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Characterising tropospheric O_3 and CO around Frankfurt over the period 1994–2012 based on MOZAIC–IAGOS aircraft measurements

Hervé Petetin et al.

Correspondence to: Hervé Petetin (hervepetetin@gmail.com)

Supplementary material

Table S1: Annual and seasonal trends of mean O_3 and CO concentrations, 5th and 95th percentiles. Trends are estimated using the Theil-Sen slope estimate without taking into account the autocorrelation of the data (i.e. uncertainties are underestimated). Uncertainties are given at the 95% confidence level (NS: non-significant trend). These results are given for comparison with the Table 1, in order to illustrate how the autocorrelation of the data (ignored here but not in Table 1) affects the uncertainties of the trend estimates. Note that the autocorrelation only influence the confidence intervals (not the best estimate). Compared to the results given in Table 1 and discussed in the manuscript, the uncertainties reported in this Table are substantially lower. Some trends that were insignificant when considering the autocorrelations appear significant (for instance the decrease of the CO 5th percentile in spring and summer). These differences highlight the importance of taking into account the serial correlation of the data in order to avoid underestimating the uncertainties affecting the trends.

		O_3 trend (%$O_{3,2000}$ yr^{-1}) (1994-2012)			CO trend (%CO_{2004} yr^{-1}) (2002-2012)		
Season	Layer	Mean	5th	95th	Mean	5th	95th
Year	UT	+0.30 [+0.12; 0.50]	+0.63 [+0.34;+0.90]	NS	-1.36 [-1.71;-0.99]	-1.22 [-1.73;-0.62]	-1.43 [-1.80;-1.08]
Year	MT	+0.20 [+0.03;+0.36]	+0.42 [+0.24;+0.65]	NS	-1.55 [-2.06;-1.09]	-1.57 [-2.08;-1.03]	-1.44 [-1.95;-0.95]
Year	LT	NS	+1.03 [+0.61;+1.53]	NS	-1.51 [-2.04;-0.93]	-1.59 [-2.14;-0.97]	-1.41 [-2.02;-0.81]
Winter	UT	+0.62 [+0.24;+1.09]	+0.96 [+0.35;+1.56]	NS	-1.64 [-2.32;-0.79]	-1.39 [-2.48;-0.56]	-1.59 [-2.34;-0.85]
Winter	MT	+0.62 [+0.22;+0.98]	+0.73 [+0.23;+1.21]	+0.46 [+0.11;+0.79]	-1.50 [-2.35;-0.73]	-1.69 [-2.68;-0.55]	-1.22 [-1.99;-0.40]
Winter	LT	+0.83 [+0.33;+1.41]	+1.63 [+0.59;+2.72]	NS	-1.32 [-2.48;-0.25]	-1.33 [-2.36;-0.19]	NS
Spring	UT	NS	NS	NS	-1.67 [-2.40;-0.89]	NS	-1.97 [-2.69;-1.15]
Spring	MT	NS	NS	NS	-2.00 [-2.92;-1.14]	-2.01 [-2.94;-0.92]	-2.01 [-3.05;-0.87]
Spring	LT	NS	NS	NS	-1.91 [-2.81;-0.88]	-1.58 [-2.67;-0.60]	-2.22 [-4.33;-0.82]
Summer	UT	NS	NS	NS	-1.22 [-2.13;-0.21]	-1.50 [-2.66;-0.19]	-1.53 [-2.27;-0.41]
Summer	MT	NS	NS	NS	-1.83 [-2.83;-0.79]	-1.50 [-2.49;-0.57]	-2.29 [-3.17;-1.24]
Summer	LT	NS	NS	NS	-2.31 [-3.30;-1.30]	-2.08 [-2.84;-1.28]	-2.63 [-3.88;-1.66]
Autumn	UT	NS	NS	NS	NS	NS	NS
Autumn	MT	NS	NS	NS	-1.44 [-2.84;-0.00]	NS	NS
Autumn	LT	NS	+1.84 [+0.64;+2.91]	NS	NS	NS	-2.21 [-4.15;-0.27]

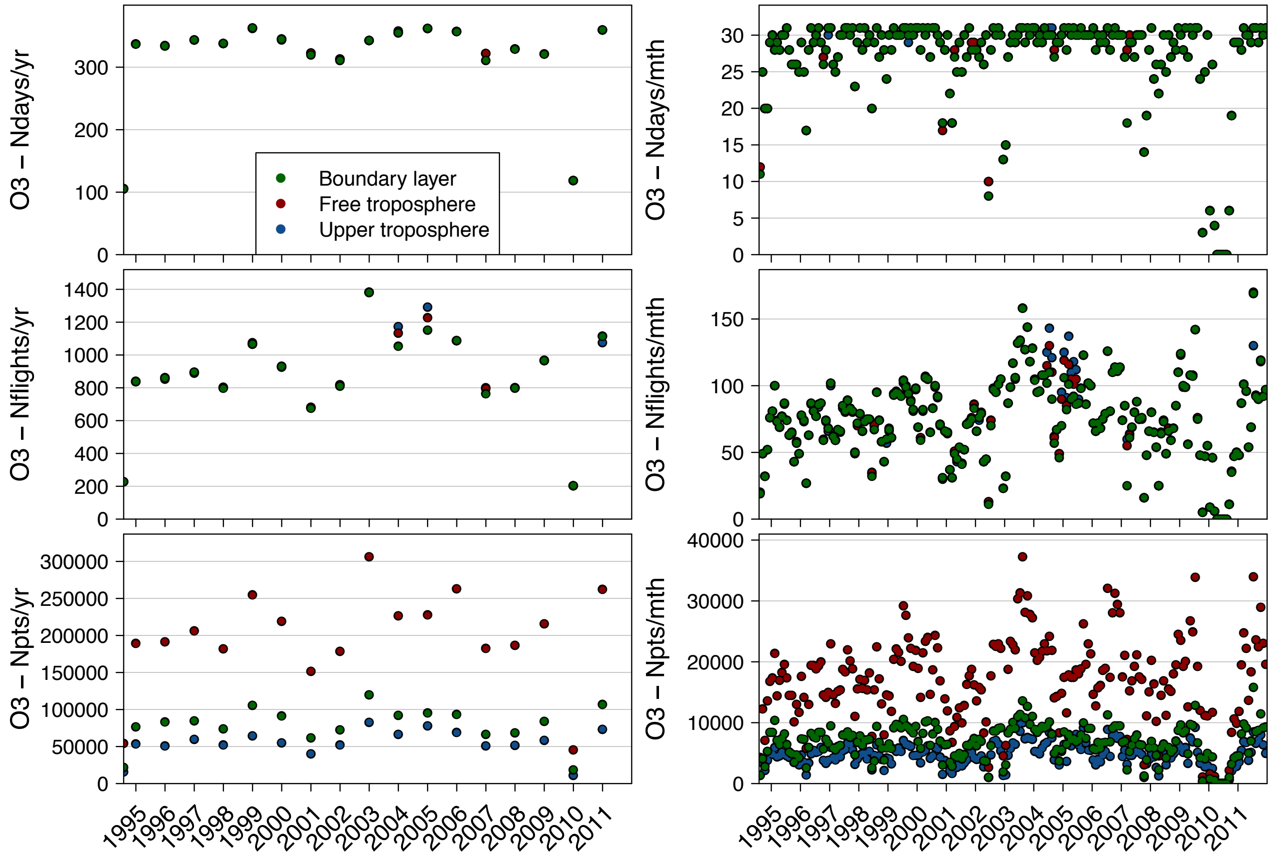

Figure S1: Number of days (top panel), flights (middle panel) and points (bottom panel) of available O_3 measurements per year (left panel) and per month (right panel), for the three different layers.

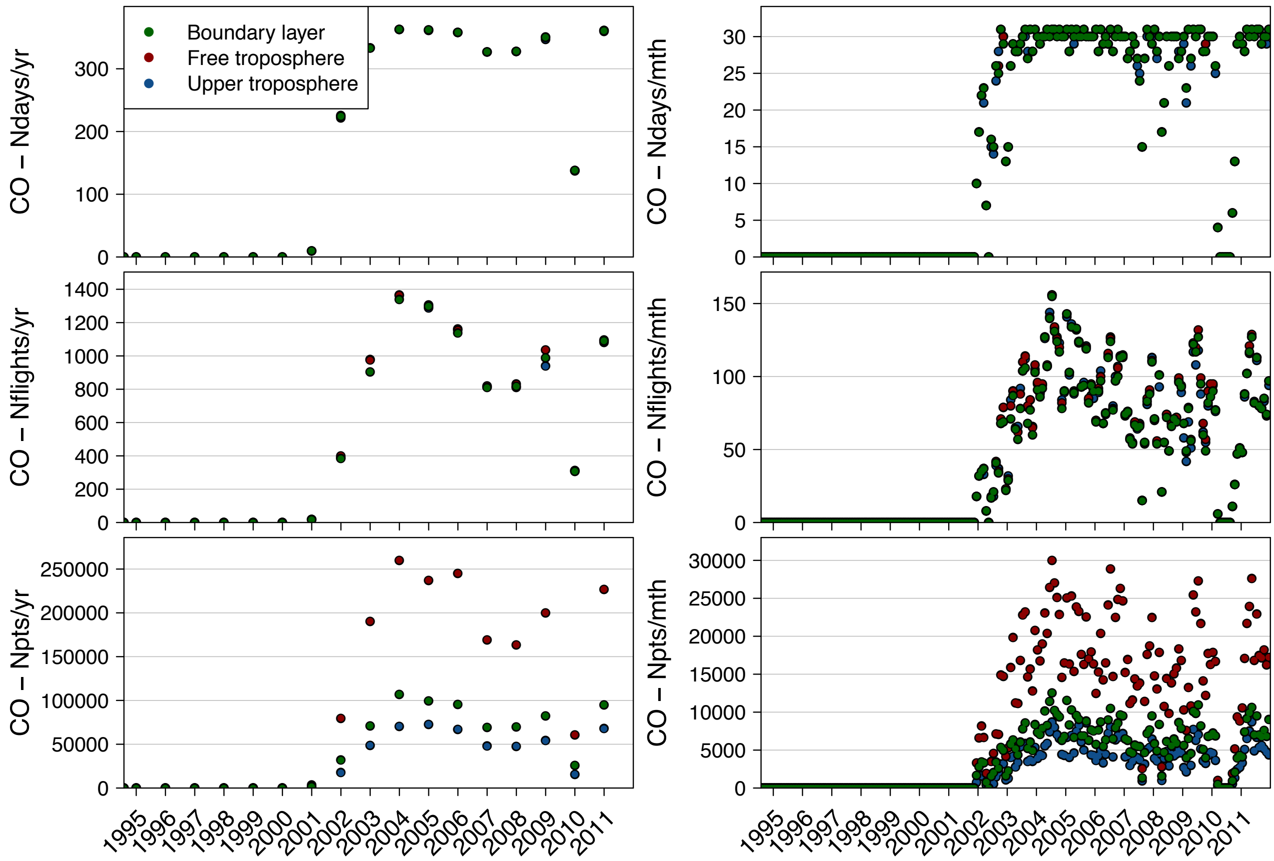

Figure S2: Same as Fig. S1 for CO.

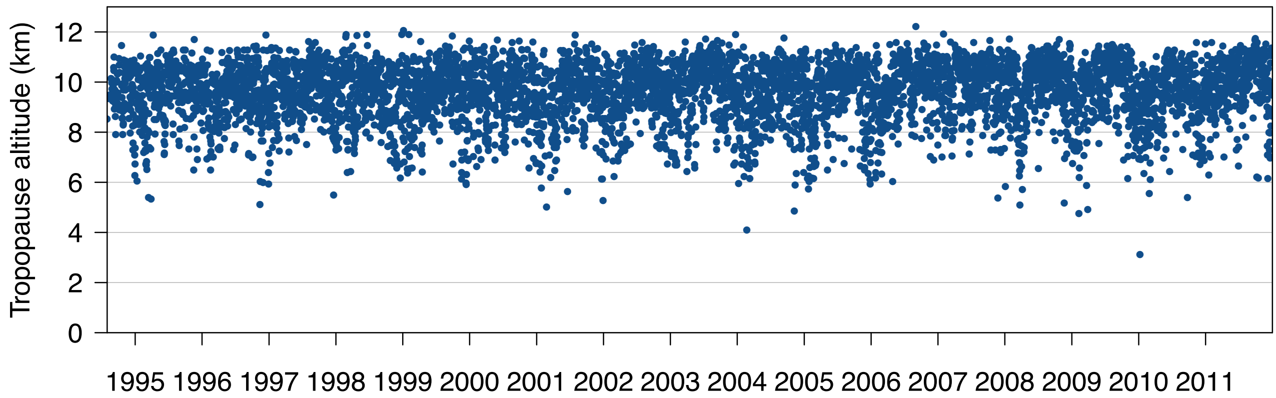

Figure S3: Daily dynamical tropopause (DT) altitude of all Frankfurt/Munich flights along the 1994-2011 period (when several flights during one day, DT is estimated for all of them and then averaged). Note that no chemical measurements (O_3, CO) are required for estimating the DT altitude, which explains the absence of gaps in data (contrary to O_3 and CO time series).

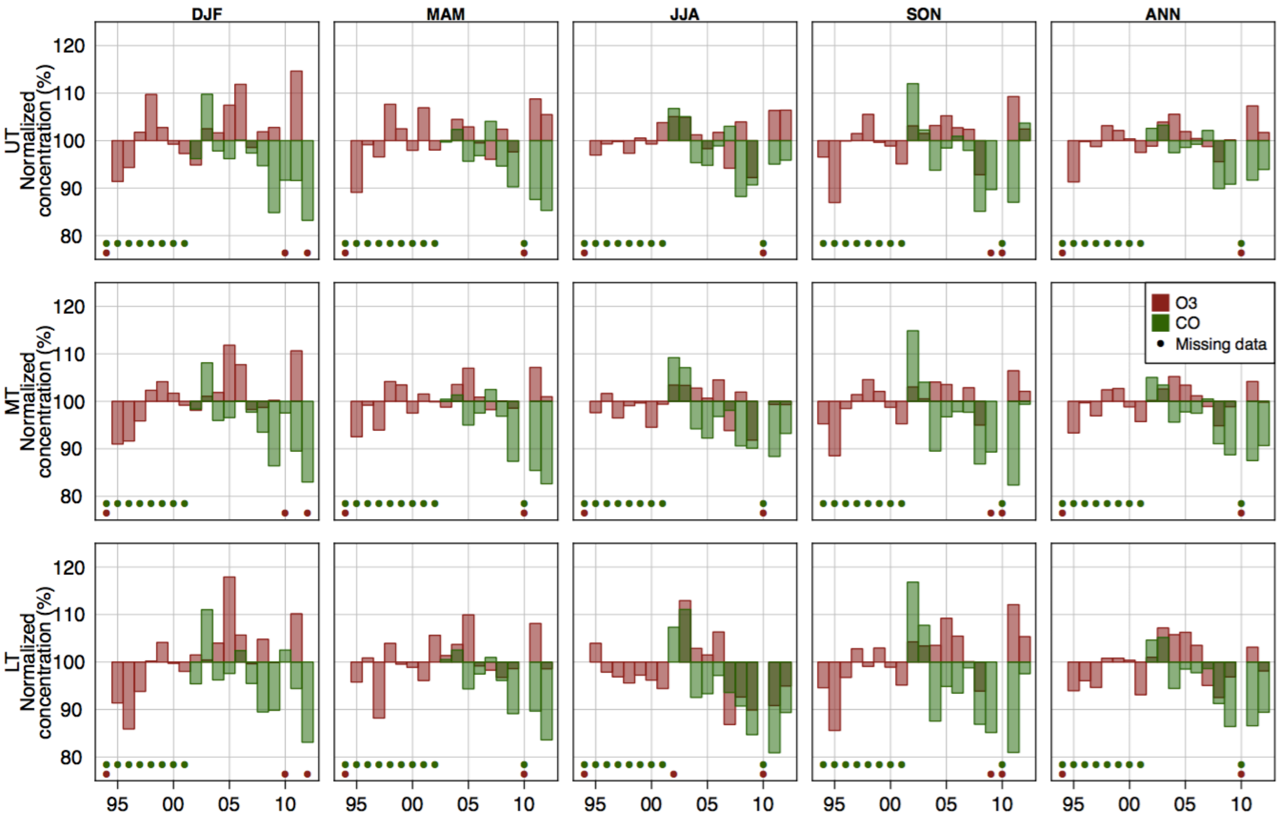

Figure S4: O_3 (in red) and CO (in green) seasonal and annual mean mixing ratios, normalized by the reference year (2000 for O_3, 2004 for CO) intercept obtained from the quadratic fit (see text), in the three tropospheric layers. Years and seasons with no data are indicated by dots.

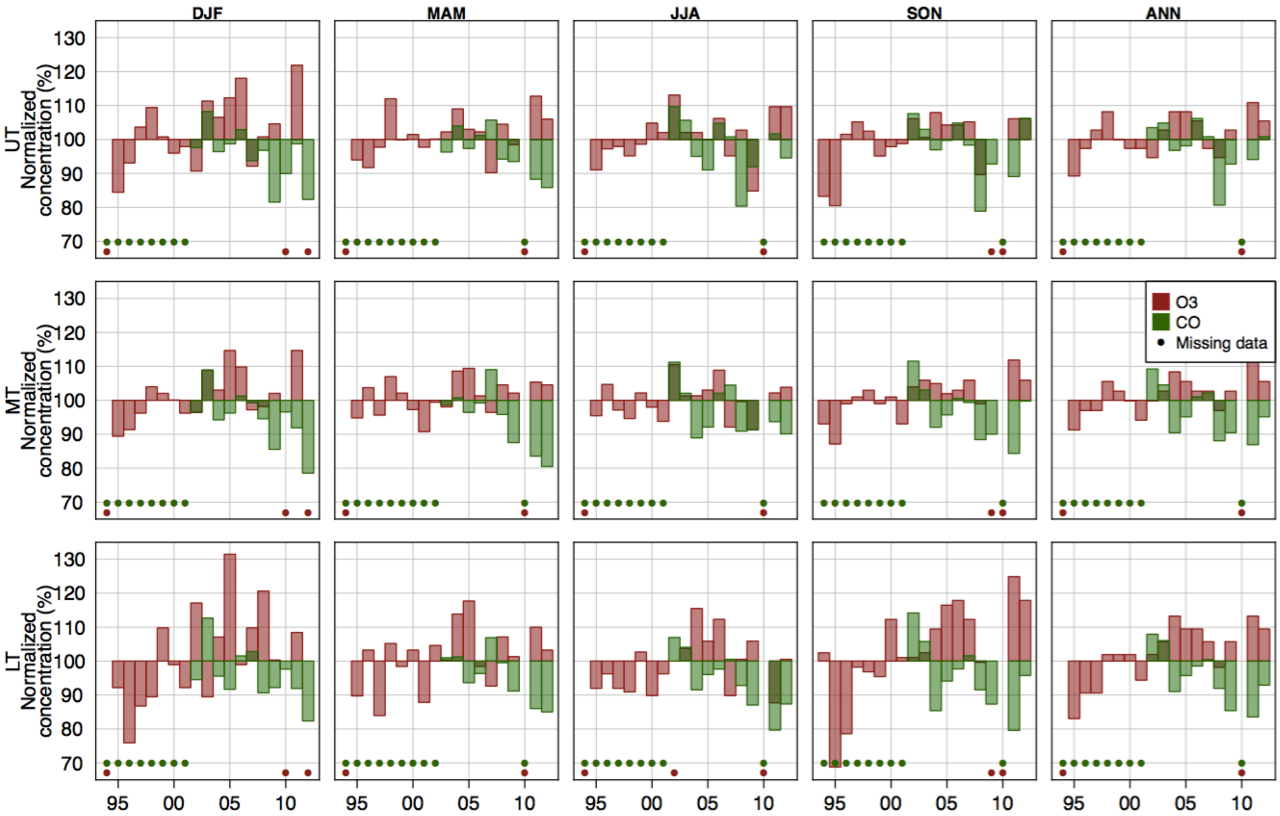

Figure S5 : O_3 (in red) and CO (in green) seasonal and annual 5th percentile concentrations, normalized by the reference year (2000 for O_3, 2004 for CO) intercept obtained from the quadratic fit (see text), in the three tropospheric layers. Years and seasons with no data are indicated by dots.

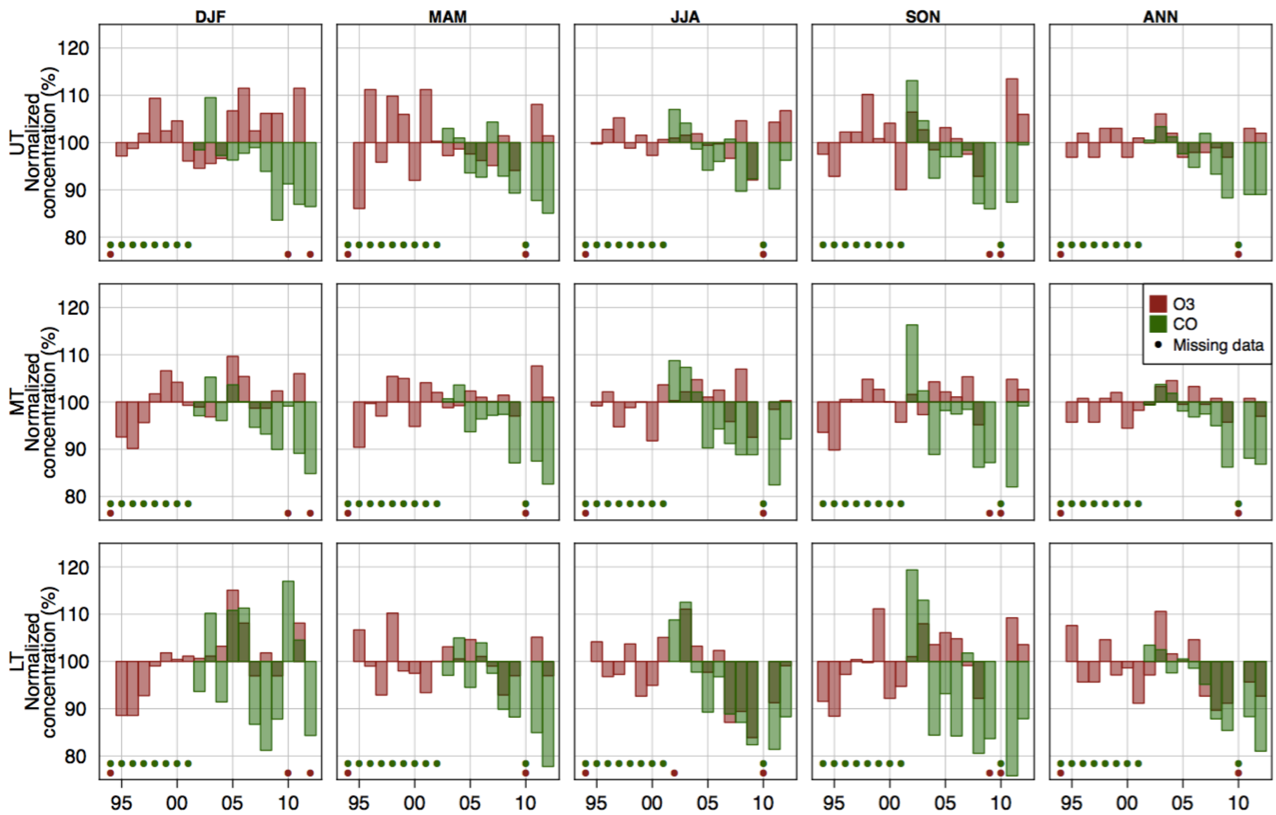

Figure S6: Same as Fig. S5 for the 95th percentile.

S.1 Annual mean CO from the GAW surface stations

In this section, we compare the CO mixing ratios measured in the LT and MT by MOZAIC-IAGOS aircraft to the CO mixing ratios measured at the GAW surface stations. Monthly data from the GAW database are downloaded on the World Data Centre for Greenhouse Gases (WDCGG) (http://ds.data.jma.go.jp/gmd/wdcgg/; data downloaded the 1st July 2016). We consider the period 2002-2012. Only the GAW surface stations located between 45°N and 55°N (i.e. ±5° from the latitude of Frankfurt) and with at least 80% of available data are retained. These criteria lead to a set of 10 stations described in Table S2.

Table S2 : Description of the GAW surface stations, annual mean CO mixing ratio over the periodf 2002-2012, and correlation (R) of the annual time series with the annual mean CO measured in the LT and MT by the MOZAIC-IAGOS aircraft.

Station name (contributor*)	Location	Altitude	Annual mean CO (ppb)	Correlation with the LT (MT) CO
Fraserdale (EC)	81.57°W, 49.88°N	210 m	135	0.68 (0.77)
Hohenpeissenberg (DWD)	11.02°E, 47.8°N	985 m	165	0.74 (0.57)
Hegyhatsal (NOAA/ESRL)	16.65°E, 46.95°N	248 m	209	0.61 (0.59)
Jungfraujoch (Empa)	7.987°E, 46.548°N	3580 m	123	0.94 (0.96)
Kollumerwaard (RIVM)	6.28°E, 53.33°N	0 m	196	0.71 (0.72)
Park Falls (NOAA/ESRL)	90.27°W, 45.92°N	868 m	141	0.74 (0.83)
Mace Head (AGAGE)	9.9°W, 53.33°N	8 m	135	0.62 (0.62)
Ochsenkopf (NOAA/ESRL)	11.8°E, 50.03°N	1185 m	160	0.41 (0.54)
Shemya Island (NOAA/ESRL)	174.08°E, 52.72°N	40 m	132	0.78 (0.85)
Schauinsland (UBA)	7.92°E, 47.92°N	1205 m	151	0.79 (0.78)

*Contributors : EC, Environment Canada; DWD, Deutscher Wetterdienst; NOAA/ESRL, National Oceanic & Atmospheric Administration / Earth System Research Laboratory; Empa, Swiss Federal Institute for Materials Science and Technology; RIVM, Dutch National Institute for Public Health and the Environment; AGAGE, Advanced Global Atmospheric Gases Experiment; UBA, Umwelt Bundesamt

The annual mean CO mixing ratio is first calculated for each station individually, and then averaged for all stations. It gives an annual mean CO mixing ratio of 155 ppb over the period 2002-2012 (the standard deviation among the stations is 28 ppb). It is 15% higher than the zonal average of ~135 ppb given by Novelli et al. (1998) in the 1990s at this latitude. As shown in Table S2, large differences among the individual stations are found, mean CO mixing ratios ranging from 132 ppb at Shemya Island (in the Pacific) to 209 ppb at Hegyhatsal (in Hungary). The standard deviation inferred from the annual mean CO of all stations is 28 ppb. The annual mean CO mixing ratio given by the MOZAIC-IAGOS data in the LT is 143 ppb for the same period. It is in the lower range of the zonal average CO inferred from the GAW surface stations at this latitude. When considering only the surface stations above 1000 m above sea level (a.s.l.) (i.e. 3 stations all located in Europe : Jungfraujoch, Ochsenkopf and Schauinsland), the zonal average is reduced to 145 ppb, thus very close to the annual mean CO observed in the LT by MOZAIC-IAGOS aircraft. The annual mean CO mixing ratio in the MT (115 ppb) is substantially lower than the zonal average given by surface stations, but the difference with the highest mountain station Jungfraujoch (located at 3580 m) is very small (-7%).

To further assess the representativeness of the MOZAIC-IAGOS observations, the correlations between the annual mean CO mixing ratios at the GAW surface stations and the CO mixing ratios observed in the LT and MT are given in Table S2. Except at Ochsenkopf where the correlation is only 0.40, all GAW stations show correlations with the MOZAIC-IAGOS data in the LT exceeding 0.60 (up to 0.94 at the mountain site Jungfraujoch, close to Frankfurt/Munich). Except at Hohenpeissenberg, higher correlations are found with the MOZAIC-IAGOS data in the MT. Thus, the interannual variation obtained in the MOZAIC-IAGOS data in the LT and MT is consistent with the interannual variation observed at regional and global surface sites at this latitude.

Therefore, although the measurements performed by the MOZAIC-IAGOS aircraft in the LT may still be influenced by some local emissions, these comparisons with the GAW surface stations highlight a good consistency, both in terms of mean annual CO mixing ratios and interannual variations. This gives confidence on the representativeness of the MOZAIC-IAGOS observations.