# Revisiting tropospheric yields of CO from CH_4 oxidation using EMAC

Sergey Gromov and Domenico Taraborrelli

Max Planck Institute for Chemistry, Mainz, Germany (sergey.gromov@mpic.de)

Among various sources of tropospheric CO, methane oxidation (MO) is commonly assumed to be least uncertain term due to the fairly well studied kinetics of the reaction of CH_4 with OH. Many studies on CO tropospheric budget (including forward and inverse modelling with CTMs and AC-GCMs) employ simplified treatment of MO source in their chemistry schemes, *i.e.* parameterising the photochemical production of CO using a "net reaction" that can be written as

$$CH_4 + OH \rightarrow \lambda\, CO + (products),$$
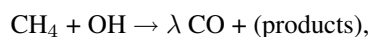
where the yield λ approximates the effect of the chemistry regime and removal of intermediates from the CH_4 oxidation chain, and is duly used as one of the fitting parameters. The estimates of λ, however, are hitherto inconsistent: Depending on the chemistry and dry/wet deposition schemes used, reckoned average tropospheric λ values vary within $0.6-1$, whilst recent model parameterisations tend to favour almost complete conversion of CH_4 to CO. The issue of such large uncertainty in CO yield from CH_4 is especially important for the SH CO, where more than 50% of its inventory is typically attributed to the MO source in austral summer.

In this study we scrutinise the MO source of CO using the **E**CHAM/**M**ESSy **A**tmospheric **C**hemistry (EMAC) model employing elaborate chemistry mechanisms and tools to directly infer the value of λ, which is a diagnosed variable rather than an assumed parameter. Three chemical mechanisms differing in complexity of the MO cycle are used in simulations based on the EMAC evaluation study setup (detailed in Jöckel *et al.*, 2010): (1) The reference (REF) mechanism which represents the "standard" MO chemistry in EMAC including CH_3O_2, CH_3OH, CH_3OOH, HCHO and HCOOH, (2) The extension of REF that resolves CH_3 and CH_3O intermediates and reactions of CH_3O_2 with peroxy radicals, foremost HO_2 (BASE mechanism), and (3) Further extension of BASE with pathways of MO involving formation and destruction of organic nitrates, plus reactions of CH_3O_2/CH_3/HCHO with O_x and HO_x from known laboratory studies that were previously unaccounted for (FULL mechanism).

We obtain yearly tropospheric value of λ in REF and BASE simulations at 0.94 and 0.96, *i.e.* in line with the more recent estimates. The NH$-$SH difference in average λ reaches 0.07 in the boundary layer (BL) and 0.02 in the free troposphere (FT), respectively. The local λ values minimise at the surface at $\sim$0.4 (continents) and $\sim$0.7 (oceans) and progressively increase with altitude. This result, however, is only partly explicable in terms of the removal processes' location, as we diagnose low sensitivity of λ to the wet scavenging and dry deposition efficiencies. In the FT, in contrast, we find local λ values often exceeding unity (*i.e.*, local CO production from MO is greater than CH_4 sink via OH), indicating efficient vertical transport of the intermediates from the BL. Despite the large spatiotemporal variations in local λ values, the tropospheric integral yield of CO from CH_4 appears to be a very robust characteristic in EMAC. A substantially lower average tropospheric λ value (below 0.9) is obtained in the FULL simulation, a clear result of the changes to the MO chain chemical regime. The largest impact on λ has the enhanced production of HCOOH in the FT (mostly due to HCHO+HO_2 and CH_3O_2+OH reactions), which augments irreversible removal of the intermediates from the $CH_4 \rightarrow$CO chain. We further discuss the details and implications of these preliminary results.

References:

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geosci. Model Dev.*, **3**, 717-752, doi: 10.5194/gmd-3-717-2010, 2010.