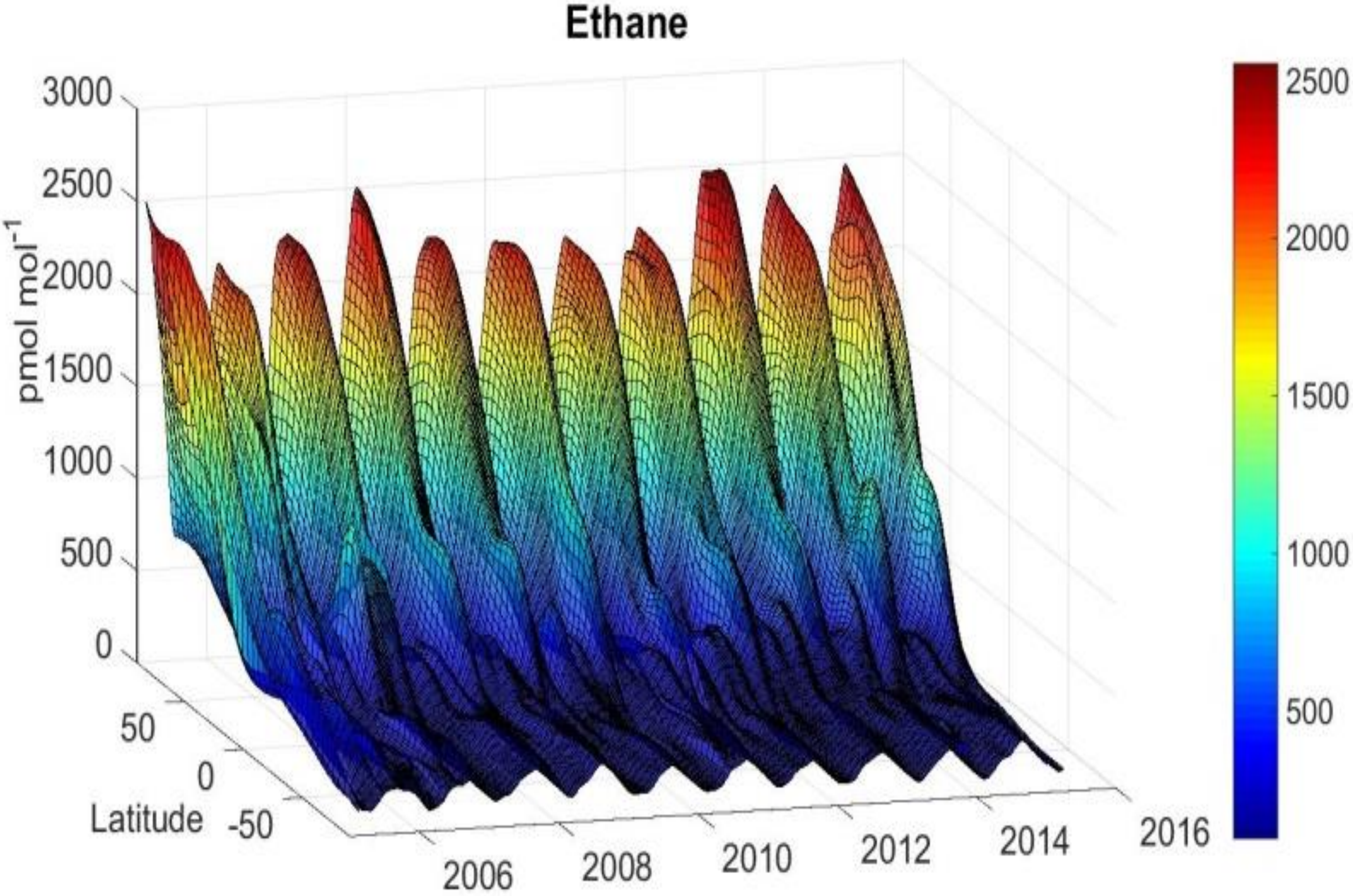
VOC currently reported:

Ethane
Propane
*iso*-Butane
*n*-Butane
*iso*-Pentane
*n*-Pentane
*n*-Hexane

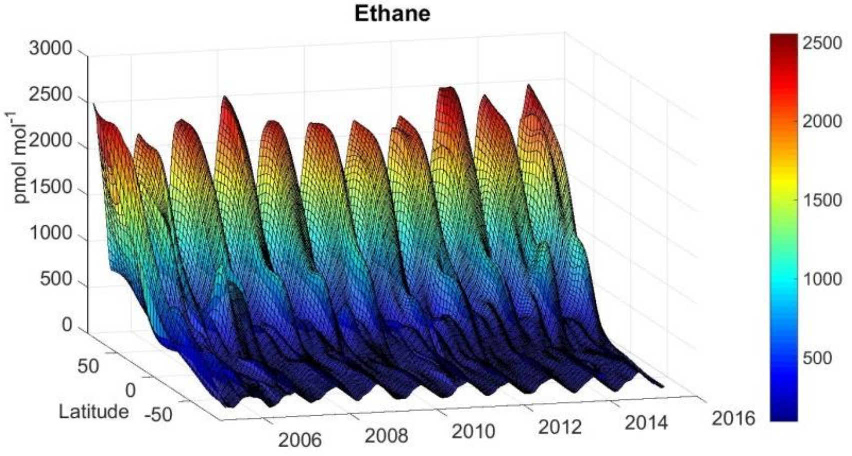
New:
Acetylene
Isoprene
Benzene

# Ethane ‘Modern’ Flask Record from Iceland

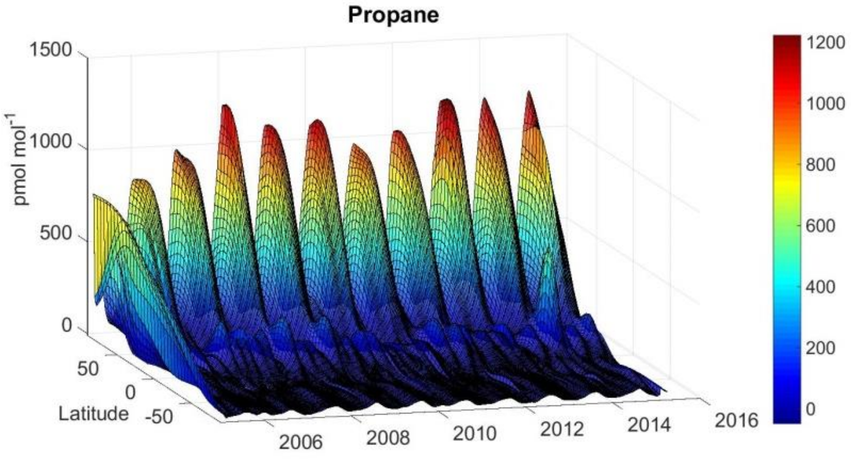



Ethane
pmol mol$^{-1}$
3000
2500
2000
1500
1000
500
0
Latitude
50
0
-50
2006
2008
2010
2012
2014
2016
2500
2000
1500
1000
500

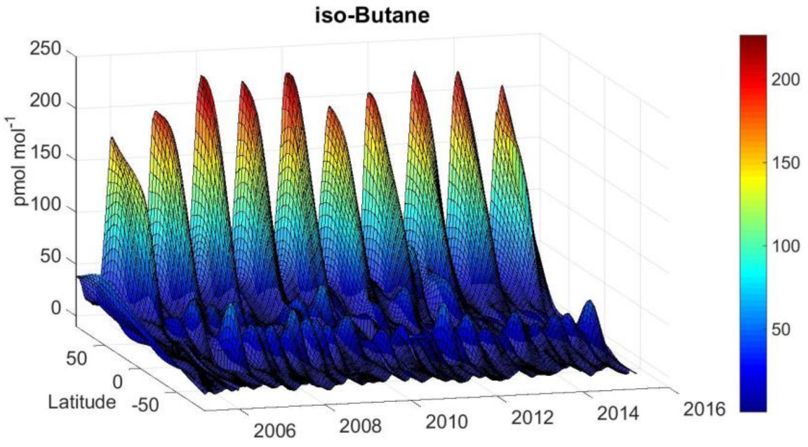
# Global Atmospheric Distribution of Light Alkanes



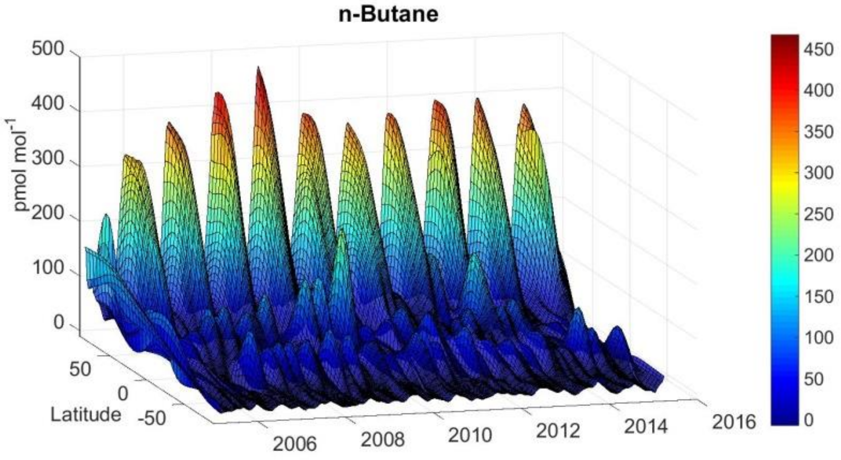
**Ethane**



**Propane**



**iso-Butane**



**n-Butane**

# Summary – Short-Lived Trace Gases Sinks and Lifetimes

Most important sinks: OH, ozone, photolysis, dry deposition, wet deposition, soils (bacterial consumption), aerosol

Lifetimes: days – many months
vary by temperature
vary by geographical location
vary by elevation
vary by time of year
estimates have relative large uncertainties

# Summary – Short-Lived Trace Gases Sinks and Lifetimes

Most important sinks: OH, ozone, photolysis, dry dep et deposition, soils (bacterial consumption), aerosol

Lifetimes: days – many mont

v

ical location

elevation

vary by time of year

estimates have relative large uncertainties

Very Complicated!!!

**Table 4.10** Estimates of sources and sinks of ammonia, $NH_3$ ($Tg\ a^{-1}$ as nitrogen)

| Process | Böttger et al. (1978) | Stedman and Shetter (1983) | Warneck (1988) | Schlesinger and Hartley (1992) | Dentener and Crutzen (1994) | Denman et al. (2007) |
|---|---|---|---|---|---|---|
| *Sources* | | | | | | |
| Coal combustion | 0.03 | <2 | ≤2 | 2 | – | 2.5 |
| Automobiles | 0.2–0.3 | – | 0.2 | 0.2 | – | – |
| Biomass burning | – | – | 2–8 | 5 | 2 | 5.4 |
| Domestic animals | 20–30 | 23 | 22 | 32 | 22 | 35 |
| Wild animals | – | 3 | 4 | – | 2.5 | – |
| Human excrements | – | 1.5 | 3 | 4 | – | 2.6 |
| Soil/plant emissions | 1 | (51)[a] | 15 | 10 | 5.1 | 2.4 |
| Fertilizer losses | 1.2–2.4 | 3.5 | 3 | 9 | 6.4 | – |
| Oceans | – | – | – | 13 | 7 | 8.2 |
| Sum of sources | 22–34 | 83 | 54 | 75 | 45 | 56.1 |
| *Sinks* | | | | | | |
| Precipitation (continents) | 15 ± 7 | 50 | 30 | 30 | 13.6[c] | – |
| Precipitation (oceans) | 6 ± 6 | 10 | 8 | 16 | 16[c] | – |
| Dry deposition (land) | [b] | 14 | 10 | 10 | 13.6[c] | – |
| Reaction with OH | 3 | 9 | 1 | 1 | 1.8[c] | – |
| Sum of sinks | 24 ± 13 | 83 | 49 | 57 | 45 | – |

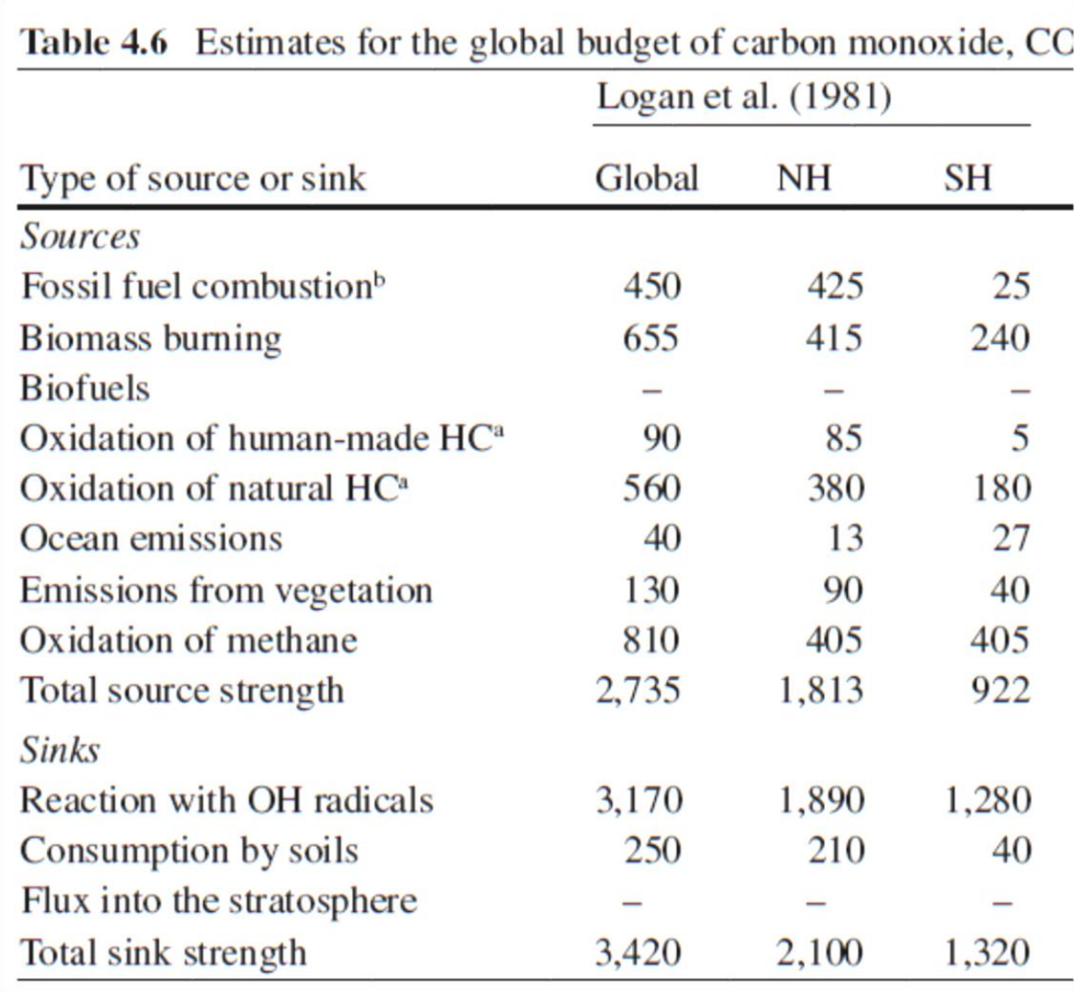


**Table 4.6** Estimates for the global budget of carbon monoxide, CC

| | Logan et al. (1981) | | |
|---|---|---|---|
| Type of source or sink | Global | NH | SH |
| *Sources* | | | |
| Fossil fuel combustion[b] | 450 | 425 | 25 |
| Biomass burning | 655 | 415 | 240 |
| Biofuels | – | – | – |
| Oxidation of human-made HC[a] | 90 | 85 | 5 |
| Oxidation of natural HC[a] | 560 | 380 | 180 |
| Ocean emissions | 40 | 13 | 27 |
| Emissions from vegetation | 130 | 90 | 40 |
| Oxidation of methane | 810 | 405 | 405 |
| Total source strength | 2,735 | 1,813 | 922 |
| *Sinks* | | | |
| Reaction with OH radicals | 3,170 | 1,890 | 1,280 |
| Consumption by soils | 250 | 210 | 40 |
| Flux into the stratosphere | – | – | – |
| Total sink strength | 3,420 | 2,100 | 1,320 |