# Revisiting tropospheric yield of CO from CH<sub>4</sub> oxidation using AC-GCM EMAC

Sergey Gromov and Domenico Taraborrelli Max Planck Institute for Chemistry, Mainz, Germany Contact: <u>sergey.gromov@mpic.de</u>



MAX-PLANCK-INSTITUT MAX-PLANCK-GESELLSCHAFT

# Abstract

Among various sources of tropospheric CO, methane oxidation is commonly assumed to be least uncertain term due to the fairly well studied kinetics of the reaction of  $CH_4$  with OH. But is it so? Many studies on CO tropospheric budget employ simplified treatment of this source in the chemistry scheme, *i.e.* parameterising the photochemical production of CO using a "net reaction" that can be written as  $CH_4 + OH \Rightarrow A CO + (products)$ ,

where the <u>yield  $\lambda$ </u> approximates the effect of the chemistry regime and removal of intermediates from the CH<sub>4</sub> oxidation chain. The estimates of  $\lambda$  are hitherto inconsistent (see below) and largely depend on the chemistry and dry/wet deposition schemes used, if not merely hypothesised.

In this study, we revisit this issue using the AC-GCM EMAC, employing comprehensive chemistry schemes and including the reaction kinetics updated according to the latest laboratory data.

## Tropospheric CO turnover and yield from CH4-

A closer look into the CO tropospheric turnover (=sources+burden+sinks) is shown in the graphic below. Essentially, there are two ways of introducing CO into the atmosphere, *viz.* direct (surface) emissions and via photochemical processing:



 $\rm CH_4$  and VOCs carbon is progressively converted into CO in the chains of chemical reactions. During this conversion, reaction intermediates are subject to transport and scavenging processes. Competing with the scavenging processes, reactions of  $\rm CH_4$ -derived carbon to the end-chain species (e.g. to HCOOH) also reduce the  $\lambda$  value. Importantly, the simplified models employed for CO budget studies usually do not resolve the CO intermediates, which implies that they assume certain yield value.

#### Previous and current estimates of $\lambda$

Depending on the chemistry and dry/wet deposition schemes used, reckoned average tropospheric  $\lambda$  values vary within 0.6–1, whilst recent model parameterisations tend to favour almost complete conversion of CH<sub>4</sub> to CO (see the table below). The large uncertainty in CO yield from CH<sub>4</sub> is especially important for the SH CO, where up to 50% of its inventory is attributed to the CH<sub>4</sub> oxidation source in austral summer (see the Detailed Results panel, Fig.  $\gamma_{\rm CH4}({\rm CO})$ ).

#### Estimates of tropospheric CO yield from $CH_4$ oxidation ( $\lambda$ )

Year	Study	λ value	Remarks	Year	Study	λ value	Remarks
1981	Logan et al.	0.5-0.78		2006	Folberth et al.	0.9	Alt. dry/wet removal param.
1991	Lelieveld & Crutzen	0.3-0.85		2007	Duncan et al.	~1	†, §, neglected wet/dry rem.
1992	Tie et al.	0.82 (0.7-0.9)		2010	Emmons et al.	~1	MOZART4
1997	Manning et al.	0.7	‡, §, ¶, ETSH	2010	Kroll (pers.comm.)	~1	†, §, CO modelling
1999	Novelli et al.	0.95	small wet/dry removal	2013	Gromov, et al.	0.94	9, EMAC, MIM1 chemistry
2000	Bergamaschi et al.	0.86 (0.8-0.9)	‡, §, ¶	2014	This work	0.87-0.96	EMAC, MIM1+ chemistry
<sup>†</sup> No chemistry used the Simplified chemistry used δ Inverse modelling study. Using stable CO isotopes							

#### References

- P. Jöckel et. al., GMD 3, 717-752, doi: 10.5194/gmd-3-717-2010, 2010.
- S. Gromov et al., GMD **3**, 337–364, doi: <u>10.5194/gmd-3-337-2010</u>, 2010 D. Taraborrelli *et al.*, 2015, *in prep.*
- P. Bergamaschi *et al.*, JGR 105, 1929–1945, doi: <u>10.1029/1999jd900819</u>, 2000.
- M. Manning et al., JGR 102, 10673–10682, doi: <u>10.1029/96jd02743</u>, 1997.
- \* Foremost the fast reactions of CH<sub>3</sub>O<sub>2</sub> with OH radicals: C. Fittschen [pers. comm., Univ. Lille, 2014], Bossolasco et al., CPL 593, 7–13, doi: <u>10.1016/j.cplett.2013.12.052</u>, 2014.

# EMAC and new methane oxidation chemistry (MIM1+)

We use the ECHAM/MESSy Atmospheric Chemistry (EMAC) model [Jöckel et al., 2010] employing elaborate chemistry mechanisms and kinetic chemistry tagging tools [Gromov et al., 2010] to directly infer the value of A, which is a diagnosed variable rather than an assumed parameter. The emission inventory resembles (with addition of CH<sub>3</sub>NO<sub>2</sub> emissions) that of EVAL2 setup of EMAC, including the following categories:

- Industrial/anthropogenic (EDGAR FT2000 v2.3)
  Biogenic (GEIA/OLSEN)
- Biomass burning (GFED v2.1)

Additionally, we incorporate three chemical mechanisms differing in complexity of the  $CH_4$  oxidation chemistry (as shown in the diagram on the right), *viz*.:

**REF:** The reference mechanism which represents the "standard" chemistry in EMAC including CH<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>OH, CH<sub>2</sub>OOH, HCHO and HCOOH

**BASE:** The extension of **REF** that resolves CH<sub>2</sub>, CH<sub>3</sub> and CH<sub>3</sub>O intermediates and reactions of CH<sub>3</sub>O<sub>2</sub> with peroxy radicals, foremost HO<sub>2</sub>

*FULL*: Further extension of *BASE* with pathways involving reactions of NO<sub>x</sub> with CH<sub>3</sub>O<sub>2</sub>/HCHO and their nitrogenated derivatives' formation and destruction of organic nitrates, plus unaccounted previously reactions of CH<sub>3</sub>O<sub>2</sub>/CH<sub>3</sub>/HCHO with O<sub>x</sub> and HO<sub>x</sub> from recent known laboratory studies that were previously unaccounted for [see refs.<sup>9</sup>].

### <u>Results: Processes determining the $\lambda$ value</u>

- REF/BASE: Intermediates are mainly removed via dry deposition (~6%)
- (Convective) transport competes with removal processes at the surface
- Local yields are attenuated in the BL, increased in the FT, at the tropopause, transported intermediates result in λ > 1 (cf. the Figure on the right)
- λ values are mostly insensitive to the deposition efficiency
- Tropospheric average yields are:  $\lambda_{CH4}$  is 0.94 (*REF*) and 0.96 (*BASE*)  $\lambda_{NMHCs}$  is 0.51–0.53 (~2.7 CO molecules, *REF*)
- FULL: Substantial additional removal via chemistry (~9%)
- New pathways allow greater removal of the methanederived carbon from the  $CH_4 \rightarrow CO$  chain
- The largest changes pertain to CH<sub>3</sub>O<sub>2</sub> + OH → ...
  ... → HCOOH chain (cf. simulated CH<sub>3</sub>O<sub>2</sub> sinks, depicted in the Figure on the right)
- Local yields are strongly attenuated in the FT and particularly TTL (>20%), ~ -6% decrease in the BL
- The share of the CH<sub>4</sub>-derived CO component (γ<sub>CH4</sub>) decreases by >1% in the ETNH, >2% in the ETSH (see the Detailed Results panel)
- Lower λ values are corroborated by the isotopeinclusive studies on CO (Manning *et al.*, Bergamaschi *et al.*)
- Tropospheric average CO yield is 0.87 (FULL)



Schematic of the methane oxidation mechanism used in this study. Black colour denotes **BASE** chemistry, green and orange colours highlight the extension of **BASE** to **FULL** mechanism.

local  $\lambda_{CH}$ 

Annual zonal average  $\lambda$  value

simulated with the RFF setur

Annual tropospheric sinks of CH3O2 simulated in BASE

(left) and FULL (right) setups. Note the substantial sink attributed to the reactions with OH in the latter.

# **Detailed Results: Simulated distributions**

Shown are distributions for the year 2000 obtained within the **BASE** setup (left) and the corresponding difference with the **FULL** setup (denoted  $\Delta = FULL-BASE$ ). Note the values quoted for averages simulated in particular domains. Panels (a)–(d) present temporal evolution of the zonal averages; panels (e)–(m) show monthly averages in the boundary layer (BL) and free troposphere (FT); in panels (n)–(r) the monthly zonal averages are shown (dash and solid line denote the tropopause and BL heights, respectively).







CO: Simulated (total) carbon monoxide mixing ratio





CO(CH4): Simulated CO component stemming from the CH4 oxidation sourc







γ<sub>CH4</sub>(CO): Share of the CO(CH<sub>4</sub>) component in the total CO burden



