Supplement to

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

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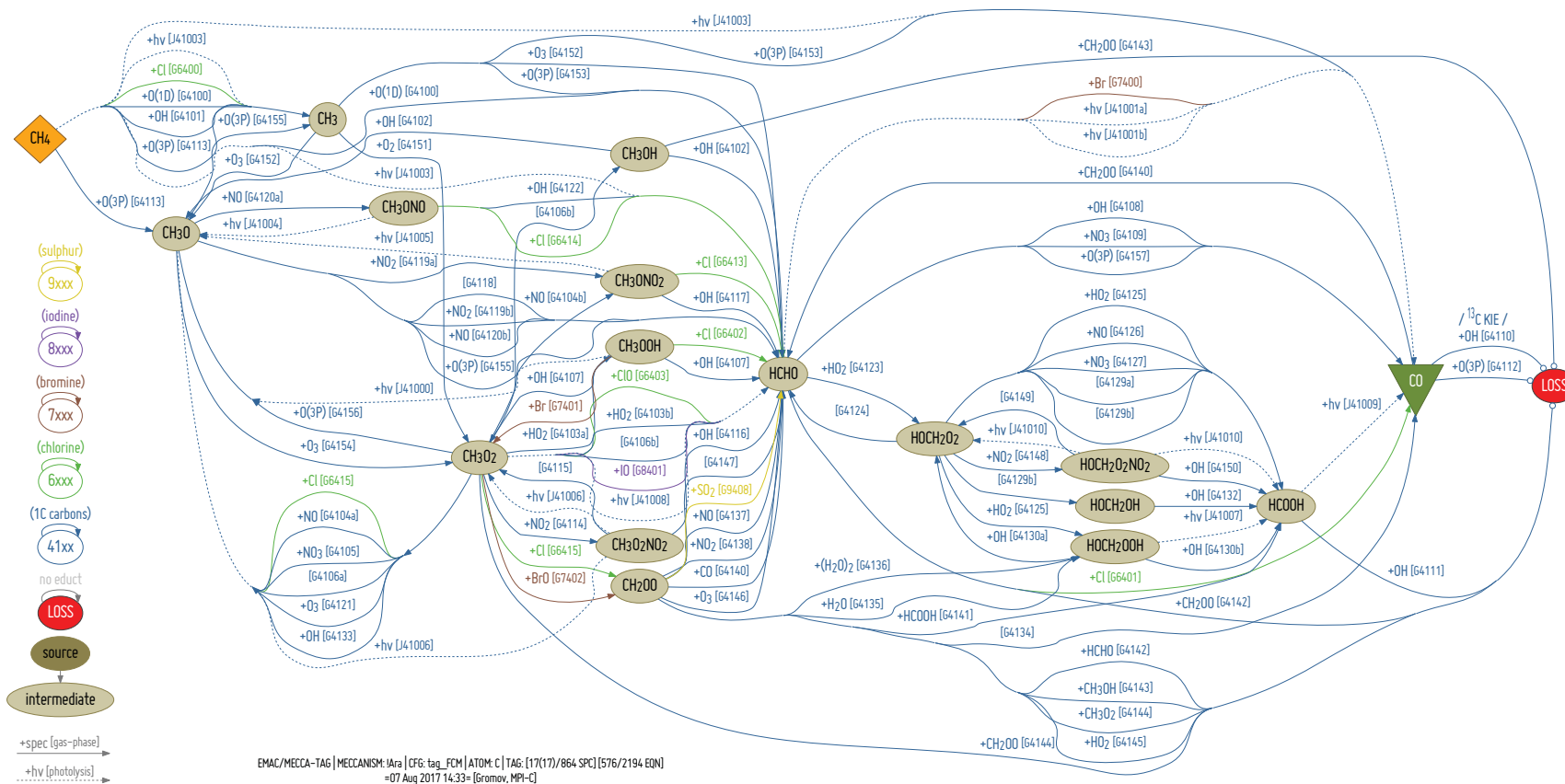
Fig. S1 Diagram of reaction pathways (following C exchanges) between CH₄ and CO as simulated in MECCA (the kinetic chemistry submodel used in EMAC, see Sect. 2.3 of the manuscript for details). Each arrow denotes a single gas-phase (solid line) or photolysis (dashed line) reaction; caption lists the 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.
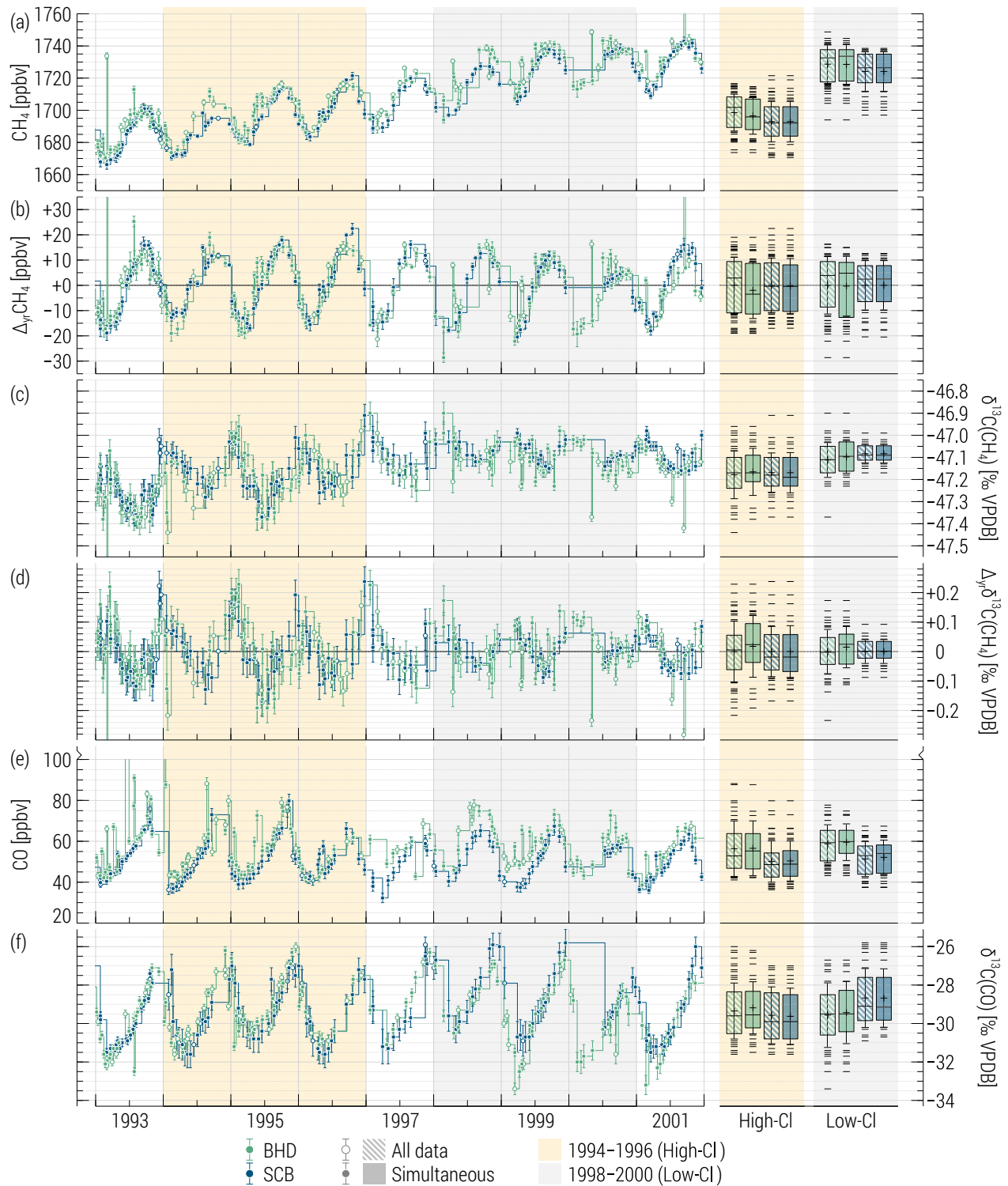
Fig. S2 Time series (left) and statistics (right, box-and-whisker plots) of the observations from Baring Head (BHD) and Scott Base (SCB) scrutinised in this study. Panels (**a**, **c**) present the mixing ratios and $\delta^{13}C$ of CH_4; panels (**b**, **d**) show anomalies with respect to the annual averages (denoted with "Δ_{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 A07 (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. Plus 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.
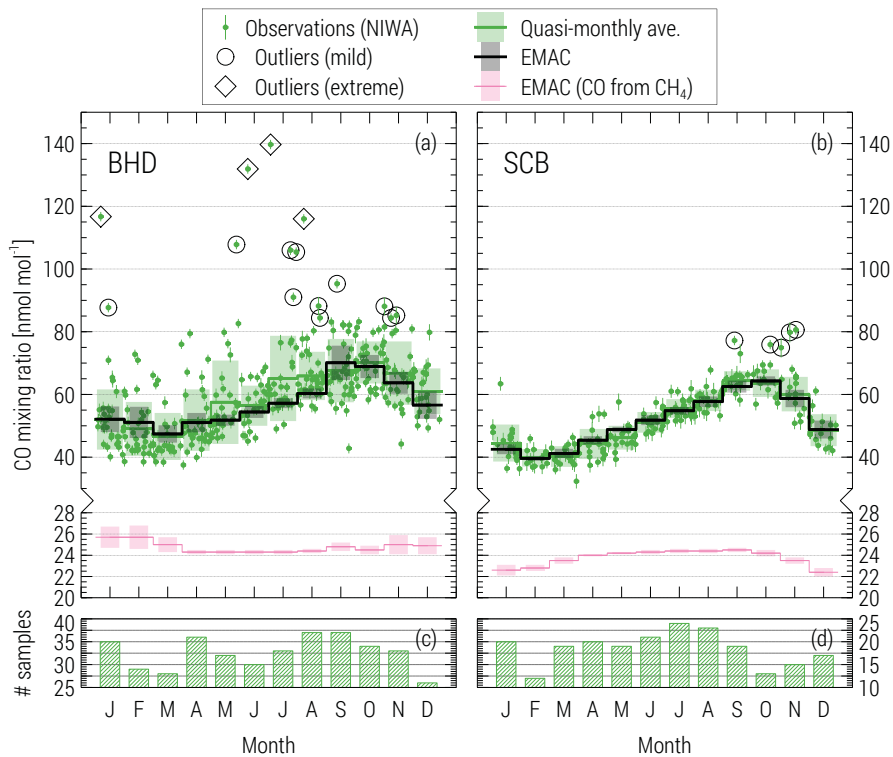
Fig. S3 Seasonal cycles CO mixing ratio at Baring Head (BHD, panel **a**) and Scott Base (SCB, panel **b**). Observations (entire data series plotted against day of year) are shown with symbols; circles and diamonds denote mild and extreme outliers (see Sect. 2.2 of the manuscript for details). Step 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 CH_4 oxidation (thin red line, lower scale). Vertical bars indicate measurement uncertainty (for observations) and $\pm 1\sigma$ (standard deviation of the subsample used for quasi-monthly averages). Panels (**c**, **d**) 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.

CO burden [Tg(C)]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	1.80	0.70	0.86	0.24	0.09	0.03
BL	12.71	5.07	5.87	1.77	0.52	0.19
MBL	6.39	1.67	3.31	1.40	0.20	0.05
FT	135.71	46.82	68.13	20.75	7.45	2.42
T	151.30	53.09	75.23	22.98	8.13	2.67
TP	4.89	2.14	1.67	1.08	0.48	0.19
LMS	15.64	6.71	4.25	4.68	1.45	0.84

Fraction of CO from CH$_4$ oxidation | γ [C/C]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	24.6%	17.1%	25.2%	44.8%	19.3%	46.0%
BL	25.7%	17.5%	27.2%	44.5%	18.9%	45.8%
MBL	32.5%	19.9%	33.5%	45.2%	19.0%	45.8%
FT	29.5%	21.2%	31.0%	43.6%	20.1%	45.4%
T	29.2%	20.7%	30.6%	43.7%	20.0%	45.5%
TP	30.5%	23.9%	32.8%	40.3%	21.8%	43.6%
LMS	40.7%	33.3%	44.7%	47.5%	30.5%	49.5%

Cl concentration [atoms cm^{-3}]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	97	56	145	47	8	10
BL	100	59	152	51	8	11
MBL	110	59	165	49	8	9
FT	269	163	352	152	36	42
T	261	157	345	146	35	40
TP	3151	1415	4945	1418	299	506
LMS	16172	15892	15630	17260	15301	20021

Yield of CO from CH$_4$ oxidation | λ [C/C]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	72%	72%	74%	62%	48%	51%
BL	81%	83%	81%	73%	55%	62%
MBL	47%	41%	45%	63%	103%	257%
FT	96%	97%	95%	96%	98%	107%
T	93%	95%	93%	93%	96%	104%
TP	123%	119%	128%	121%	120%	120%
LMS	102%	103%	101%	103%	103%	102%

CH$_4$ sink | S [Tg(C) yr^{-1}]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	7.0	1.1	5.2	0.69	0.01	0.01
BL	49.2	7.9	36.1	5.1	0.07	0.06
MBL	32.7	2.9	25.9	3.9	0.03	0.01
FT	313.8	49.5	227.8	36.5	2.22	1.01
T	372.7	59.2	270.6	42.8	2.32	1.09
TP	1.83	0.59	0.74	0.50	0.07	0.05
LMS	20.2	5.5	9.1	5.59	0.67	0.67

(via OH) [C/C]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	99.9%	99.9%	99.9%	99.8%	99.8%	99.8%
BL	99.9%	99.9%	99.9%	99.8%	99.8%	99.8%
MBL	99.9%	99.9%	99.9%	99.8%	99.8%	99.8%
FT	99.7%	99.7%	99.7%	99.7%	99.7%	99.6%
T	99.7%	99.7%	99.7%	99.7%	99.7%	99.6%
TP	90.9%	94.2%	86.4%	93.7%	97.8%	96.5%
LMS	53.4%	58.7%	47.9%	57.1%	64.7%	60.4%

(via O^{1}D) [C/C]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	0.01%	0.01%	0.01%	0.01%	0.02%	0.04%
BL	0.01%	0.02%	0.01%	0.01%	0.02%	0.05%
MBL	0.01%	0.01%	0.01%	0.01%	0.02%	0.03%
FT	0.07%	0.08%	0.07%	0.07%	0.06%	0.09%
T	0.06%	0.07%	0.06%	0.06%	0.06%	0.09%
TP	1.94%	1.13%	3.20%	1.05%	0.38%	0.40%
LMS	33.0%	26.8%	40.3%	27.1%	18.6%	18.4%

(via Cl) [C/C]

vertical	GLOB	ETNH	IT	ETSH	AR	AN
SRF	0.13%	0.11%	0.13%	0.14%	0.14%	0.19%
BL	0.13%	0.12%	0.13%	0.15%	0.15%	0.19%
MBL	0.14%	0.13%	0.14%	0.15%	0.15%	0.18%
FT	0.25%	0.24%	0.25%	0.27%	0.22%	0.30%
T	0.23%	0.22%	0.23%	0.25%	0.22%	0.29%
TP	7.2%	4.7%	10.4%	5.2%	1.8%	3.1%
LMS	13.7%	14.6%	11.8%	15.8%	16.7%	21.2%

Domain abbreviations

zonal:	GLOB	Globe (90°S–90°N)
	IT/ET	Intra/Extra-Tropics (separated at 23.4 N/ S)
vertical:	SRF/TP	Surface (lowest model layer)
	(M)BL	(Marine) Boundary Layer
	TP	Tropopause

NH/SH	Northern/Southern Hemisphere
AR/AN	Arctic/Antarctic (above 66 N/ S)
T	Troposphere (below the TP)
FT	Free Troposphere (above the BL, below the TP)
LMS	Lowermost Stratosphere (above the TP)