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Supplement of

A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane

Sergey Gromov et al.

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Fig. S1 Diagram of reaction pathways (following C exchanges) between CH₄ and CO as simulated in MECCA (the kinetic chemistry submodel used in EMAC, see Sect. 2.3 of the manuscript for details). Each arrow denotes a single gas-phase (solid line) or photolysis (dashed line) reaction; caption lists the reaction partner and label; colours refer to the chemical mechanism groups defined in MECCA. Pathways ending at the loss reservoir remove C from the CH₄ → CO conversion chain. Note that non-chemical removal of C from the system (e.g. dry/wet deposition of CH₃O₂, CH₃OH, HCHO, HCOOH intermediates) is not shown, however, simulated by the model. See Supplement to Lelieveld et al. (2016) (p. S18, https://www.atmos-chem-phys.net/16/12477/2016/acp-16-12477-2016-supplement.pdf) for the complete listing of the respective MECCA reaction mechanism.
Fig. S2 Time series (left) and statistics (right, box-and-whisker plots) of the observations from Baring Head (BHD) and Scott Base (SCB) scrutinised in this study. Panels (a, c) present the mixing ratios and \(\delta^{13}C\) of CH\(_4\); panels (b, d) show anomalies with respect to the annual averages (denoted with “\(\Delta_{yr}\)”). Panels (e, f) display the mixing ratios and \(\delta^{13}C\) of CO. The number of samples in each subset is presented in the manuscript (Fig. 1, panel (g)). Shaded areas denote the ETSH MBL high-Cl (orange shaded) and low-Cl (grey shaded) periods hypothesised by AO7 (see text for details). Step lines navigate through the entire time series at each station. Boxes and whiskers present the median/interquartile range and \(\pm1\sigma\) (of the population) of the selected data. Circles and minus symbols denote the averages and samples falling outside \(\pm1\sigma\), respectively. Solid symbols/boxes refer to the data when CH\(_4\) and CO samples were taken simultaneously (up to 7 days apart); hollow symbols/hatched boxes refer to all data.
Fig. S3 Seasonal cycles CO mixing ratio at Baring Head (BHD, panel a) and Scott Base (SCB, panel b). Observations (entire data series plotted against day of year) are shown with symbols; circles and diamonds denote mild and extreme outliers (see Sect. 2.2 of the manuscript for details). Step lines refer to quasi-monthly averages derived from the observations (green) and from the EMAC model (1996–2005) for total CO (black) and its component derived from CH₄ oxidation (thin red line, lower scale). Panels (c, d) present the simulated effective sink $^{13}$CO enrichment, respectively. Vertical bars indicate ±1σ of the subsample used for quasi-monthly averages. Panels (e, f) show the number of samples in observational data. Mind the breaks and different scales of the ordinate axes.
Table S1 Annual average CO- and CH$_4$-related integrals by domain simulated in EMAC for 1996–2005.

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