



Isotope-informed analysis of changes in the global CO budget over the past 30 years

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27 **Abstract**

28 Carbon monoxide (CO) is an active intermediate in the cycling of carbon compounds in the atmosphere
29 and affects the atmosphere's oxidation capacity through its own and related reactions. Global monitoring
30 of CO mole fractions has been extensively carried out by the National Oceanic and Atmospheric
31 Administration (NOAA) Global Monitoring Laboratory (GML) since the 1990s. The sources and sinks of
32 CO can be partially distinguished with isotope measurements, but observations of the CO isotopic
33 composition are sparse. A network of independent global observatories measured $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$
34 between 1995-2001, but the only continuous monitoring until now has been performed at Baring Head,
35 New Zealand. As part of the Iron Salt Aerosol Methane Oxidation (ISAMO) project, regular
36 measurements of $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ have resumed at seven stations, three of which (ZEP, IZO, RPB)
37 overlap with the older network. In this study, we use the new and existing CO mole fraction and isotope
38 data together with model simulations to derive empirical constraints for changes to the global and
39 regional CO budget over the past three decades. We find a strong reduction in wintertime CO at mid-to-
40 high latitudes in the Northern Hemisphere and relatively stable CO mole fractions across the entire
41 Southern Hemisphere. We validate the trend of increasing CH_4 in the atmosphere concurrent with
42 decreasing CO emissions from fossil fuel combustion, though our findings suggest that reductions in
43 fossil fuel CO emissions in the Northern Hemisphere may be underestimated. This trend, coupled with
44 increasing summer wildfire activity in the Northern Hemisphere, is substantially changing our
45 understanding of CO, $\delta^{13}\text{C}_{\text{CO}}$, and $\delta^{18}\text{O}_{\text{CO}}$ seasonality.

46



47 **Main Text**

48

49 **1 Introduction**

50 **1.1 CO Background**

51 Carbon monoxide (CO) is an important, ubiquitous trace gas, which impacts tropospheric chemistry through
52 numerous pathways. In particular, the reaction of CO with hydroxyl (OH) radicals acts as the primary sink
53 for both constituents (Crutzen and Zimmermann; 1991). Therefore, changes in the abundance of CO can
54 substantially influence the lifetime of other species which are also oxidized by OH, including the
55 greenhouse gas methane (CH₄). This makes CO an indirect greenhouse gas (Szopa et al., 2021). The CO +
56 OH reaction also produces hydroperoxyl radicals (HO₂) which lead to ozone (O₃) formation in high NO_x
57 environments and alternatively, O₃ destruction in low-NO_x environments, thus influencing the severity of
58 ground level pollution and related human health effects.

59

60 Tropospheric CO sources are categorized as “primary” or “secondary” based on their respective origins.
61 Primary sources are those that emit CO directly from Earth’s surface to the atmosphere, occurring mainly
62 through incomplete combustion of fossil fuels and organic matter. Vegetation emits a small amount of
63 primary CO through processes associated with leaf litter decomposition, as well as stress signaling in living
64 plants (van Asperen et al., 2024; Derendorp et al., 2011; Muller et al., 2025). Additionally, bacterial
65 production and photolysis of dissolved organic material in ocean surface water contributes a minor fraction
66 to total CO (Conte et al., 2019). Secondary sources stem from hydrocarbon precursor species that are
67 oxidized to yield CO in the atmosphere, primarily by OH but also nitrate, ozone and chlorine (Cl) radicals.
68 The most abundant precursor species is CH₄, which yields approximately 1/3 of total CO, followed by
69 numerous anthropogenic and biogenic non-methane volatile organic compounds (NMVOC).

70

71 The many CO sources exhibit a wide range in isotopic source signature for the two most abundant
72 isotopologues, ¹³CO and C¹⁸O (discussed in Sections 1.2 and 1.3). Due to rapid removal by OH, the
73 chemical lifetime of CO ranges from several weeks near the equator to several months at high latitudes
74 (Levy, 1971). This results in large spatial and temporal variability in both CO mole fraction and the isotopic
75 composition. At background locations, the carbon isotopic composition of CO (δ¹³C_{CO}) has been observed
76 to vary between -34‰ to -23‰ in the Northern Hemisphere and between -34‰ to -26‰ in the Southern
77 Hemisphere. A larger spread has been observed in the background oxygen isotopic composition (δ¹⁸O_{CO}),
78 ranging from -4‰ to +11‰ and from -7‰ to +2‰ in the Northern and Southern Hemispheres, respectively
79 (Bräunlich, 2000; Brenninkmeijer, 1993; Gros et al., 2001; Kato et al., 2000; Mak et al., 2003; Mak & Kra,



1999; Röckmann et al., 2002). Studying this variability is a powerful tool for mapping source emissions and tracking long-term trends in CO, which may have considerable implications for atmospheric chemistry.

1.2 $\delta^{13}\text{C}_{\text{CO}}$ Source Isotopic Signatures

CO derived from methane oxidation is the most ^{13}C -depleted of all sources due to 1) the existing low ^{13}C content of background CH_4 (current average $\delta^{13}\text{C}_{\text{CH}_4} = -48\text{‰}$) in combination with 2) the strong kinetic isotopic effects ($^{13}\text{C}\text{KIE} = k(^{12}\text{CH}_4)/k(^{13}\text{CH}_4)$) occurring in the reactions $\text{OH} + \text{CH}_4$ and $\text{Cl} + \text{CH}_4$. The OH oxidative sink is associated with a moderate $^{13}\text{C}\text{KIE}$ of 1.0039 (3.9‰ slower reaction rate constant for ^{13}C than for ^{12}C) which further depletes the produced CO to a $\delta^{13}\text{C}$ signature of approximately -52‰ (Saueressig et al., 2001) according to:

$$\delta^{13}\text{C}_{\text{CO}} = \alpha_{\text{CH}_4+\text{OH}} (\delta^{13}\text{C}_{\text{CH}_4} + 1) - 1 = (0.9961 * 0.952) - 1 = -52\text{‰} \quad (1)$$

where α is the fractionation factor equal to $1/\text{KIE}$. The Cl oxidative sink imparts a much stronger $^{13}\text{C}\text{KIE}$ of approximately 1.066 (66‰), producing CO with a substantially lower $\delta^{13}\text{C}$ signature near -107‰ (Crowley et al., 1999; Röckmann et al., 2024; Saueressig et al., 1995).

Relative to CO from CH_4 oxidation, the remaining major sources (i.e. fossil combustion, biomass burning, NMVOC oxidation) produce more ^{13}C -enriched CO. Fossil fuel combustion is a relatively well studied source and is associated with an average $\delta^{13}\text{C}$ value of -27.5‰, reflecting that of the precursor oil-based fuel (Popa et al., 2015; Saurer et al., 2008; Stevens et al., 1972). However, this typical $\delta^{13}\text{C}$ source signature may be shifting with the growth of recycled carbon and biofuels.

CO produced from biomass burning (i.e. combustion of organic matter) exhibits a larger spread in $\delta^{13}\text{C}$ source signature due to differences in how C3 and C4 plants fix carbon. In C3 plants (e.g. trees, rice, wheat, soybeans, potatoes, etc.), the enzyme Rubisco converts carbon dioxide (CO_2) to sugar via the Calvin-Benson cycle. Though C3 plants are more widespread, this mechanism has two key consequences: energy is expended due to photorespiration and water vapor is lost when stomata are open to accept CO_2 . Thus, C3 plants are better adapted to cool, humid regions. C4 plants (e.g. corn, sugarcane, sorghum, tropical grasses, etc.) use an additional evolutionary process that reduces photorespiration and moisture loss. This pathway allows C4 plants to thrive in dry and hot environments. Carbon fixation discriminates against the heavier ^{13}C isotope of ambient CO_2 (current average $\delta^{13}\text{C} = -8\text{‰}$) in both C3 and C4 plants, but the fractionation effect is much stronger in C3 plants (Dawson et al., 2002; Farquhar et al., 1989). This difference is reflected



112 in the typical carbon isotopic composition of each variety, around -27‰ for C3 and -12‰ for C4 plants,
113 which drives the geographically variable source signature of CO from biomass burning (Bender, 1971;
114 Bergamaschi et al., 2000; Gromov et al., 2017). Aside from this, combustion conditions play an important
115 role. It has been shown that CO from smoldering combustion is associated with a normal fractionation
116 effect (i.e. ^{12}CO is combusted faster than ^{13}CO) while flaming combustion exhibits the opposite (Kato et
117 al., 1999). Because CO production is enhanced in a smoldering fire, the $\delta^{13}\text{C}$ source composition of CO
118 from biomass burning is typically depleted (-2.1 to -6.8‰) relative to the fuel.

119
120 Constraints on the $\delta^{13}\text{C}$ source signature of CO from NMVOCs are limited due to the large variety of
121 relevant species and complicated oxidative pathways. As for CH_4 (Equation 1), the abundance of ^{13}C in
122 NMVOC-derived CO reflects the isotopic composition of the precursor material plus any fractionation
123 effects during NMVOC emission and subsequent oxidation to CO. For most biogenically derived
124 NMVOCs, plants are the primary emitter and so the isotopic composition of the precursor material is
125 modulated by the reservoir of fixed atmospheric CO_2 and the isotopic discrimination during carbon fixation
126 (Dawson et al., 2002; Farquhar et al., 1989; Gromov et al., 2017; Sharkey et al., 1991). As mentioned above,
127 this leads to a typical carbon isotopic composition of -27‰ for C3 and -12‰ for C4 plants. For many
128 NMVOCs, emissions from vegetation are associated with negligible fractionations (Conny & Currie, 1996).
129 Exceptions include isoprene, the most abundant biogenic NMVOC, with a reported emission ^{13}C KIE of
130 1.004-1.011 (4-11‰) and methanol, which exhibits a strong ^{13}C KIE of approximately 1.040 (40‰) (Affek
131 & Yakir, 2003; Keppler et al., 2004; Yamada et al., 2010). Considering the fractionation associated with
132 NMVOC oxidation to CO, Anderson et al. (2004a; 2004b) and Rudolph et al. (2000) report ^{13}C KIEs in the
133 reaction with OH for a list of biogenic species relevant to the CO inventory. All KIEs are normal (i.e. ^{12}C
134 isotopologues are oxidized faster than ^{13}C ones) and generally range between 1.002-1.012 (2-12‰). Still,
135 the fractionation effects are not known for most compounds and individual reaction steps.

136
137 Two observational studies are in close agreement regarding the $\delta^{13}\text{C}$ source signature of biogenic NMVOC-
138 derived CO, finding a value around -32.5‰ based on analysis of air in the midwestern USA (Stevens &
139 Wagner, 1989; Vimont et al., 2019). The NMVOC-derived CO is presumed to originate primarily from
140 isoprene and terpenes emitted by regional vegetation. Gromov et al. (2017) estimates a globally average
141 biogenic emitted CO $\delta^{13}\text{C}$ signature of -24.2‰, which is considerably higher than what was derived by
142 Stevens and Wagner (1989) and Vimont et al. (2019) but includes a larger portion of CO produced from
143 C4 plants (i.e. isotopically enriched precursor material) and does not consider KIE's associated with
144 NMVOC + OH reactions.

145



Human activities (e.g. fossil and biofuel combustion for power generation or transport, waste incineration, land use, manufacturing of various consumer products, etc.) also release NMVOCs and their breakdown in the atmosphere yields significant amounts of CO. At this time, no observational studies have isolated the anthropogenic NMVOC-derived CO $\delta^{13}\text{C}$ source signature. However, Gromov et al. (2017) estimates a globally averaged $\delta^{13}\text{C}$ source signature of -26.15‰ using a bottom-up model assessment, which primarily reflects the two largest contributing NMVOC categories: fossil and biofuel combustion.

1.3 $\delta^{18}\text{O}_{\text{CO}}$ Source Isotopic Signatures

The oxygen isotopic composition of CO primarily assists in tracing combustion contributions to the CO inventory. The $\delta^{18}\text{O}$ source signature of CO from fossil fuel combustion is expected to reflect the significantly enriched $\delta^{18}\text{O}$ of oxygen in air (+23.5‰) due to the negligible isotopic fractionation that is associated with high temperature combustion (Brenninkmeijer & Röckmann, 1997; Kroopnick & Craig, 1972). However, recent studies investigating the oxygen isotopic signature of urban and vehicle emissions show considerable spread (+11-25‰) in this value depending on fuel type and combustion conditions (Naus et al., 2018; Vimont et al., 2017).

A comprehensive study of CO from biomass burning shows that, regardless of plant type, the $\delta^{18}\text{O}$ source signature is significantly depleted (+3-18‰) or comparable (+16-26‰) to oxygen in air (+23.5‰) during smoldering and flaming conditions, respectively (Kato et al., 1999). In other words, C^{16}O is emitted faster than C^{18}O when vegetation combustion occurs at lower temperature. It has also been suggested that the $\delta^{18}\text{O}$ source signature may be influenced by the oxygen isotopic composition of cellulose which is influenced by soil moisture and ambient humidity (Saurer et al., 1997). Several additional studies have reported similar average $\delta^{18}\text{O}$ source signatures, though combustion temperatures or $\delta^{18}\text{O}$ of organic matter were not explicitly discerned. Stevens and Wagner (1989) report a signature of +18‰ for controlled burns of pine, grass and brush while Bergamaschi et al. (1998) derives a signature of +10‰ from enhanced CO linked to biomass burning in Siberia. Brenninkmeijer (1993) reports a $\delta^{18}\text{O}$ signature of +16.3‰ from analysis of unidentified burned organic matter in the laboratory.

Currently, the $\delta^{18}\text{O}$ signatures of secondary CO sources (i.e. CH_4 and NMVOC oxidation) are not well constrained. With respect to CO from NMVOC oxidation, Stevens and Wagner (1989) suggest a $\delta^{18}\text{O}$ signature of +15‰ while Brenninkmeijer and Röckmann (1997) and Vimont (2019) derived substantially depleted signatures of 0‰ and +3.6‰, respectively. All studies utilize isotopic observations of $\delta^{18}\text{O}_{\text{CO}}$, though the Stevens and Wagner (1989) and Vimont (2019) interpret the data via Keeling plot analysis and Brenninkmeijer and Röckmann (1997) derive the number from closing a larger scale isotopic mass balance.



180 Regarding CO from CH₄ oxidation, Brenninkmeijer and Röckmann (1997) estimated a $\delta^{18}\text{O}$ signature as
181 low as 0‰ based on Southern Hemisphere observations while Stevens and Wagner (1989) simply adopt
182 the same signature calculated for NMVOC oxidation (15‰). An incomplete understanding of oxygen KIEs
183 occurring in the CH₄ and NMVOC oxidation pathways and uncertainty surrounding water vapor exchange
184 with intermediate species, such as HCHO, contributes to low confidence in these $\delta^{18}\text{O}$ source signatures.

185

186 There are no studies of the $\delta^{18}\text{O}$ source signature for CO from Cl-initiated oxidation of CH₄. However, the
187 oxygen isotopic composition of the formed CO is likely independent of the initial H abstraction reaction
188 and so the $\delta^{18}\text{O}$ source signature should reflect that of OH-initiated oxidation.

189

190 **1.4 Isotope Effects from the Main Sink Reaction CO + OH**

191 Once emitted, the isotopic composition of CO is altered by kinetic fractionation in its removal processes.
192 Reaction with OH preferentially removes ¹²CO and is associated with a ¹³C KIE in the range of 1.005 to
193 1.007 (5-7‰) for standard atmospheric pressure, but it decreases as pressure drops (Stevens et al., 1980;
194 Röckmann et al., 1998). Accounting for decreasing pressure with increasing altitude, the average
195 tropospheric ¹³C KIE for CO + OH can be estimated to be about 1.003 (3‰). The CO + OH reaction exhibits
196 a stronger and inverse fractionation for oxygen, preferentially removing C¹⁸O. The ¹⁸O KIE of 0.990 (-10‰
197 faster reaction rate constant for ¹⁸O than for ¹⁶O) is pressure independent in the range 0.2-1.0 atm (Stevens
198 et al., 1980; Röckmann et al., 1998). Taken together, removal by OH causes residual CO in air to become
199 isotopically enriched in $\delta^{13}\text{C}$ and depleted in $\delta^{18}\text{O}$ as an air mass ages. The temperature dependencies of
200 the KIEs in this reaction have not yet been investigated, but they could have a non-negligible effect of up
201 to 1‰ additional enrichment for $\delta^{13}\text{C}_{\text{CO}}$ (Gromov, 2013).

202

203 **1.5 Modern Observations of CO, $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$**

204 The National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Laboratory (GML)
205 has measured CO mole fractions weekly from 1988 to present across a globally distributed network of air
206 sampling sites (Novelli et al., 1992; Novelli et al., 1998; Petron et al., 2026). The NOAA-GML sampling
207 sites were selected based on the criteria that these locations are distant from centers of human activity and
208 represent the background atmosphere (Fig. 1a). This network is further categorized into Marine Boundary
209 Layer (MBL) and Continental Outflow (COF) sites. MBL sites are situated at sea level, where the
210 atmosphere is well mixed and prevailing winds travel from the remote ocean towards the land-based
211 sampling location. Conversely, the COF sites are situated at several altitudes and may receive additional
212 emissions from upwind industrialized regions or natural sources.

213



214 Remote sensing of total column CO has also been carried out, with the primary advantage of enhanced
215 geographic coverage for emission quantification. The longest running dataset (2000-2025) was collected
216 by the Measurement of Pollution in the Troposphere (MOPITT) instrument onboard the NASA Terra
217 satellite. An additional NASA instrument, the Atmospheric Infrared Sounder (AIRS), was launched with
218 the Aqua satellite in 2002 and still collects total column CO data today. As part of a European initiative,
219 the Tropospheric Monitoring Instrument (TROPOMI) onboard the Sentinel-5 Precursor (S5P) satellite was
220 launched in 2017, providing another data product for global CO monitoring.

221

222 High-resolution observations of CO isotopic composition are also available, although sparser. A network
223 of independent global observatories monitored $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ (in addition to CO mole fractions) at the
224 turn of the 21st century (Bräunlich, 2000; Brenninkmeijer, 1993; Gros et al., 2001; Kato et al., 2000; Mak
225 et al., 2003; Mak & Kra, 1999; Röckmann et al., 2002). Since that time, the only continuous in-situ
226 monitoring of CO isotopic composition has been carried out at Baring Head, New Zealand by Earth
227 Sciences New Zealand (formerly the National Institute of Water and Atmospheric Research).

228

229 Beginning in 2023, regular monitoring of $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ resumed at seven globally distributed stations
230 as part of the ISAMO (Iron Salt Aerosol Methane Oxidation) project. At its inception, the primary goal of
231 the ISAMO project was to better constrain the current atmospheric chlorine sink of CH_4 . Because prior
232 measurements of CO, $\delta^{13}\text{C}_{\text{CO}}$, and $\delta^{18}\text{O}_{\text{CO}}$ were collected at three of the seven stations (ZEP, IZO, and RPB)
233 between 1996-2001, an additional utility has been identified: comparing average values and seasonal trends
234 in CO isotopic composition over three decades to understand long-term shifts in global atmospheric
235 composition, as they relate to CO. In this study, we 1) analyze the NOAA-GML CO timeseries to quantify
236 temporal trends in atmospheric CO at a global scale, 2) present the new stable isotope data from the ISAMO
237 network, 3) compare these observations to previous datasets, and finally 4) interpret the observed isotopic
238 shifts in terms of underlying budget changes obtained from CO source emission inventories.

239

240 **2 Methods**

241 **2.1 ISAMO**

242 **2.1.1 Air Sampling**

243 The ISAMO network is constituted by air sampling twice per week at seven locations: IZO (Izaña
244 Atmospheric Observatory, Tenerife, Spain), IEO (Spanish Institute of Oceanography, Tenerife, Spain),
245 CVAO (Cape Verde Atmospheric Observatory, Cape Verde), RPB (Ragged Point Barbados, Barbados),
246 ATTO (Amazon Tall Tower Observatory, Brazil), ZEP (Zeppelin Observatory, Svalbard, Norway), and
247 CMN (Monte Cimone, Italy). Air sampling methods are relatively uniform among all monitoring stations.



248 Using a diaphragm pump, ambient air is flushed through a 1-2 L borosilicate glass flask for five minutes at
249 midday and compressed to a target pressure of 1.7 bar. At ZEP, 1.4 L Entech Silonite™ coated stainless
250 steel canisters are used in place of borosilicate glass flasks. During flushing and filling, water vapor is
251 chemically removed using a magnesium perchlorate trap to avoid moisture accumulation in the flask. Flasks
252 are sealed and transported to Utrecht University for isotopic analysis typically within 3 months of sample
253 collection. Sample pressures are measured again on the analysis date and a flag is applied if flask leakage
254 is evident.

255

256 2.1.2 Analytical Methods at UU

257 The mole fraction and isotopic composition of CO is measured on a continuous flow isotope ratio mass
258 spectrometer (CF-IRMS) system that was described in Pathirana et al. (2015) and has been used for several
259 previous studies (Dasari et al., 2022; Kirago et al., 2023; Naus et al., 2018; Vernooij et al., 2022). Glass
260 flasks are connected to the inlet ports of a 12-port Valco Dead-end Flowpath Selector with Ultra-Torr
261 vacuum fittings. The system can accommodate up to eight flasks, three reference tanks, and one blank (i.e.
262 capped port) for each automated measurement sequence. Whole dry air is supplied to the extraction system
263 through a mass flow controller (MFC) at 20 mL min⁻¹ for 5 minutes. Flow rate and injection time can be
264 altered depending on sample mole fraction to optimize CO yield.

265

266 Upon injection, CO₂ is removed by a chemical trap containing Ascarite® (i.e. sodium hydroxide coated
267 silica). The adsorption of CO₂ releases H₂O, which is subsequently removed by magnesium perchlorate. A
268 U-shaped 6 mm glass trap filled with US mesh 40-60 glass beads (approximately 0.25-0.4 mm diameter)
269 is lowered into a liquid nitrogen bath (-196° C) to trap other condensable gases, such as N₂O, and
270 remaining H₂O and CO₂. Due to its lower freezing point (-205° C), CO passes through the cryogenic trap
271 and is directed to an oxidation reactor, another U-shaped glass tube filled with 3 g of Schütze reagent
272 (iodine pentoxide coated silica gel) (Schütze, 1944; Smiley, 1965). At room temperature, Schütze reagent
273 selectively oxidizes CO to CO₂ without inducing isotopic exchange between the original and additional
274 oxygen atoms (Schütze, 1944; Smiley, 1965). The introduction of an additional oxygen atom from
275 Schütze is later corrected for in $\delta^{18}\text{O}_{\text{CO}}$ calculations as described in Section 2.1.6.

276

277 The CO-derived CO₂ is then collected in a pre-concentration trap, consisting of 1/16 inch stainless steel
278 tubing submerged in liquid nitrogen. Here, bulk O₂ and N₂ are not trapped and pumped away from the
279 sample. The CO₂ sample is warmed to room temperature (25° C) by lifting the pre-concentration trap out
280 of the liquid nitrogen bath and carried by a helium carrier gas via a 6-port 2-position Valco valve to a
281 focus trap (silica capillary encased by 1/16-inch stainless steel tubing and submerged in liquid nitrogen).



282 Focusing further consolidates the CO₂ sample, which translates to sharper peaks during sample detection
 283 by the IRMS. Following focusing, a PoraPLOT Q Gas Chromatography (GC) column held at 50° C
 284 separates the sample from residual contaminants. The sample is dried by Nafion and finally introduced to
 285 a Thermo Scientific Delta V Advantage IRMS via a custom made open split interface as described in
 286 Röckmann et al. (2003).

287

288 2.1.3 Blank Correction

289 A blank correction is applied to $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ measurements to remove the integrated influence of
 290 CO and CO₂ generated by the CF-IRMS system itself. The methods described in Section 2.1.2 are applied
 291 to a capped manifold port to quantify contamination attributed to CO₂ produced by the Schütze reagent,
 292 CO and CO₂ emitted by materials along the extraction line, or CO and CO₂ entering the system via an
 293 external leak (Pathirana et al., 2015). We assume the total isotopic abundance detected by the IRMS is
 294 constituted by the sample plus the blank:

295

$$\delta_{\text{total}}m_{\text{total}} = \delta_{\text{sample}}m_{\text{sample}} + \delta_{\text{blank}}m_{\text{blank}} \quad (2)$$

296

297 where m represents the mole fraction and δ represent the isotopic abundance. By rearranging Equation 2,
 298 the corrected isotopic abundance of the sample is defined as:

299

$$\delta_{\text{sample}} = \frac{\delta_{\text{total}}m_{\text{total}} - \delta_{\text{blank}}m_{\text{blank}}}{m_{\text{sample}}} \quad (3)$$

300

301 2.1.4 CO Mole Fraction Calibration

302 The current daily reference cylinder has an assigned CO mole fraction value of 235.0 ppb and is set on the
 303 WMO X2004 scale via calibration of a previous daily reference cylinder at the Max Planck Institute for
 304 Biogeochemistry (MPI-BGC). Calibrated CO mole fractions of flask samples and monitoring cylinders are
 305 determined by multiplying the ratio of sample versus daily reference peak area by the daily reference CO
 306 mole fraction. Monitoring cylinders are regularly run against the daily reference to assess potential CO
 307 drift. No detectable drift has occurred during measurement collection of the dataset presented here (i.e.
 308 2022-2025).

309

310 2.1.5 Delta Notation

311 Stable isotope measurements are reported in delta notation (‰), as the relative difference in isotope ratio
 312 between sample and international standard:



313

$$\delta = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \text{ ‰} \quad (4)$$

314

315 For analysis of $\delta^{13}\text{C}_{\text{CO}}$, R is defined as $^{13}\text{C}/^{12}\text{C}$ and VPDB (Vienna PeeDee Belemnite) is recognized as a
 316 the primary standard (Craig, 1957). For analysis of $\delta^{18}\text{O}_{\text{CO}}$, R is defined as $^{18}\text{O}/^{16}\text{O}$ and VSMOW (Vienna
 317 Standard Mean Ocean Water) is recognized as the primary standard (Gonfiantini, 1978). All
 318 measurements discussed here have been set on the $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ international scales by using a
 319 calibration gas developed by Carl Brenninkmeijer when he started the early CO isotope measurements at
 320 Earth Sciences New Zealand (formerly NIWA) against NZCH (IAEA-CO-9) with $\delta^{13}\text{C} = -47.23\text{‰}$ and
 321 $\delta^{18}\text{O} = -15.6\text{‰}$ on the VPDB scale (Brenninkmeijer, 1993; Brenninkmeijer, 1995; Coplen et al., 2006;
 322 Stichler, 1995). The calibration gas was produced by mixing chemically pure CO with N_2 in an aluminum
 323 cylinder at a high mole fraction of 259 ppm, and the isotopic calibration was verified using an
 324 independent method in Brenninkmeijer and Röckmann (1997).

325

326 2.1.6 Schütze Correction

327 During conversion of CO to CO_2 using Schütze reagent ($5\text{CO} + \text{I}_2\text{O}_5 \rightarrow 5\text{CO}_2 + \text{I}_2$), the addition of an
 328 oxygen atom does not induce isotopic exchange (Stevens & Krout, 1972), thereby allowing the original
 329 isotopic composition of CO to be determined mathematically. Following Brenninkmeijer (1993), we correct
 330 the $\delta^{18}\text{O}_{\text{CO}}$ of our samples using:

331

$$\delta_s = 2\delta_{\text{ms}} - \delta_i \quad (5)$$

332

333 where δ_s is the corrected $\delta^{18}\text{O}$ of sample, δ_{ms} is the measured $\delta^{18}\text{O}$ of CO-derived CO_2 and δ_i is the $\delta^{18}\text{O}$ of
 334 O from the I_2O_5 , which is also defined as:

335

$$\delta_i = 2\delta_{\text{mc}} - \delta_c \quad (6)$$

336

337 where δ_{mc} is the measured $\delta^{18}\text{O}$ of CO-derived CO_2 from the reference gas and δ_c is the $\delta^{18}\text{O}$ of CO in the
 338 reference gas, which is established previously through calibration techniques.

339

340 2.1.7 Uncertainty

341 The stability and variability of the CF-IRMS system is evaluated using long-term monitoring of samples
 342 taken from a reference tank. For the duration of the ISAMO project, three cylinders of air (two spiked to



approximately 400 ppb CO and one containing background air with 90 ppb CO) are measured alongside whole-air flask samples. The derived standard deviations from over three years of measurements are provided in Table 1. Sample uncertainty (± 1 ppb for CO, $\pm 0.1\%$ for $\delta^{13}\text{C}_{\text{CO}}$ and $\pm 0.2\%$ for $\delta^{18}\text{O}_{\text{CO}}$) is calculated as the mean daily standard deviation of the background monitoring tank (Cyl_IZANA). The highest degree of sample uncertainty (± 1 ppb for CO, $\pm 0.2\%$ for $\delta^{13}\text{C}_{\text{CO}}$ and $\pm 0.4\%$ for $\delta^{18}\text{O}_{\text{CO}}$) is calculated as the long-term standard deviation of the background monitoring tank. Daily and long-term standard deviations of the spiked monitoring tanks (NAT_311 and Cyl_JENA) are lower than the background tank for both $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$, as increased signal leads to greater measurement precision.

	CO (ppb)		$\delta^{13}\text{C}_{\text{CO}}$ (‰ VPDB)		$\delta^{18}\text{O}_{\text{CO}}$ (‰ VSMOW)	
	Mean	SD	Mean	SD	Mean	SD
NAT_311	434	1.2 (2.9)	-26.9	0.06 (0.11)	+16.6	0.12 (0.24)
Cyl_Jena	387	2.9 (4.4)	-27.8	0.07 (0.13)	+10.9	0.14 (0.29)
Cyl_IZANA	88	0.6 (0.8)	-29.0	0.09 (0.17)	-1.6	0.24 (0.38)

Table 1 | Cylinder statistics (mean and standard deviation) for the period Jan 01, 2023 – May 02, 2026; SD values without parentheses are the average of daily standard deviations, whereas values inside parentheses are the standard deviation of all measurements within timeframe

2.2 Used Datasets

2.2.1 NOAA-GML CO Mole Fraction Methods

Air samples are collected and pressurized in 2.2 L borosilicate glass flasks at the Cooperative Global Air Sampling Network sites within NOAA-GML's Global Greenhouse Gas Reference Network. Three analytical methods have been used since the start of CO monitoring. Between 1988 to 2008, measurements were made using gas chromatography (GC) with a mercuric oxide (HgO) detector, though this method had a nonlinear response over the range of CO in the remote troposphere (Novelli et al., 1991). In 2008, one of two GC-HgO systems was replaced by an analyzer using vacuum ultraviolet (VUV) fluorescence. From August 2019, all measurements of CO mole fraction have been obtained using Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS), which is calibrated monthly and has a linear response in the range of 23 to 486 ppb.

The NOAA-GML sites used in this analysis were filtered based on the following criteria. To control for elevated, non-background CO mole fractions, sites with regular excursions above 260 ppb in the Northern Hemisphere (e.g. AMY, BAL, BSC, DSI, HUN, KDZ, LLN, SDZ, TAP, TPI) and 120 ppb in the Southern Hemisphere (e.g. ASC) were removed. The excluded high CO sites in the Northern Hemisphere



are subject to elevated CO emissions from nearby industrialized regions, whereas the Southern Hemisphere site ASC is regularly affected by Sub-Saharan biomass burning. In addition, sites with less than 25% temporal coverage (i.e. monitoring for < 7.5 years) of the study period 1995-2025 were removed (e.g. ABP, LLB, MBC, KCO, TIK). Finally, ship transect observations were not included.

2.2.2 CO Isotope Measurements from Large Compressed Air Samples

During the extensive CO isotope monitoring period in the 1990s, before the implementation of CF-IRMS, measurements were carried out after extraction and purification of CO from high volume air samples. At the sampling locations ZEP, IZO, and RPB, 1 m³ air samples were compressed into 10 L aluminum cylinders (Mak and Brenninkmeijer, 1994). At BHD, 70 L stainless steel tanks were filled to 17 bar using a membrane compressor. In 2004, this shifted to 50 L aluminum cylinders that are more stable and reduce the need to rapidly extract the samples after collection. Large air samples were processed using a laboratory extraction system, cryogenically removing CO₂ before oxidizing the CO to CO₂ using Schütze reagent (Brenninkmeijer, 1991; Brenninkmeijer and Röckmann, 1996). The overall yield was determined manometrically to establish the CO mole fraction. The isotopic composition of the CO-derived CO₂ was determined using a Dual Inlet IRMS.

2.3 Emissions Inventories and Model Data

The analysis below is assisted by model-based estimates of tropospheric CO turnover (direct emissions, photochemical production and sink, transport) simulated with the ECHAM/MESSy Atmospheric Chemistry (EMAC) model. EMAC is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2010). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5) (Roeckner et al., 2006). The physics subroutines of the original ECHAM code have been modularized and reimplemented as MESSy submodels and are under continuous development. Only the spectral transform core, the flux-form semi-Lagrangian large scale advection scheme, and the nudging routines for the Newtonian relaxation are remaining from ECHAM.

For the present study we applied EMAC (MESSy version 2.55.2) in the T63L31ECMWF-resolution, with a spherical truncation of T63 (corresponding to a quadratic Gaussian grid of approximately 1.88° by 1.88° in latitude and longitude) with 31 vertical hybrid pressure levels up to 10 hPa. The applied model configuration is based on the RD1SD setup according to the Chemistry-Climate Modelling Initiative



(CCMI) 2022 refD1 protocol (Jöckel et al., 2024) with atmospheric dynamics nudged towards the observed atmospheric state (ERA5 reanalysis) (Hersbach et al., 2020). In this hind-cast simulation throughout the 1979-2019 period, online comprehensive gas-phase and aerosol kinetic chemistry integration and transient emissions/boundary conditions are used; the latter closely follow the specifications of the CMIP6 SSP2-4.5 scenario. Jöckel (2016) provide a detailed evaluation of earlier CCMI simulations with EMAC with their results of the RC1SD-base-10 setup being comparable to the one used here.

3 Results

3.1 Global trends in CO from the NOAA-GML flask sampling network

The NOAA-GML CO timeseries data exhibits a strong interhemispheric gradient, with the highest CO mole fractions in the mid and high latitudes of the Northern Hemisphere. Seasonal variation is observed in both hemispheres, where the monthly-averaged CO extrema range from approximately 70-200 ppb in the Northern Hemisphere and 40-70 ppb in the Southern Hemisphere (Fig. 1c).

Since monitoring of atmospheric CO began in the 1990s, the seasonal amplitude at mid and high latitudes (i.e. extra-tropical) of the Northern Hemisphere has decreased due to a gradual reduction in the wintertime CO maxima (Fig. 2a). Between 1995-1999, the winter maxima averaged 170 ppb while the summer minima averaged 100 ppb. Twenty-five years later (2020-2024), the average summer minima are largely unchanged, yet the winter maxima now average 135 ppb. A similar yet dampened trend is found in the low latitude (i.e. tropical) Northern Hemisphere (Fig. 2b). Here, summer minima have remained around 75 ppb while the winter maxima have decreased from approximately 120 ppb to 105 ppb. Across the entire Northern Hemisphere, the mean summertime minimum in 2023 is the highest on record since 2003.

In the extra-tropical Southern Hemisphere, seasonal CO variation has remained relatively consistent since 1995 with an averaged winter maximum of 65 ppb and a summer minimum of 45 ppb (Fig. 2c). One exception is the summertime CO in 2020, which is elevated by ~10 ppb, resulting from unusually strong biomass burning in Australia (Bègue et al., 2024). The tropical Southern Hemisphere exhibits similar stability with average extrema approximately 5 ppb higher than the extra-tropics, although fewer observations exist in this region (Fig. 2d). During the 2024 winter period, the entire Southern Hemisphere exhibited exceptionally high CO mole fractions. The 2024 excursions deviate furthest from the long-term mean in the tropical Southern Hemisphere, suggesting the additional CO originated within this latitude band and was later transported to higher latitudes.



Variation also exists between the Marine Boundary Layer (MBL) and Continental Outflow (COF) sites. In the extra-tropical Northern Hemisphere, the MBL annual minima are consistently 20 ppb lower than the COF locations, while the annual maxima are generally aligned. The MBL sites exhibit approximately half the variability as the COF sites. Monthly-resolved CO standard deviations for both categories show insignificant change over the monitoring period (Fig. 1d, 3a). In the extra-tropical Southern Hemisphere, the annual minima and maxima are similar, though the past two decades exhibit a growing divide. Specifically, the extrema of the COF sites are approximately 5-10 ppb higher in the past several years, relative to the MBL sites. Similarly, variability at the COF sites appears to increase over time.

3.2 CO Mole Fraction and Isotopic Analysis from the ISAMO network

The ISAMO project provides high temporal resolution measurements of CO mole fraction and isotopic composition at seven stations: IZO, IEO, CVAO, RPB, ATTO, CMN, and ZEP. The first five stations are representative of the “low-latitude” atmosphere, while CMN and ZEP provide information about “mid-latitude” and “high-latitude” air, respectively. In the following description, we first discuss trends in CO mole fraction at mid and high latitudes followed by a summary of the low-latitude station observations and then describe the isotope time series.

3.2.1 CO Mole Fraction

The ZEP and CMN CO mole fraction timeseries exhibit strong seasonality with sustained annual maxima in February-March and minima in July (Fig 4a). The range in CO extrema at ZEP is larger, as both the winter maximum and summer minimum are approximately 10 ppb higher and lower, respectively, than those at CMN. An interesting element of the mid- and high-latitude CO timeseries is the occurrence of secondary autumn maxima (up to 150 ppb) detected at ZEP in 2023 and at both ZEP and CMN in 2024. Finally, we note that ZEP CO mole fraction exhibits the lowest week-to-week variability as compared to the other stations. This is partially related to lower sampling frequency (1 sample per week at ZEP vs. 2-3 at others), but it is also due to the geographic remoteness from regions with large and variable CO sources or sinks, which causes the local CO inventory to be well-mixed.

Low-latitude background CO mole fractions exhibit very low seasonality throughout 2023 (Fig. 4a). Excluding the summer ATTO biomass burning season, CO fluctuates between 70-150 ppb with no clear extrema at each of the tropical stations (IZO, IEO, CVAO and RPB). In 2024, RPB again exhibits very low seasonal CO variation, similar to that observed in 2023. The 2024 CO timeseries at CVAO is nearly identical to that in 2023, but there is slightly greater seasonality due to a more pronounced minimum in



473 June. IZO and IEO also show a more distinct seasonal cycle in 2024 due to higher CO between January-
474 June (~125 ppb) and lower CO in the remaining months (~100 ppb), relative to 2023.

475

476 The large summer-to-autumn CO peak at ATTO, occurring in both 2023 and 2024, is due to this site's
477 proximity to biomass burning emissions. Based on our observations, the burn season gradually begins in
478 June and is strongest from July to November (Fig. 4a). We capture 600 ppb or greater spikes in CO mole
479 fraction, though there is likely high hourly to daily variation during this period. Outside of this time frame,
480 CO mole fractions at ATTO fall within the background range of the other tropical stations. This indicates
481 that air arriving at ATTO originates in the lower latitudes of the Northern Hemisphere despite the site
482 location being 2 degrees south of the equator (Andreae et al., 2015).

483

484 3.2.2 Carbon Isotopic Composition

485 In section 3.2.1, relatively similar CO mole fractions are described for the mid-latitude station CMN and
486 high-latitude station ZEP. The associated $\delta^{13}\text{C}_{\text{CO}}$ timeseries are nearly identical during the winter period
487 (i.e. November 2023 through March 2024) and then diverge slightly through the spring and summer (Fig.
488 4b). At the onset of CO mole fraction decline in April, a 1‰ enrichment (-27 to -26‰) in $\delta^{13}\text{C}_{\text{CO}}$ is observed
489 at ZEP, while no shift is observed at CMN. The annual maxima for both locations are reached shortly
490 thereafter in May, before declining in parallel to minima in August. During the CMN summertime
491 minimum, we document several $\delta^{13}\text{C}_{\text{CO}}$ observations lower than -32‰, which is approximately ~2‰ lower
492 than at ZEP, but relatively in line with minima at the tropical stations CVAO, IZO and IEO.

493

494 Among the low-latitude tropical monitoring stations, $\delta^{13}\text{C}_{\text{CO}}$ varies between -27 and -35‰ within an annual
495 period though interestingly, isotopic shifts do not occur simultaneously (Fig. 4b). For both 2023 and 2024,
496 springtime $\delta^{13}\text{C}_{\text{CO}}$ (i.e. March-June) shows a large divergence between the eastern Atlantic (i.e. IZO, IEO
497 and CVAO) and western Atlantic (i.e. RPB, ATTO) regions. At the most extreme point, ATTO is ~6‰
498 lower than IZO, IEO, and CVAO, while RPB falls approximately midway.

499

500 A general timeline of the observed deviations is as follows. At mid-winter (i.e. January), the average δ
501 $^{13}\text{C}_{\text{CO}}$ of all tropical stations falls within a 2‰ range, with an average background of -29‰. By March, RPB
502 and ATTO have already hit a seasonal maximum and are beginning an initial decrease towards their
503 respective seasonal minima. ATTO decreases at a faster rate, already reaching a seasonal minimum by May.
504 Of all observations presented in Figure 4, ATTO experiences the lowest multi-week $\delta^{13}\text{C}_{\text{CO}}$ at this time,
505 reaching -34‰ or lower two years in a row, despite comparable CO mole fraction to the other tropical
506 stations. At this same time, the eastern Atlantic stations (i.e. IZO, IEO, and CVAO) are reaching their



seasonal maxima. RPB does not reach a minimum until late summer. In 2023, the seasonal minimum occurs in August, with the caveat that we did not have data for September and October. The 2024 minimum occurs in July, with two consecutive data observations below -34‰. From mid-to-late May, the eastern Atlantic stations begin decreasing towards a seasonal minimum, which occurs consistently from July-August at IZO, but is not as predictable at IEO and CVAO. The coastal Tenerife station, IEO (0 m above sea level (ASL)), exhibits a similar seasonal pattern to IZO (Tenerife; 2373 m ASL) in that winter and spring observed $\delta^{13}\text{C}_{\text{CO}}$ values are typically high and an average minimum is reached in summer, but IEO also exhibited a strong multi-week depletion from December 2023-January 2024 obscuring the expected oscillation. At CVAO, the seasonal minimum appears to occur twice: the first minimum is reached in July/August followed by another in October/November. The minima appear as short-lived negative $\delta^{13}\text{C}_{\text{CO}}$ departures from the monthly average. This pattern is evident in 2023 and 2024. By November, average $\delta^{13}\text{C}_{\text{CO}}$ among all tropical stations converges to a background of $-29 \pm 1\text{‰}$ and remains relatively stable throughout the winter.

Another interesting feature of the low-latitude $\delta^{13}\text{C}_{\text{CO}}$ timeseries is the isotopic shift associated with biomass burning near ATTO (Fig. 4b). As mentioned in Section 3.2.1, the burn season begins in June (concurrent with the seasonal minimum in $\delta^{13}\text{C}_{\text{CO}}$ at ATTO). From this point until the burning emissions subside, our observations are greatly influenced by the $\delta^{13}\text{C}$ source signature of organic combustion and are not representative of the background CO inventory. Using a Keeling plot analysis, additional CO in the ATTO inventory is found to have a $\delta^{13}\text{C}$ source signature = $-30.3 \pm 0.25\text{‰}$ ($r^2 = 0.50$; uncertainty calculated as standard error of y-intercept), which is consistent with smoldering emissions from high C3:C4 plant matter. This addition tips the combined $\delta^{13}\text{C}_{\text{CO}}$ towards more enriched values, which vary between -30 to -31.7‰ during the height of the burn season.

3.2.3 Oxygen Isotopic Composition

Aside from ATTO, all stations exhibit the same seasonal trend in $\delta^{18}\text{O}_{\text{CO}}$, characterized by annual maxima in February and minima in July. At the high-latitude station ZEP, the maxima occur at values of approximately +7‰ and fall to about -1‰ in the summertime. The mid-latitude station CMN exhibits a nearly identical winter peak to ZEP, though the average summer minimum only reaches +1‰. The winter maxima at low-latitude stations IZO, IEO, CVAO, and RPB are significantly lower (approximately +3‰ in 2024) than at ZEP and CMN, though the summertime minima are similar to that of ZEP.

The utility of $\delta^{18}\text{O}_{\text{CO}}$ as a tracer of combustion-derived CO is evident in the ATTO timeseries data (Fig. 4c). The seasonal cycle of ATTO diverges from the other six stations due to the large contribution of biomass burning emissions in the latter half of the year. The seasonal minima are instead reached in May,



prior to elevated burning, and the seasonal maxima around October, when CO mole fractions are consistently double or more than background conditions. For this period, a Keeling plot analysis indicates the additional CO has a $\delta^{18}\text{O}$ source signature = $+8.3 \pm 0.32\text{‰}$ ($r^2 = 0.76$; uncertainty calculated as standard error of y-intercept). This finding is consistent with the $\delta^{13}\text{C}$ Keeling analysis in Section 3.2.2, which points to enhanced biomass burning emissions in the smoldering stage.

3.3 Longterm Shifts in CO and Model Comparison

	CO (ppb)		$\delta^{13}\text{C}_{\text{CO}}$ (‰ VPDB)		$\delta^{18}\text{O}_{\text{CO}}$ (‰ VSMOW)	
	shift	SEM	shift	SEM	shift	SEM
ZEP	-17.9	± 5.6	-2.09	± 0.26	-1.64	± 0.60
IZO	9.9	± 6.4	-2.43	± 0.37	+1.31	± 0.87
RPB	-7.5	± 6.1	-1.43	± 0.47	-2.12	± 0.64
BHD	n/a	n/a	-1.92	± 0.27	-1.49	± 0.63

Table 2 | Shift in moving averages (Fig. 5) from 1996-2001 vs 2023-2024 (ZEP, IZO, RPB) and from 1996-2000 vs 2020-2023 (BHD); For each station, reported standard error of the mean (SEM) values are calculated as the square root of the sum of squared mean SEM for each period (RSS method)

3.3.1 CO Mole Fraction

CO seasonality is driven primarily by cyclical variation in UV light and by extension, the availability of OH radicals. This interplay is evident in observations from high-latitude Northern Hemisphere monitoring stations where we observe the largest average range in CO extrema (Fig. 2a). For example, the station ZEP experiences a period of Arctic polar night (mid-November to end of January) when the sun remains below the horizon 24 hours a day, thereby preventing any substantial OH production and CO removal. During this time, CO transported from lower latitudes is subject to less removal and accumulates in the northern latitudes. Upon termination of the polar night, OH formation resumes at high-latitudes while increasing at mid-latitudes. Thus, we observe CO maxima between February-March across high Northern latitudes, followed by a swift decline to the annual minima in July-August when the OH sink is strongest. Removal by OH similarly drives CO seasonality at mid and low latitudes, but these regions experience less extreme variation. In the Southern Hemisphere, the timing of OH sink strength fluctuations are shifted and correspondingly the CO maxima occur between September-October and minima between January-March.



567 When evaluating long-term changes in Northern Hemisphere CO mole fractions, we find that the 2023-
568 2024 observations exhibit a dampened CO seasonal cycle, relative to observations in the late 1990s. This
569 finding is consistent with long-term trends in the NOAA CO monitoring network presented in Section 3.1.

570

571 At ZEP and RPB, reduced seasonality is primarily driven by a reduction in wintertime CO over the past
572 several decades (Fig. 5). The 2024 maximum at ZEP of 140 ppb is significantly lower than the average
573 seasonal maxima of 150-175 ppb occurring from 1996-2001. For these same years at ZEP, the seasonal
574 minima range of 80-100 ppb in July are similar between the 1990s and 2020s (~90 ppb). In both years 2023
575 and 2024, CO levels increase quickly after the summer minimum to a secondary maximum in October. A
576 similar atypical autumn peak was documented in 1998 at ZEP and ultimately linked to a strong Northern
577 Hemisphere biomass burning season using isotopic characterization (Röckmann et al., 2002). At RPB, low
578 CO (70-110 ppb) is documented from January-April in both 2023 and 2024, whereas it had previously
579 ranged from 100-140 ppb during the years 1996-2000 (Mak et al. 2003). For all years on record, average
580 summertime minima (75-95 ppb) are aligned.

581

582 In contrast to ZEP and RPB, dampened seasonality at IZO in 2023-2024 is driven by elevated summer and
583 autumn CO (Fig. 5). The 1996-2001 CO measurements at IZO exhibit consistent average seasonal minima
584 in the range of 70-90 ppb (Bräunlich, 2000). The 2023 and 2024 average summertime minima reached 100
585 and 115 ppb, respectively, due to frequent positive excursions in CO mole fraction. Interestingly, the
586 average wintertime maximum at IZO has remained roughly unchanged over the past three decades.

587

588 In line with the large-scale trends derived from the NOAA-GML observations, average seasonal extrema
589 have remained relatively constant between 1999-2024 at BHD, varying from 40-55 ppb during summer and
590 from 60-80 ppb during winter (Fig. 5). Individual years (e.g. 2003, 2005, and 2024) exhibit anomalously
591 high wintertime CO events at BHD, reaching upwards of 90 ppb. As mentioned in Section 3.1, the NOAA-
592 GML monitoring network also detected exceptionally high mean CO mole fractions in both the tropical and
593 extra-tropical Southern Hemisphere during 2024.

594

595 3.3.2 Carbon Isotopic Composition

596 The seasonal cycle of background $\delta^{13}\text{C}_{\text{CO}}$ is largely driven by the balance between CO from ^{13}C -depleted
597 sources, such as $\text{OH} + \text{CH}_4$, versus ^{13}C -enriched sources, such as fossil and biomass combustion. Because
598 CO from CH_4 oxidation is both produced and destroyed via OH, its absolute contribution can be calculated
599 from a steady-state model:

600



$$\frac{d[\text{CO}]}{dt} = k_{\text{CH}_4+\text{OH}}[\text{CH}_4][\text{OH}] - k_{\text{CO}+\text{OH}}[\text{CO}][\text{OH}] = 0 \quad (7)$$

601

602 where $k_{\text{CH}_4+\text{OH}} (=2.5 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ s}^{-1})$ and $k_{\text{CO}+\text{OH}} (=1.5 \times 10^{-13} \times (1+0.6P_{\text{atm}}) \text{ cm}^3 \text{ s}^{-1})$ are the rate
 603 coefficients of the temperature-dependent production and pressure-dependent removal pathways,
 604 respectively (DeMoore et al., 1997). Rearranging, the absolute amount of CO from OH+CH₄ is equal to
 605 $k_{\text{CH}_4+\text{OH}} / k_{\text{CO}+\text{OH}} [\text{CH}_4]$ because the most variable parameter [OH] cancels out. Elevated OH in summer forms
 606 more CO via CH₄ oxidation, while simultaneously removing it faster; winter months are characterized by
 607 lower CH₄-derived CO formation and slower removal due to OH. Minor variations still occur due to the
 608 temperature and pressure dependence of the rate coefficients, seasonal and latitudinal variations in CH₄,
 609 and the effect of transport. Conversely, the other globally dominant source, CO from fossil combustion, is
 610 continuously and consistently emitted but subject to seasonally varying removal. Winter periods in the
 611 Northern Hemisphere experience reduced OH availability which leads to enhanced CO accumulation,
 612 predominantly due to isotopically enriched fossil CO. Therefore, the winter CO inventory is characterized
 613 by higher relative contribution from combustion CO and a lower relative contribution of CO from CH₄
 614 oxidation, which causes an increase in the observed $\delta^{13}\text{C}_{\text{CO}}$. Entering summer, as the OH sink gains
 615 importance and total CO decreases, the relative contribution of CO from OH+CH₄ increases and tips the
 616 observed $\delta^{13}\text{C}_{\text{CO}}$ in the negative direction to an eventual minimum. However, the extent of depletion due to
 617 summertime CH₄ oxidation is counteracted by the KIE in OH+CO (i.e. preferential removal of ¹²CO), which
 618 peaks concurrently.

619

620 At all four CO isotope monitoring locations in this comparison (ZEP, IZO, RPB and BHD), $\delta^{13}\text{C}_{\text{CO}}$
 621 observations in 2023-2024 are approximately 1.4-2.4‰ lower compared to the measurements taken in the
 622 1990s (Table 2, Fig. 5). At IZO and RPB, this divergence lessens during the late summer and autumn
 623 months. At ZEP, the divergence is greatest during summertime and diminishes during other seasons of the
 624 year. At BHD, the ~2‰ $\delta^{13}\text{C}_{\text{CO}}$ offset appears consistent across all months (Fig. 5).

625

626 An obvious contribution to the negative $\delta^{13}\text{C}_{\text{CO}}$ shift is ¹³C-depleted CO from CH₄ oxidation, which must
 627 have increased due to globally increasing CH₄ mole fractions over the last several decades (Lan et al., 2022).
 628 Based on Equation 7, the increase in CO from OH-initiated CH₄ oxidation, $\Delta\text{CO}_{\text{CH}_4}$, scales directly with
 629 the increase in CH₄, ΔCH_4 , and can be calculated as:

630

$$\Delta\text{CO}_{\text{CH}_4} = \frac{k_{\text{CH}_4+\text{OH}}}{k_{\text{CO}+\text{OH}}} (\Delta\text{CH}_4)(x) = 4 \text{ ppb} \quad (8)$$



631

632 where $k_{\text{CH}_4+\text{OH}} = 5.16 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at global average temperature $T=288 \text{ K}$, $k_{\text{CO}+\text{OH}} = 2.04 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at
633 average tropospheric pressure $P_{\text{atm}}=0.6 \text{ atm}$, $\Delta\text{CH}_4 = \text{CH}_{4,2025} - \text{CH}_{4,1995} = 1930-1750 \text{ ppb} = 180 \text{ ppb}$, and x
634 $= 0.9$ is an assumed yield for CO formation from CH₄ taking into account loss due to deposition of HCHO.
635 Holding the remaining inventory constant at 110 ppb and -27‰, an additional production of 4 ppb CO from
636 increased CH₄ with $\delta^{13}\text{C}_{\text{CO}}$ signature = -52‰, would shift the background $\delta^{13}\text{C}_{\text{CO}}$ by 0.8‰ according to:
637

$$\delta^{13}\text{C}_{\text{CO},2025} = \frac{(110 \text{ ppb})(-27\text{‰}) + (4 \text{ ppb})(-52\text{‰})}{114 \text{ ppb}} = -27.8\text{‰} \quad (9)$$

638

639 The increase of the CH₄-derived CO fraction is also incorporated into the emissions inventories. Due to the
640 strongly depleted $\delta^{13}\text{C}_{\text{CO}}$ source signature (-52‰) and high emission rate, CO from CH₄ oxidation
641 dominates the total $\delta^{13}\text{C}_{\text{CO}}$ source mix in both hemispheres (Fig. 9). Over two decades (1995-1999 vs 2015-
642 2019), the average percent contribution to the total emission inventory shows a 2.8% and 2.4% increase in
643 the Northern and Southern Hemisphere, respectively (Fig. 6a). Globally, this imparts a depleting effect on
644 the combined $\delta^{13}\text{C}_{\text{CO}}$ source mix.

645

646 Following CH₄ oxidation, the model output shows that the Northern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$ source mix is most
647 sensitive to CO from NMVOC oxidation and fossil fuel combustion due to their large emission rates. In the
648 model, average NMVOC oxidation emission exhibits a 0.8% increase over two decades, further lowering
649 the $\delta^{13}\text{C}_{\text{CO}}$ source mix. The same timeframe exhibits a 2.4% decrease in the average percent contribution
650 from fossil fuel combustion CO (Fig. 6a), linked to the introduction of catalytic converters on motor
651 vehicles and stricter air quality regulations beginning in the 1970s. This shift counteracts the depleting
652 influence of enhanced hydrocarbon oxidation to some degree (Fig. 9a). Biomass burning emissions are
653 another important contributor, though they are highly variable year-to-year (e.g. 2015-2019 average may
654 not be indicative of 2023-2024). The Northern Hemisphere emission inventories used as an input to the
655 model show an average 1.0% decreasing contribution from biomass burning over 20 years, with emissions
656 actually increasing during June, July and August (Fig. 6a, 7a). This trend also offsets the depletion from
657 hydrocarbon oxidation, with the strongest effect during the summer months. Other emission source
658 categories (agricultural waste burning and direct vegetation emissions) do not exhibit significant changes.
659 The overall impact of these changes in the inventory is a 0.7‰ decrease in the combined modeled Northern
660 Hemisphere $\delta^{13}\text{C}_{\text{CO}}$ source mix, from -33.8 to -34.5‰ over two decades (Fig. 9a). Figure 8 shows the
661 seasonal cycle of this shift. Interestingly, no shift is evident during July and August due to enhanced
662 biomass burning emissions (Fig. 8a).



663

664 The modeled Southern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$ source mix is most sensitive to increasing CH_4 oxidation,
665 followed by NMVOC oxidation, which has decreased 1.0% in relative contribution since the 1990's (Fig.
666 9b). This counteracts the strong depleting effect from CH_4 oxidation. The Southern Hemisphere also shows
667 sensitivity to biomass burning emissions, which show a declining trend on average, with short-term
668 increases during the warmer months of November, December and January (Fig. 7b). Taken together, the
669 combined modeled Southern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$ source mix has decreased 0.6‰, from -34.9 to -35.5‰,
670 over two decades. The depletion is strongest from May-October and weaker during the remaining months
671 of the year (Fig. 8c).

672

673 3.3.3 Oxygen Isotopic Composition

674 Seasonal variation in $\delta^{18}\text{O}_{\text{CO}}$ is similarly related to the ratio of the ^{18}O -depleted (e.g. photochemical
675 production) versus ^{18}O -enriched (e.g. fossil and biomass combustion) CO sources that constitute the total
676 inventory, although it is amplified by the KIE occurring in $\text{OH}+\text{CO}$ (i.e. preferential removal of C^{18}O). For
677 instance, winter months are characterized by higher accumulation of combustion CO causing a net positive
678 influence on the $\delta^{18}\text{O}_{\text{CO}}$ signal, while the isotopic depletion due to the sink effect is minimal. This
679 relationship is especially evident at mid and high latitudes. Increased photochemical removal during
680 summer both lowers the relative contribution of combustion CO and preferentially removes C^{18}O , causing
681 a strong depleting effect in the observed $\delta^{18}\text{O}_{\text{CO}}$, thus explaining the broader range in seasonal extrema
682 relative to $\delta^{13}\text{C}_{\text{CO}}$.

683

684 When comparing across decades, we find that $\delta^{18}\text{O}_{\text{CO}}$ seasonality exhibits nonuniform and site-specific
685 changes, though all long-term shifts in $\delta^{18}\text{O}_{\text{CO}}$ move in phase with long-term shifts in CO mole fraction
686 (Fig. 5). Positive concurrent shifts in both CO and $\delta^{18}\text{O}_{\text{CO}}$, relative to the background, generally indicate
687 additional emissions from biomass or fossil fuel combustion sources due to their enriched source signatures.
688 For example, the 2023 and 2024 autumn CO peaks at ZEP are associated with higher $\delta^{18}\text{O}_{\text{CO}}$, and utilizing
689 satellite observations of CO, anomalous plumes reaching Svalbard can be traced to North American forest
690 fires during this time (Copernicus Sentinel-5P, 2021). Similarly, we document positive shifts in CO and
691 $\delta^{18}\text{O}_{\text{CO}}$ during the summer and autumn months at IZO. Remote sensing indicates that this location also
692 received CO-rich air during periods of enhanced North American biomass burning. Similar circumstances
693 were detected in the Southern Hemisphere at BHD during 2024. A subsampling campaign revealed
694 exceptionally high CO between August-December, with a seasonal maximum 40% larger than the average
695 for the previous decade. Remote sensing shows large swathes of CO originating in South America and



696 Africa and later being transported east to Oceania during the latter half of 2024 (Copernicus Sentinel-5P,
 697 2021; de Laat et al., 2026).

698

699 The inverse is also observed. During periods of reduced CO, the $\delta^{18}\text{O}_{\text{CO}}$ becomes more negative indicating
 700 a lower contribution of combustion CO to the total inventory. We document this pattern at ZEP and RPB
 701 during the winter and spring periods of 2023-2024, relative to the 1990s. At BHD, we also see a reduction
 702 in $\delta^{18}\text{O}_{\text{CO}}$ during the winter since 1996-2001, though this cannot be compared with CO mole fraction
 703 measurements which only began in 1999.

704

705 According to the emission inventory, fossil fuel combustion dominates the Northern Hemisphere $\delta^{18}\text{O}_{\text{CO}}$
 706 source mix signal due to the relatively high emission of this category and the enriched source signature
 707 (+23‰) (Fig. 6b, 9a). As mentioned in Section 3.3.2, the Northern Hemisphere experienced the following
 708 proportional shifts to the CO emissions inventory over twenty years (1995-1999 vs 2015-2019): 2.4%
 709 decrease from fossil combustion, 1.0% decrease from biomass burning, 2.8% increase from CH₄ oxidation,
 710 0.8% increase from NMVOC oxidation, and negligible shifts (<0.3%) from agriculture waste burning and
 711 vegetation. The result is a strong depleting effect from reduced direct combustion sources, which is slightly
 712 offset by an enrichment due to increased hydrocarbon oxidation emissions. Within this timeframe, the
 713 combined modeled $\delta^{18}\text{O}_{\text{CO}}$ source mix declined 0.6‰ on average, from +12.4 to +11.8‰.

714

715 In contrast, relatively low emissions from combustion CO sources in the Southern Hemisphere produce a
 716 $\delta^{18}\text{O}_{\text{CO}}$ source mix that is not overtly influenced by any one category (Fig. 6b, 9a). Despite 0.6% increase
 717 from fossil combustion, 1.7% decrease from biomass burning, 2.4% increase from CH₄ oxidation, 1.0%
 718 decrease from NMVOC oxidation, and negligible shifts (<0.2%) from agriculture waste burning and
 719 vegetation, the combined modeled $\delta^{18}\text{O}_{\text{CO}}$ source mix shifts only 0.1‰ lower over twenty years.

720



$^{13}\text{C}_{\text{CO}}$

	pp-m (-52‰)	pp-n (-28‰)	em-ff (-27.5‰)	em-bb (-25‰)	em-awb (-22‰)	em-veg (-25‰)	total
NH	-1.45	-0.22	+0.66	+0.25	+0.06	-0.02	-0.72
SH	-1.26	+0.30	-0.17	+0.44	+0.03	+0.02	-0.64

$^{18}\text{O}_{\text{CO}}$

	pp-m (+5‰)	pp-n (+5‰)	em-ff (+23.5‰)	em-bb (+15‰)	em-awb (+15‰)	em-veg (+15‰)	total
NH	+0.14	+0.04	-0.57	-0.15	-0.04	+0.01	-0.57
SH	+0.12	-0.05	+0.14	-0.26	-0.02	-0.01	-0.08

Table 3 | Per mil shift to combined $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ source mix (Fig. 9) by emission category (pp-m = methane oxidation; pp-n = NMVOC oxidation; em-ff = fossil fuel; em-awb = agriculture waste burning; em-veg = vegetation; em-bb = biomass burning) between 1995-1999 and 2015-2019 average; source mixes are calculated as the product of percent contribution and associated average source signature (in parentheses below emission abbreviations)

4 Discussion

Emission inventories help approximate average hemispheric source mixes, although the observed $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ are subject to a complex mix of factors including atmospheric transport at varying scales, photochemical removal KIEs, unidentified CO emissions or removal processes, and variation in local isotopic source signatures. It's also important to note that the CO emissions inventories obtained from the model used here were only available until 2020, so direct comparisons cannot be made to 2023-2024 when new measurements were gathered. Still, examination of the emission inventories offers a framework for interpreting long-term shifts in isotopic observations.

Considering only $\delta^{13}\text{C}_{\text{CO}}$, the well documented increase in atmospheric CH_4 over the past decades has increased the relative share of CO produced by $\text{CH}_4 + \text{OH}$ oxidation. Since this category has a very ^{13}C -depleted isotopic source signature (-52‰), it leads to a negative trend in atmospheric $\delta^{13}\text{C}_{\text{CO}}$. However, the magnitude of influence is underestimated by the source changes derived from the model inventories. Specifically, we observe a -2‰ $\delta^{13}\text{C}_{\text{CO}}$ shift at all sampling stations between 1996-2024, while the model suggests an average shift of -0.7‰ and -0.6‰ over two decades for the Northern and Southern Hemispheres, respectively. Thus, other changes must have occurred to explain our observations.



745

746 In the North, one possibility is that the discrepancy arises from inflated estimates of fossil CO emissions in
 747 recent years. According to the model, the relative share of CO from fossil fuel combustion has decreased
 748 by 2.4% between the two periods (i.e. 1995-1999 versus 2015-2019). Reducing this category further would
 749 increase the relative share of ^{13}C -depleted CO from CH_4 oxidation, which would further decrease the total
 750 $\delta^{13}\text{C}_{\text{CO}}$ source mix shift towards the observed value of -2‰. As CO from fossil fuel combustion is the most
 751 ^{18}O -enriched source, decreasing the emission from this source category would also lessen the discrepancy
 752 between the observations and the $\delta^{18}\text{O}_{\text{CO}}$ source mix shift in the model. For example, averaging the observed
 753 $\delta^{18}\text{O}_{\text{CO}}$ changes at ZEP, IZO and RPB yields a -0.82‰ North Hemisphere shift, while the changes that are
 754 presently included in the inventories point to -0.57‰ shift. This explanation is consistent with the strong
 755 dampening of CO seasonality in the Northern Hemisphere, as wintertime CO mole fraction is particularly
 756 sensitive to fossil combustion emissions.

757

758 Another possible but highly uncertain factor of the $\delta^{13}\text{C}_{\text{CO}}$ budget is the contribution of CO produced by Cl
 759 + CH_4 oxidation. Due to its extremely ^{13}C -depleted source signature (lower than -100‰), small amounts
 760 can disproportionately alter $^{13}\text{C}_{\text{CO}}$ source mixes. Thus, an increasing role of chlorine in the oxidation of CH_4
 761 may contribute to the observed -2‰ shift in $\delta^{13}\text{C}_{\text{CO}}$ since the 1990s. The emission inventories do not
 762 consider CO from chlorine oxidation, but we test the effect in the following section.

763

764 Figure A1 shows how multi-decadal shifts in the $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ source mixes change when the modeled
 765 2015-2019 CO emissions from fossil combustion and Cl + CH_4 are covaried. In this test, the fossil emission
 766 category is varied between 10-100% of the 2015-2019 average and an additional contribution of CO from
 767 Cl + CH_4 varies between 1-9% of the average OH + CH_4 emission for the same years. The observed
 768 Northern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$ shift (-1.43‰ to -2.43‰) can be explained by reducing fossil fuel related
 769 emissions by 15-70% or by increasing Cl + CH_4 by 1.5-7% of the OH sink, or by a linear combination of
 770 these changes to both categories.

771

772 Changes in the tropospheric Cl sink are highly uncertain. Despite reductions in total atmospheric chlorine
 773 prompted by the Montreal Protocol, recent increases in anthropogenic emissions of very short-lived Cl
 774 containing compounds, namely dichloromethane (CH_2Cl_2), have been documented and could lead to an
 775 increase in this extremely depleted source of CO (Hossaini et al., 2017; Raymond et al., 2026). Increases
 776 in dust-driven production of tropospheric Cl have also been proposed. Changes near the upper range of our
 777 sensitivity study (1.5-7%) are unlikely, because this would also lead to strong changes in the carbon isotopic
 778 composition of CH_4 (van Herpen et al., 2023). Conversely, underestimated reductions in CO from fossil



779 fuel combustion near the low end of our sensitivity study (~15%) are likely within the uncertainties of
780 present emission inventories, given the large range of emission factors dependent on fuel and engine type,
781 combustion efficiency, and post-emission mitigation measures (Popa et al., 2014; Naus et al., 2018; Kato
782 et al., 1999; Vimont et al., 2017). Considering the observations of $\delta^{18}\text{O}_{\text{CO}}$, the strong negative shifts at ZEP
783 and RPB (-1.64‰ and -2.12‰, respectively) cannot be explained unless the emission of fossil CO is
784 reduced in our sensitivity study. Taken together, our isotope observations suggest the reduction in CO from
785 fossil fuel combustion since the 1990s likely proceeded faster than represented in the emission inventories.
786 This is consistent with findings from Zheng et al. (2019).

787

788 The station IZO has a distinctly different trend (i.e. positive) in $\delta^{18}\text{O}_{\text{CO}}$, compared to the other two Northern
789 Hemisphere stations, suggesting different source changes. Exceptionally active wildfire seasons were
790 documented in Canada for both 2023 and 2024, with 2023 surpassing historical records of burnt area, carbon
791 emitted, and PM_{2.5} transport during a given year (Copernicus Atmosphere Monitoring Service, 2022;
792 Pelletier et al., 2024; Zhang et al., 2025). Increased contributions from boreal biomass burning, which emits
793 CO with relatively high $\delta^{18}\text{O}_{\text{CO}}$, could explain the differing trend at IZO. This station is situated on a
794 mountain plateau at 2373 m ASL, and likely captured high-altitude, long-range fire emissions during 2023
795 and 2024. This is consistent with lowered CO mole fraction seasonality as observed in the ISAMO and
796 NOAA-GML samples. Whereas a clear summer minimum was observed in the late 1990s, the seasonal
797 cycle is much flatter in our new dataset, likely reflecting higher CO contributions from biomass burning
798 during the hot and dry summer season. Increasing wildfire activity is expected as global mean temperatures
799 continue to rise and regional humidity drops (Wang et al., 2025; Barnes et al., 2023; IPCC). Aside from the
800 clear risks to human and ecosystem health, this trend raises concerns about evolving CO patterns and the
801 indirect effects on atmospheric chemistry.

802

803 For the Southern Hemisphere station BHD, the observed $\delta^{18}\text{O}_{\text{CO}}$ shift is stronger than derived from both
804 the baseline model inventory changes and the scenario presented in Figure A1 (covarying fossil and $\text{Cl} +$
805 CH_4 emissions). Due to the substantially different CO emission breakdown in the Southern Hemisphere
806 relative to the North, the categories of CO from $\text{OH} + \text{CH}_4$ oxidation, NMVOC oxidation, and biomass
807 burning also act as substantial levers on the combined $\delta^{18}\text{O}_{\text{CO}}$ source mix. Because CO from $\text{OH} + \text{CH}_4$ is
808 relatively well quantified, we investigate how additional changes in the NMVOC and biomass burning
809 emissions would affect the hemispheric isotope source mix.

810

811 In Figure A2, biomass burning CO is decreased between 10-100% of the 2015-2019 average and NMVOC
812 oxidation is increased from 100-190% of the average for the same years. Based on this evaluation, the



813 observed isotopic shifts at BHD (-1.9‰ $\delta^{13}\text{C}_{\text{CO}}$ and -1.5‰ $\delta^{18}\text{O}_{\text{CO}}$) can only be reproduced when CO from
814 biomass burning is dramatically reduced by 70-90% and CO from NMVOC oxidation is increased up to
815 20% from the 2015-2019 average. These changes lower the contribution of CO from biomass burning by
816 an order of magnitude in Tg CO (~ 100 Tg), which is not consistent with GFED5 satellite-based estimates.
817 For example, the five-year biomass burning emission average following the 2015-2019 period (until but
818 not including 2024) is consistently only 10% lower than the 2015-2019 average, primarily due to a large
819 peak in the latter half of 2015 (van der Werf et al., 2025). As mentioned above, $\delta^{13}\text{C}_{\text{CO}}$ is sensitive to
820 changes in the tropospheric Cl sink. Assuming a reasonable 10% decrease in CO emissions from biomass
821 burning, then our results for $\delta^{13}\text{C}_{\text{CO}}$ would require Cl + CH₄ to increase to at least 11% of the total OH sink,
822 which is excessive. In this same scenario, the $\delta^{18}\text{O}_{\text{CO}}$ shift can only be explained by increasing CO from
823 NMVOC oxidation by 60%, which is also extreme though multiple studies have concluded that NMVOC
824 emissions in the Southern Hemisphere atmosphere are underestimated by models (Rocco et al., 2021;
825 Ferracci et al., 2024; Wohl et al., 2023). Thus, the observed shift in CO isotopic composition at BHD would
826 require unrealistically large changes in the emission inventories utilized here. We conclude that data from
827 a single remote station is not sufficient to constrain the Southern Hemisphere emissions robustly.

828

829 5 Conclusion

830 Atmospheric monitoring has revealed substantial and geographically diverse changes in the seasonality of
831 CO within three decades. The most dramatic change has occurred in the extra-tropical Northern
832 Hemisphere where the average winter maximum has decreased approximately 20% between 1995 to
833 2025, in effect flattening the seasonal cycle. Above average summertime CO emissions, which occurred
834 for example during 2023, further contribute to this loss in amplitude. In the Southern Hemisphere, CO
835 mole fractions have remained relatively stable since the 1990s, apart from 2020 and 2024 which showed
836 the highest summer and wintertime CO on record, respectively. In this study, we explore the utility of
837 atmospheric $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ observations in constraining these long-term changes to the global CO
838 budget.

839

840 Our findings from the Northern Hemisphere strongly indicate that wintertime CO has lowered due to
841 decreasing CO emissions from fossil fuels. Stricter air quality standards have forced the implementation
842 of catalytic converters on motor vehicles and adoption of cleaner burning fuel, such as natural gas, for
843 energy requirements across the United States, the European Union and Eastern China. This is a promising
844 example of how technology and policy have aligned to address an atmospheric pollutant, in this case one
845 that acts as an indirect greenhouse gas through competing reactions with CH₄ and can contribute to



846 hazardous ground-level ozone. The results presented here even show that reductions in fossil-derived CO
847 emissions may have been larger than predicted by the model inventories used, and that further monitoring
848 of the isotopic composition of CO could assist in improved emission quantification. At the same time, our
849 results serve as a reminder that atmospheric CH₄ continues to increase, as this trend disproportionately
850 affects the $\delta^{13}\text{C}_{\text{CO}}$, and that coordinated steps across industry, policy, and technology will be necessary to
851 address this potent greenhouse gas (UNEP and Climate and Clean Air Coalition, 2021; National
852 Academies of Sciences, Engineering, and Medicine, 2024).

853

854 The findings from the Southern Hemisphere pose a unique challenge, as long-term CO isotope monitoring
855 has only been available in one location and the CO emissions inventories used are spatially integrated. It
856 is therefore important to establish and maintain routine air sampling at numerous locations, ideally with
857 enhanced coverage across the latitudinal gradient of CO. This is feasible given the advances in
858 continuous-flow CO isotope analysis, which has allowed the ISAMO program to collect a large amount
859 of air samples and promptly measure them.

860

861 Lastly, extreme wildfire seasons are frequently reflected in the presented datasets in recent years, for
862 example Australia in 2020, Canada in 2023, and South American and Africa in 2024. These events show
863 clear, and sometimes unprecedented, perturbations to the seasonal cycle of CO at background monitoring
864 sites. Numerous studies, at both regional and global scales, have shown that anthropogenic climate
865 change has increased the likelihood of extreme fire events and future warming will intensify this risk
866 (Abatzoglou et al., 2025; Burton et al., 2024; Jolly et al., 2015; Kirchmeier-Young et al., 2024; van
867 Oldenborgh et al., 2021). Therefore, CO emission estimates aided by CO isotopic analysis may become
868 more uncertain due the large spread in $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ source signatures associated with biomass
869 burning. The continuation of tropospheric CO mole fraction monitoring and remote sensing of wildfire
870 temperature and total column CO will be greatly beneficial to isotopic evaluations, as these approaches
871 inform the geographic distribution of vegetation that is combusted (i.e. C3 vs C4) and the temperature of
872 combustion (i.e. smoldering vs flaming).



Figures

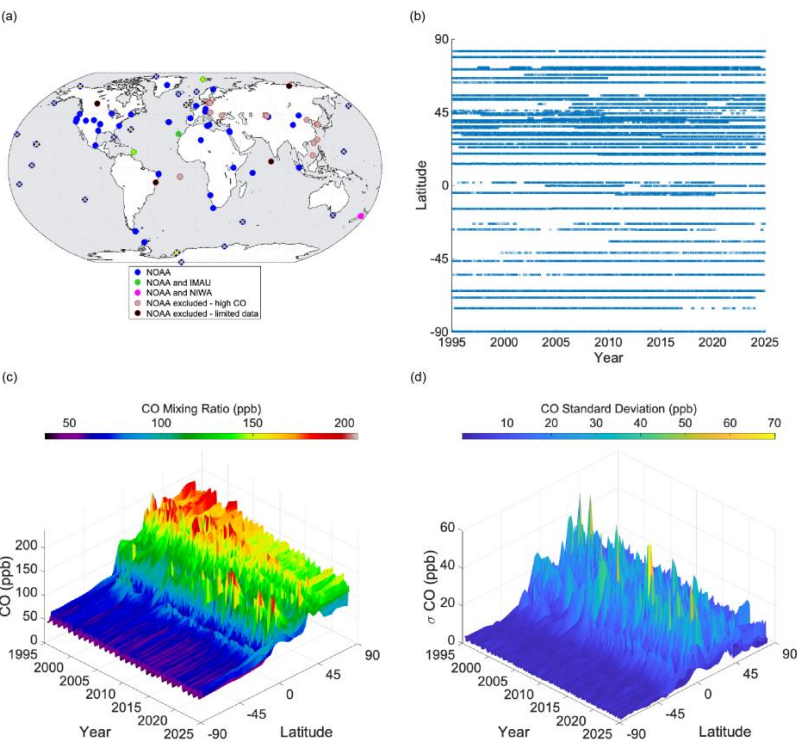


Figure 1 | (a) Sites from the NOAA-GML monitoring network represented in panels c and d; Marine Boundary Layer (MBL) sites are marked with a yellow 'x'; Sites showing evidence of elevated CO from nearby sources (AMY, ASC, BAL, BSC, DSI, HUN, KDZ, LLN, SDZ, TAP, TPI) have been removed; Sites with temporally limited observations (ABP, LLB, MBC, KCO, TIK) have been removed; (b) Sampling frequency of CO monitoring sites represented in panel a; (c) interpolated moving mean of NOAA-GML CO observations (window size = 30 days, centered on each observation); (d) interpolated moving standard deviation of NOAA-GML CO observations (window size = 30 days, centered on each observation)

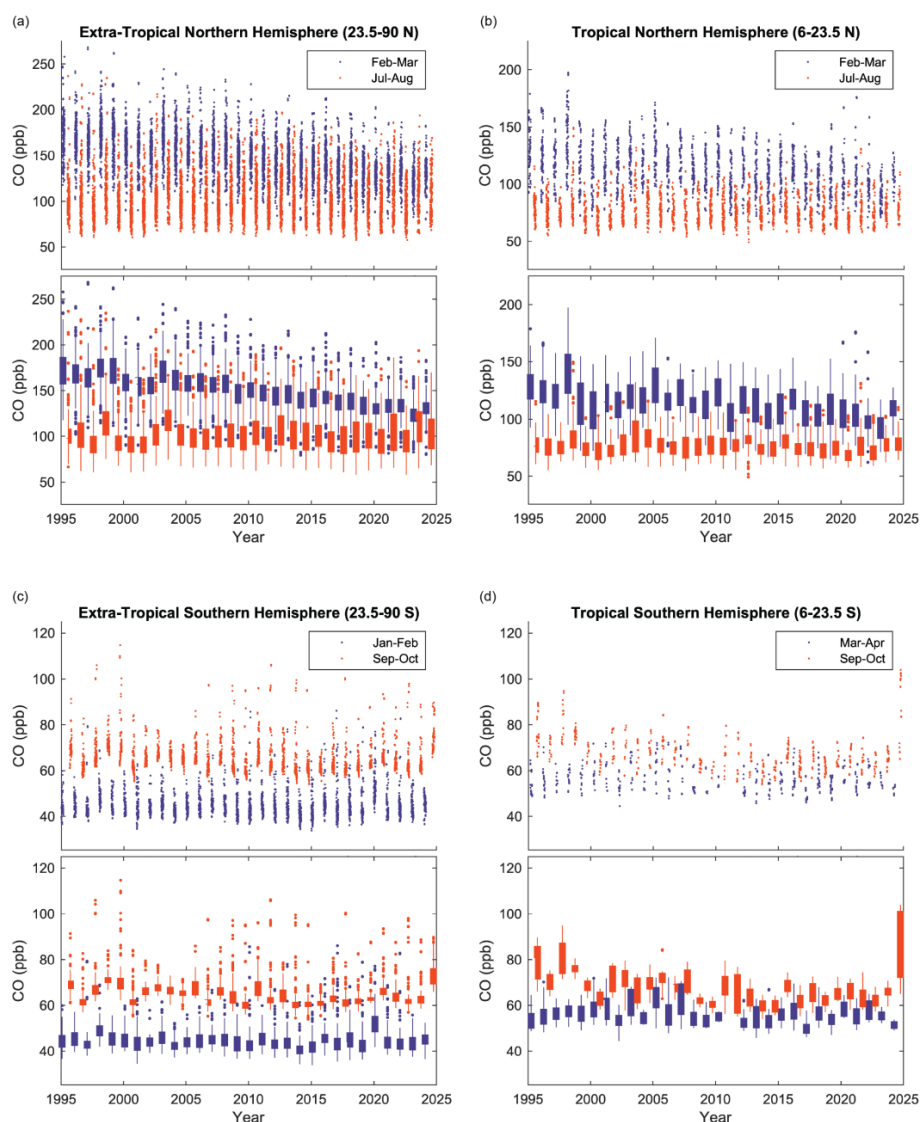
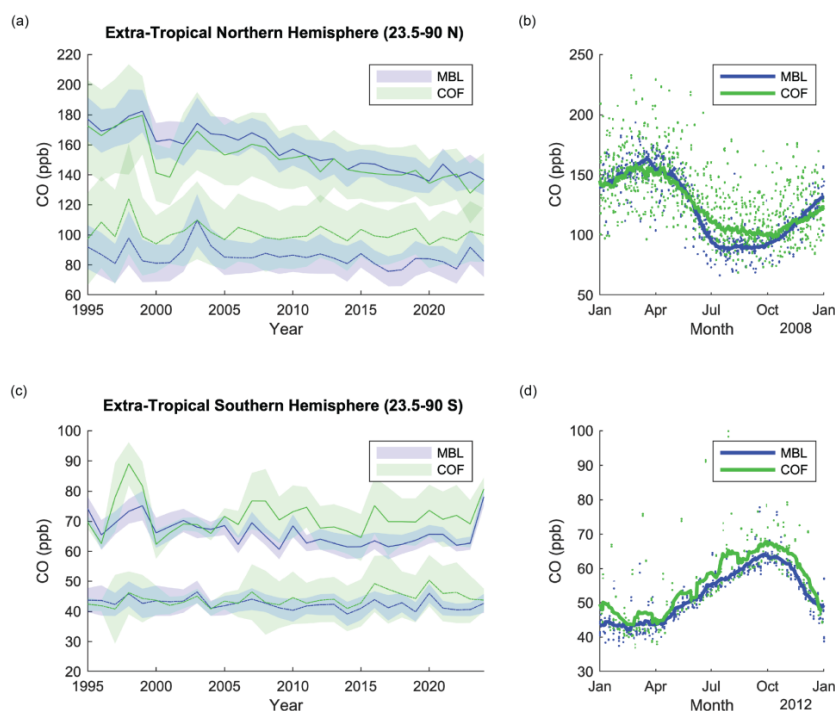


Figure 2 | For panels a-d, upper subplots show NOAA-GML CO observations grouped by 60-day windows centered on expected seasonal maxima (purple in Northern Hemisphere, orange in Southern Hemisphere) and seasonal minima (orange in Northern Hemisphere, purple in Southern Hemisphere); lower subplots show boxplots for extrema data groupings where box edges extend to the 25th and 75th percentiles, whiskers extend to furthest data not considered outliers, and outliers are marked by circles; Analysis is shown for the following latitude bands **(a)** extra-tropical Northern Hemisphere (23.5-90 N), **(b)** tropical Northern Hemisphere (6-23.5 N), **(c)** extra-tropical Southern Hemisphere (23.5-90 S), and **(d)** tropical Southern Hemisphere (6-23.5 S); Analysis does not include data from sites showing evidence of elevated CO from nearby sources (AMY, ASC, BAL, BSC, DSI, HUN, KDZ, LLN, SDZ, TAP, TPI) or from sites with temporally limited observations (ABP, LLB, MBC, KCO, TIK); Analysis does not include observations with first position (i.e. rejection) or second position (i.e. non-background) flags



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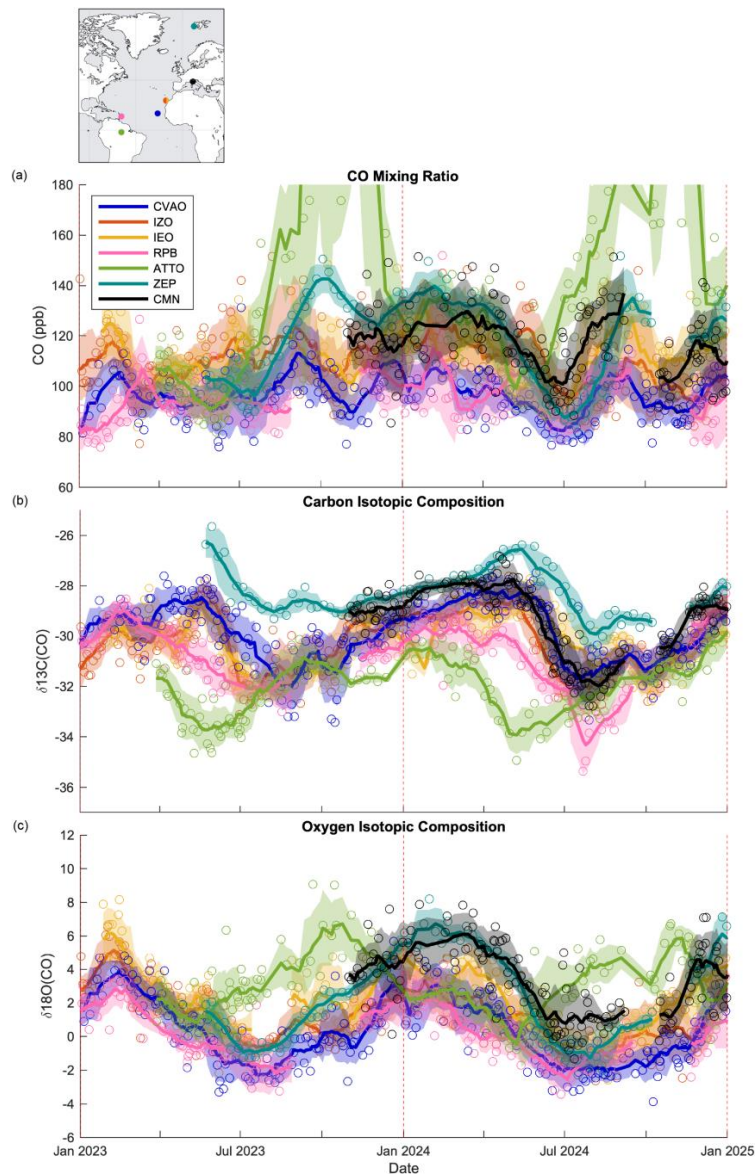
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Figure 3 | Comparison between Marine Boundary Layer (MBL) and Continental Outflow (COF) sites in the NOAA-GML network; Annual minima and maxima (solid line) of the moving mean (window size = 30 days, centered on each observation) of MBL vs COF aggregated data in the (a) extra-tropical Northern Hemisphere (ETNH) and (c) extra-tropical Southern Hemisphere (ETSH) between 1995-2024; Shading corresponds to the yearly average standard deviation of aggregated data; Panels (b) and (d) show examples of the aggregated data and 30-day moving mean for a randomized year



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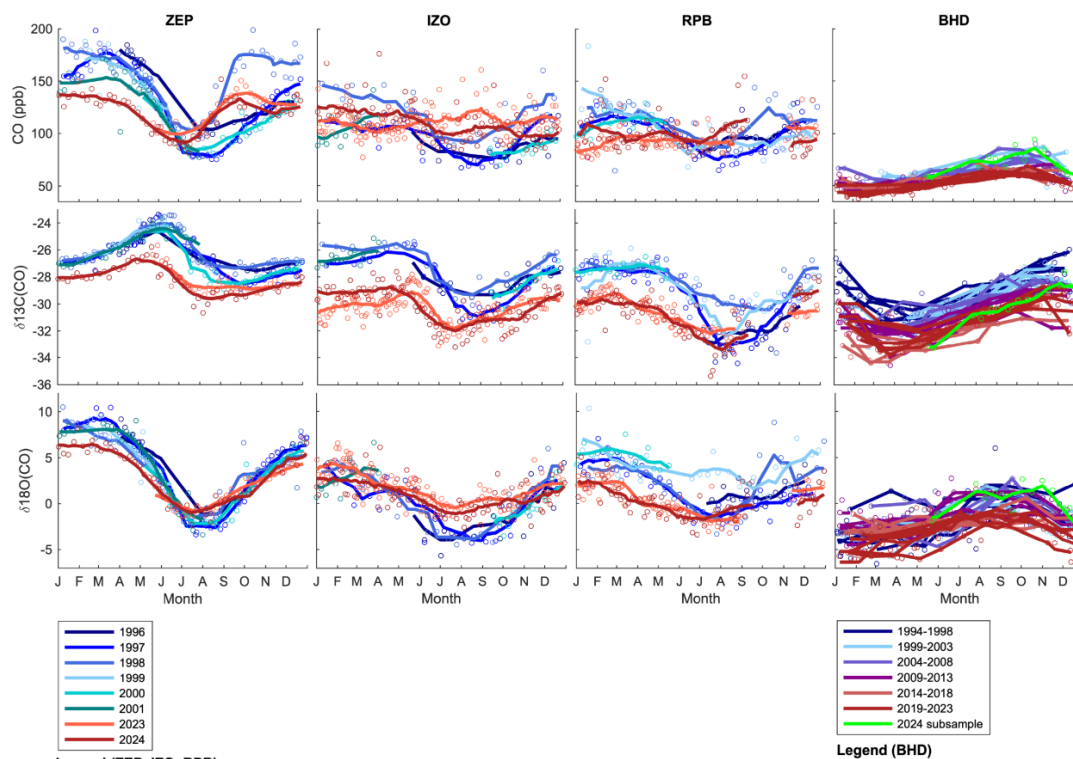
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Figure 4 | Timeseries observations of CO (a) mole fraction, (b) carbon isotopic composition ($\delta^{13}C$), and (c) oxygen isotopic composition ($\delta^{18}O$) for the stations CVAO (dark blue), IZO (red), IEO (yellow), RPB (pink), ATTO (green), ZEP (light blue) and CMN (black) during 2023-2024; Open circle markers indicate measurement values; Solid lines indicate moving mean (window size = 30 days, centered on each observation); Colored shading delineates moving standard deviation (window size = 30 days, centered on each observation); With the exception of ATTO, non-background CO observations have been removed



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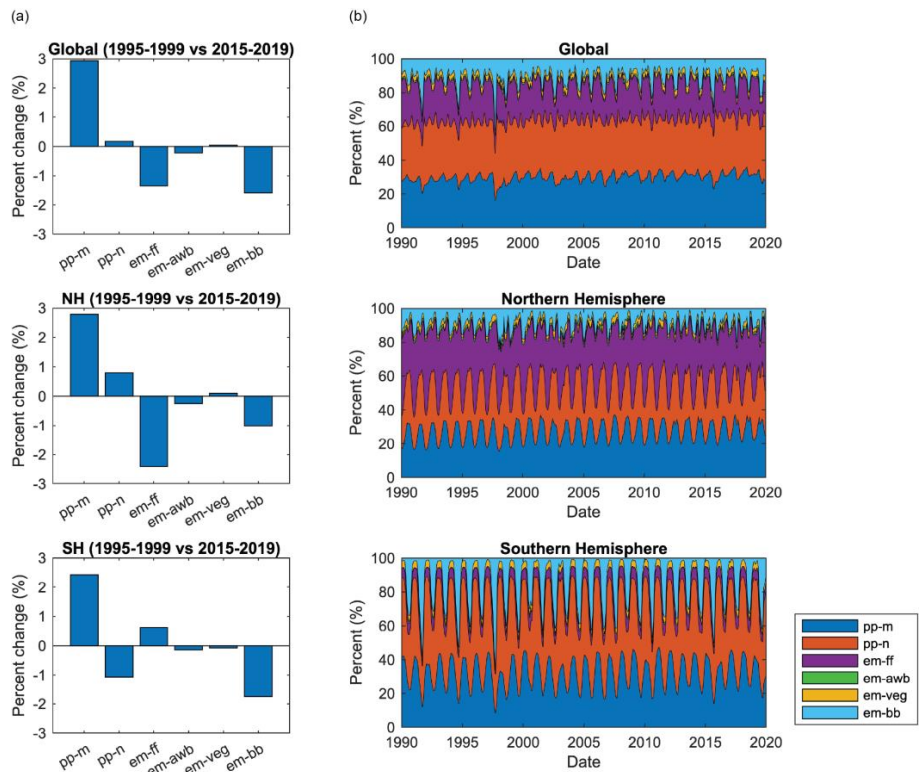


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Figure 5 | Comparisons of CO mole fraction, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ between 1996-2001 (blues) and 2023-2024 (reds) for the stations ZEP, IZO and RPB; A continuous comparison from 1994 through 2024 is made on CO, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ observations for the station BHD (note: no CO mole fraction data is available for the timeframe 1994-1998); Open circle markers indicate measurement values; Solid lines indicate moving mean (window size = 60 days, centered on each observation)



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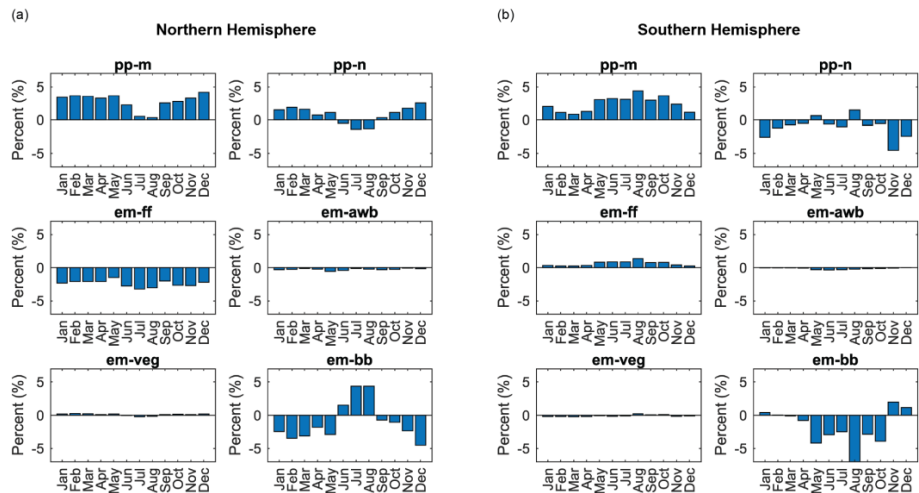


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Figure 6 | (a) Percent change in relative contribution of CO emission categories (pp-m = methane oxidation; pp-n = NMVOC oxidation; em-ff = fossil fuel; em-awb = agriculture waste burning; em-veg = vegetation; em-bb = biomass burning) between 1995-1999 average and 2015-2019 average; **(b)** Relative contribution of various CO emission categories to total CO emission inventory from 1990-2019



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Figure 7 | Monthly breakdown of total percent changes depicted in Figure 6a for **(a)** Northern Hemisphere and **(b)** Southern Hemisphere

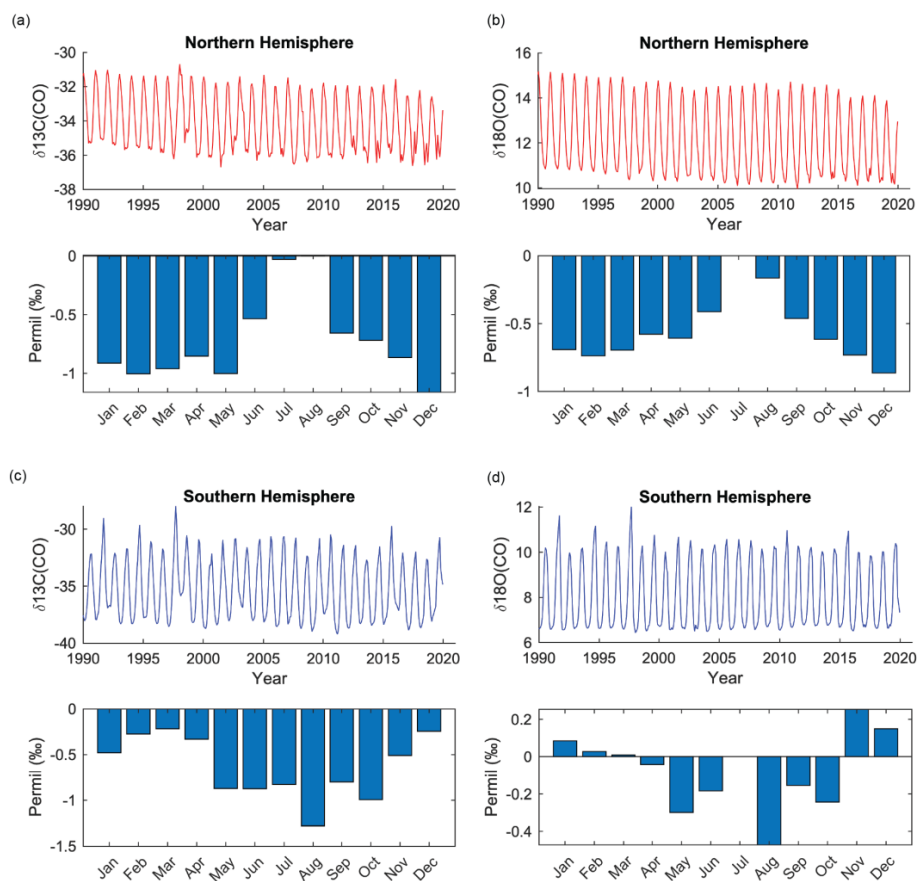


Figure 8 | Upper panels show the 1990-2020 total isotopic source mix timeseries for (a) Northern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$, (b) Northern Hemisphere $\delta^{18}\text{O}_{\text{CO}}$, (c) Southern Hemisphere $\delta^{13}\text{C}_{\text{CO}}$, and (d) Southern Hemisphere $\delta^{18}\text{O}_{\text{CO}}$; Lower panels show the monthly breakdown of per mil shift in total isotopic source mix between 1995-1999 average versus 2015-2019 average

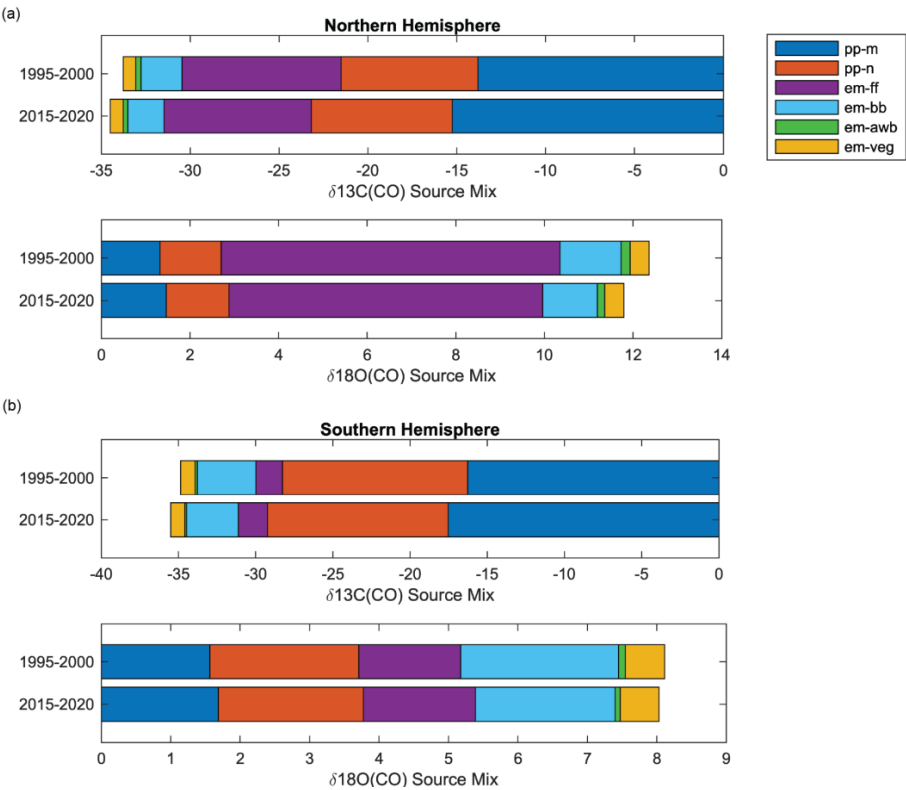


Figure 9 | Contribution of each CO emission category to the combined source mix for (a) $\delta^{13}\text{C}_{\text{CO}}$ and (b) $\delta^{18}\text{O}_{\text{CO}}$, calculated as the product of percent contribution and associated average source signature



Appendix A: Figures

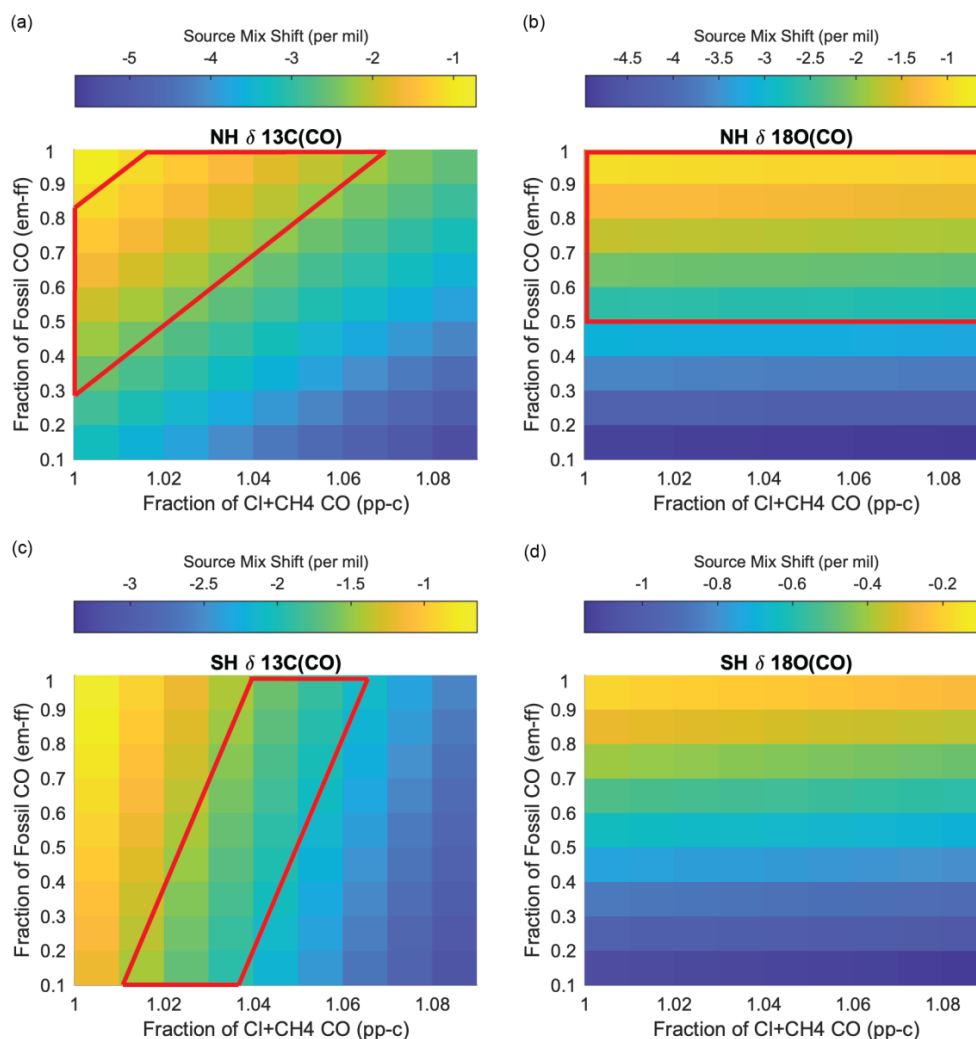


Figure A1 | Shift in 1995-1999 versus 2015-2019 source mix isotopic composition for (a,b) Northern Hemisphere and (c,d) Southern Hemisphere when the 2015-2019 CO inventory is adjusted for a decrease in CO from fossil fuel combustion and an increase in CO from Cl + CH₄ oxidation; area outlined in red represents the observed shift with uncertainty

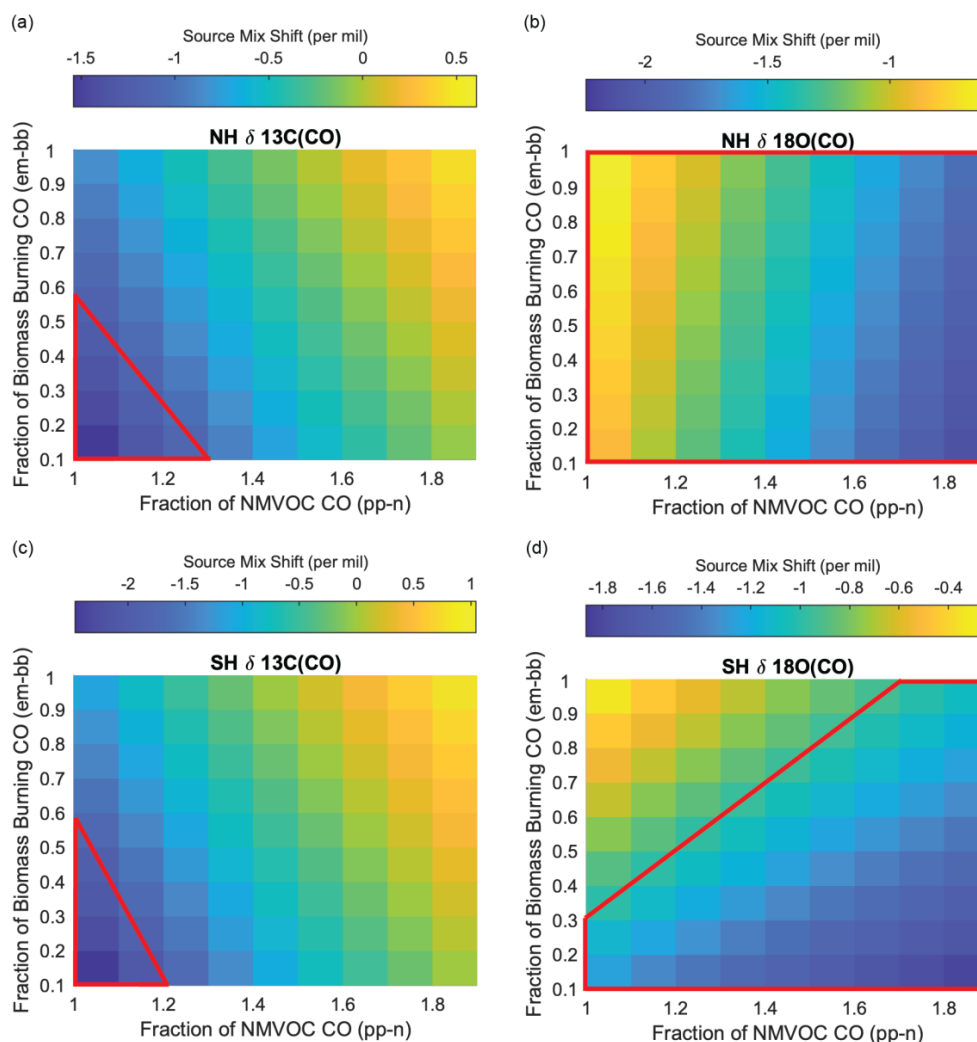


Figure A2 | Shift in 1995-1999 versus 2015-2019 source mix isotopic composition for (a,b) Northern Hemisphere and (c,d) Southern Hemisphere when the 2015-2019 CO inventory is adjusted for a decrease in CO from biomass burning and an increase in CO from NMVOC oxidation; area outlined in red represents the observed shift with uncertainty



Data Availability. The CO isotope dataset from Utrecht University can be found at <https://doi.org/10.18160/ZFZ1-Z7WD> (pending upload). The CO isotope dataset from Earth Science New Zealand is available upon request. The NOAA-GML CO dataset is available to the public through the official government website.

Author Contributions. CAB wrote this article. TR, MMJWvH, SG, XY, and MSJ contributed to and reviewed the article. CAB and CvdV measured the CO isotope data at UU. BvdK managed logistics for the ISAMO network. HT, SZ, AJ, HM, AB, NP, IB, JA, DY, PS, HvA, SM, PS, SMP, OH, and CLM supported whole air sampling in the field. PS, RM, and SN measured the CO isotope data at Earth Sciences New Zealand. GP, AD, and IV maintain the NOAA-GML CO monitoring network.

Competing Interests. The authors declare that they have no conflict of interest.

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References

- Abatzoglou, J. T., Kolden, C. A., Cullen, A. C., Sadegh, M., Williams, E. L., Turco, M., & Jones, M. W. (2025). Climate change has increased the odds of extreme regional forest fire years globally. *Nature Communications*, 16(1), 6390. <https://doi.org/10.1038/s41467-025-61608-1>
- Affek, H. P., & Yakir, D. (2003). Natural abundance carbon isotope composition of isoprene reflects incomplete coupling between isoprene synthesis and photosynthetic carbon flow. *Plant Physiology*, 131(4), 1727–1736. <https://doi.org/10.1104/pp.102.012294>
- Anderson, R. S., Huang, L., Iannone, R., Thompson, A. E., & Rudolph, J. (2004). Carbon Kinetic Isotope Effects in the Gas Phase Reactions of Light Alkanes and Ethene with the OH Radical at 296 ± 4 K. *The Journal of Physical Chemistry A*, 108(52), 11537–11544. <https://doi.org/10.1021/jp0472008>



- Anderson, R. S., Iannone, R., Thompson, A. E., Rudolph, J., & Huang, L. (2004). Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K. *Geophysical Research Letters*, 31(15). <https://doi.org/10.1029/2004GL020089>
- Andreae, M. O., Acevedo, O. C., Araújo, A., Artaxo, P., Barbosa, C. G. G., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Cintra, B. B. L., Da Silva, N. F., Dias, N. L., Dias-Júnior, C. Q., Ditas, F., Ditz, R., Godoi, A. F. L., Godoi, R. H. M., Heimann, M., Hoffmann, T., ... Yáñez-Serrano, A. M. (2015). The Amazon Tall Tower Observatory (ATTO): Overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols. *Atmospheric Chemistry and Physics*, 15(18), 10723–10776. <https://doi.org/10.5194/acp-15-10723-2015>
- Barnes, C., Boulanger, Y., Keeping, T., Gachon, P., Gillett, N., Boucher, J., Roberge, F., Kew, S., Haas, O., Heinrich, D., Vahlberg, M., Singh, R., Elbe, M., Sivanu, S., Arrighi, J., van Aalst, M., Otto, F., Zachariah, M., Krikken, F., & Wang, X. (2023). *Climate change more than doubled the likelihood of extreme fire weather conditions in Eastern Canada*. <https://doi.org/10.25561/105981>
- Bègue, N., Baron, A., Krysztofiak, G., Berthet, G., Kloss, C., Jégou, F., Khaykin, S., Ranaivombola, M., Millet, T., Portafaix, T., Duflo, V., Keckhut, P., Vèrèmes, H., Payen, G., Sha, M. K., Coheur, P.-F., Clerbaux, C., Sicard, M., Sakai, T., Querel, R., Liley, B., Smale, D., Morino, I., Uchino, O., Nagai, T., Smale, P., Robinson, J., and Bencherif, H.: Evidence of a dual African and Australian biomass burning influence on the vertical distribution of aerosol and carbon monoxide over the southwest Indian Ocean basin in early 2020, *Atmos. Chem. Phys.*, 24, 8031–8048, <https://doi.org/10.5194/acp-24-8031-2024>, 2024
- Bender, M. M. (1971). Variations in the $^{13}\text{C}/^{12}\text{C}$ ratios of plants in relation to the pathway of photosynthetic carbon dioxide fixation. *Phytochemistry*, 10(6), 1239–1244. [https://doi.org/10.1016/S0031-9422\(00\)84324-1](https://doi.org/10.1016/S0031-9422(00)84324-1)
- Bergamaschi, P., Brenninkmeijer, C. a. M., Hahn, M., Röckmann, T., Scharffe, D. H., Crutzen, P. J., Elansky, N. F., Belikov, I. B., Trivett, N. B. A., & Worthy, D. E. J. (1998). Isotope analysis based source identification for atmospheric CH_4 and CO sampled across Russia using the Trans-Siberian railroad. *Journal of Geophysical Research: Atmospheres*, 103(D7), 8227–8235. <https://doi.org/10.1029/97JD03738>
- Bergamaschi, P., Hein, R., Brenninkmeijer, C. A. M., & Crutzen, P. J. (2000). Inverse modeling of the global CO cycle: 2. Inversion of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios. *Journal of Geophysical Research: Atmospheres*, 105(D2), 1929–1945. <https://doi.org/10.1029/1999JD900819>
- Bräunlich, M. (2000). *Study of atmospheric carbon monoxide and methane* [Dissertation]. <https://doi.org/10.11588/heidok.00000934>
- Brenninkmeijer, C. A. M. (1991). Robust, high-efficiency, high-capacity cryogenic trap. *Analytical Chemistry*, 63(11), 1182–1184. <https://doi.org/10.1021/ac00011a024>
- Brenninkmeijer, C. A. M. (1993). Measurement of the abundance of ^{14}CO in the atmosphere and the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric CO with applications in New Zealand and Antarctica. *Journal of Geophysical Research: Atmospheres*, 98(D6), 10595–10614. <https://doi.org/10.1029/93JD00587>
- Brenninkmeijer, C. A. M., D. C. Lowe, M. R. Manning, R. J. Sparks, and P. F. J. vanVelthoven (1995). The ^{13}C , ^{14}C , and ^{18}O isotopic composition of CO , CH_4 , and CO_2 in the higher southern latitudes lower stratosphere, *Journal of Geophysical Research: Atmospheres*, 100(D12), 26163–26172. <https://doi.org/10.1029/95JD02528>
- Brenninkmeijer, C. A. M., & Röckmann, T. (1996). Russian Doll Type Cryogenic Traps: Improved Design and Isotope Separation Effects. *Analytical Chemistry*, 68(17), 3050–3053. <https://doi.org/10.1021/ac960208w>
- Brenninkmeijer, C. A. M., & Röckmann, T. (1997). Principal factors determining the $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric CO as derived from observations in the southern hemispheric troposphere and lowermost stratosphere. *Journal of Geophysical Research: Atmospheres*, 102(D21), 25477–25485. <https://doi.org/10.1029/97JD02291>



- 1052 Burton, C., Lampe, S., Kelley, D. I., Thiery, W., Hantson, S., Christidis, N., Gudmundsson, L., Forrest,
1053 M., Burke, E., Chang, J., Huang, H., Ito, A., Kou-Giesbrecht, S., Lasslop, G., Li, W., Nieradzick,
1054 L., Li, F., Chen, Y., Randerson, J., ... Mengel, M. (2024). Global burned area increasingly
1055 explained by climate change. *Nature Climate Change*, 14(11), 1186–1192.
1056 <https://doi.org/10.1038/s41558-024-02140-w>
- 1057 Copernicus Atmosphere Monitoring Service (2022): CAMS global biomass burning emissions based on
1058 fire radiative power (GFAS). Copernicus Atmosphere Monitoring Service (CAMS) Atmosphere
1059 Data Store, DOI: 10.24381/a05253c7 (Accessed on 26-05-2026)
- 1060 Copernicus Sentinel-5P (processed by ESA). (2021). TROPOMI Level 2 Carbon Monoxide Products.
1061 Version 02. European Space Agency. <https://doi.org/10.5270/S5P-bj3nry0>
- 1062 Coplen, T. B., Brand, W. A., Gehre, M., Gröning, M., Meijer, H. A. J., Toman, B., & Verkouteren, R. M.
1063 (2006). New guidelines for delta13C measurements. *Analytical Chemistry*, 78(7), 2439–2441.
1064 <https://doi.org/10.1021/ac052027c>
- 1065 Conny, J. M., & Currie, L. A. (1996). The isotopic characterization of methane, non-methane
1066 hydrocarbons and formaldehyde in the troposphere. *Atmospheric Environment*, 30(4), 621–638.
1067 [https://doi.org/10.1016/1352-2310\(95\)00305-3](https://doi.org/10.1016/1352-2310(95)00305-3)
- 1068 Conte, L., Szopa, S., Séférian, R., & Bopp, L. (2018). The oceanic cycle of carbon monoxide and its
1069 emissions to the atmosphere. *Biogeosciences Discussions*, 1–33. <https://doi.org/10.5194/bg-2018-410>
- 1071 Craig, H. (1957). Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric
1072 analysis of carbon dioxide. *Geochimica et Cosmochimica Acta*, 12(1), 133–149.
1073 [https://doi.org/10.1016/0016-7037\(57\)90024-8](https://doi.org/10.1016/0016-7037(57)90024-8)
- 1074 Crowley, J. N., Saueressig, G., Bergamaschi, P., Fischer, H., & Harris, G. W. (1999). Carbon kinetic
1075 isotope effect in the reaction CH₄+Cl: A relative rate study using FTIR spectroscopy. *Chemical*
1076 *Physics Letters*, 303(3–4), 268–274. [https://doi.org/10.1016/S0009-2614\(99\)00243-2](https://doi.org/10.1016/S0009-2614(99)00243-2)
- 1077 Crutzen, P. J., & Zimmermann, P. H. (1991). The changing photochemistry of the troposphere. *Tellus B*,
1078 43(4), 136–151. <https://doi.org/10.1034/j.1600-0889.1991.t01-1-00012.x>
- 1079 Dasari, S., Andersson, A., Popa, M. E., Röckmann, T., Holmstrand, H., Budhavant, K., & Gustafsson, Ö.
1080 (2022). Observational Evidence of Large Contribution from Primary Sources for Carbon
1081 Monoxide in the South Asian Outflow. *Environmental Science & Technology*, 56(1), 165–174.
1082 <https://doi.org/10.1021/acs.est.1c05486>
- 1083 Dawson, T. E., Mambelli, S., Plamboeck, A. H., Templer, P. H., & Tu, K. P. (2002). Stable Isotopes in
1084 Plant Ecology. *Annual Review of Ecology, Evolution, and Systematics*, 33(Volume 33, 2002),
1085 507–559. <https://doi.org/10.1146/annurev.ecolsys.33.020602.095451>
- 1086 DeMore, W. B., Howard, C. J., Sander, S. P., Ravishankara, A. R., Golden, D. M., Kolb, C. E., Hampson,
1087 R. F., Molina, M. J., & Kurylo, M. J. (1997). Chemical Kinetics and Photochemical Data for Use
1088 in Stratospheric Modeling. 97-4.
1089 <https://ntrs.nasa.gov/api/citations/19970037557/downloads/19970037557.pdf>
- 1090 Derendorp, L., Quist, J. B., Holzinger, R., & Röckmann, T. (2011). Emissions of H₂ and CO from leaf
1091 litter of *Sequoiadendron giganteum*, and their dependence on UV radiation and temperature.
1092 *Atmospheric Environment*, 45(39), 7520–7524. <https://doi.org/10.1016/j.atmosenv.2011.09.044>
- 1093 de Laat, A. T. J., Andela, N., Forkel, M., Huijnen, V., Kinalczyk, D., & van Wees, D. (2026). *Sentinel-5p*
1094 *Reveals Unexplained Large Wildfire Carbon Emissions in the Amazon in 2024*. 53(5).
1095 <https://doi.org/10.1029/2025GL115123>
- 1096 Farquhar, G. D., Ehleringer, J. R., & Hubick, K. T. (1989). Carbon Isotope Discrimination and
1097 Photosynthesis. *Annual Review of Plant Biology*, 40(Volume 40, 1989), 503–537.
1098 <https://doi.org/10.1146/annurev.pp.40.060189.002443>
- 1099 Ferracci, V., Weber, J., Bolas, C. G., Robinson, A. D., Tummon, F., Rodríguez-Ros, P., Cortés-Greus, P.,
1100 Baccarini, A., Jones, R. L., Galí, M., Simó, R., Schmale, J., & Harris, Neil. R. P. (2024).
1101 Atmospheric isoprene measurements reveal larger-than-expected Southern Ocean emissions.
1102 *Nature Communications*, 15(1), 2571. <https://doi.org/10.1038/s41467-024-46744-4>



- 1103 Gonfiantini, R. (1978). Standards for stable isotope measurements in natural compounds. *Nature*,
1104 271(5645), 534–536. <https://doi.org/10.1038/271534a0>
- 1105 Gromov, S. (2013). *Stable isotope composition of atmospheric carbon monoxide: A modelling study*.
1106 <https://doi.org/10.13140/RG.2.2.30769.17760>
- 1107 Gromov, S., Brenninkmeijer, C., & Jöckel, P. (2017). Uncertainties of fluxes and $^{13}\text{C}/^{12}\text{C}$ ratios of
1108 atmospheric reactive-gas emissions. *Atmospheric Chemistry and Physics*, 17, 8525–8552.
1109 <https://doi.org/10.5194/acp-17-8525-2017>
- 1110 Gros, V., Bräunlich, M., Röckmann, T., Jöckel, P., Bergamaschi, P., Brenninkmeijer, C. a. M., Rom, W.,
1111 Kutschera, W., Kaiser, A., Scheel, H. E., Mandl, M., van der Plicht, J., & Possnert, G. (2001).
1112 Detailed analysis of the isotopic composition of CO and characterization of the air masses
1113 arriving at Mount Sonnblick (Austrian Alps). *Journal of Geophysical Research: Atmospheres*,
1114 106(D3), 3179–3193. <https://doi.org/10.1029/2000JD900509>
- 1115 Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Peubey,
1116 C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G.,
1117 Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., ... Thépaut, J.-N. (2020). The ERA5 global
1118 reanalysis. *Quarterly Journal of the Royal Meteorological Society*, 146(730), 1999–2049.
1119 <https://doi.org/10.1002/qj.3803>
- 1120 Hossaini, R., Chipperfield, M. P., Montzka, S. A., Leeson, A. A., Dhomse, S. S., & Pyle, J. A. (2017).
1121 The increasing threat to stratospheric ozone from dichloromethane. *Nature Communications*,
1122 8(1), 15962. <https://doi.org/10.1038/ncomms15962>
- 1123 IPCC. Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth
1124 Assessment Report of the Intergovernmental Panel on Climate Change (Cambridge University
1125 Press, 2021).
- 1126 Intergovernmental Panel on Climate Change (IPCC). (2023). *Climate Change 2021 – The Physical*
1127 *Science Basis: Working Group I Contribution to the Sixth Assessment Report of the*
1128 *Intergovernmental Panel on Climate Change*. Cambridge: Cambridge University Press.
1129 <https://doi.org/10.1017/9781009157896>
- 1130 Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., et al. (2010). Development cycle 2 of
1131 the modular earth submodel system (MESSy2). *Geoscientific Model Development*, 3(2),
1132 717–752. <https://doi.org/10.5194/gmd-3-717-2010>
- 1133 Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S.,
1134 Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K.-D., Graf, P., Grewe, V., Kerkweg,
1135 A., Kern, B., Matthes, S., Mertens, M., ... Zahn, A. (2016). Earth System Chemistry integrated
1136 Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy) version 2.51.
1137 *Geoscientific Model Development*, 9(3), 1153–1200. <https://doi.org/10.5194/gmd-9-1153-2016>
- 1138 Jöckel, P., Brinkop, S., Graf, P., Eichinger, R., Garny, H., Mertens, M., et al. (2024). RD1SD: EMAC
1139 CCMi-2022 hindcast simulations with specified dynamics, ERA-5, 1979–2019 [Data set]. World
1140 Data Center for Climate (WDCC) at DKRZ. https://doi.org/10.26050/WDCC/ESCiMo2_RD1SD
- 1141 Jolly, W. M., Cochrane, M. A., Freeborn, P. H., Holden, Z. A., Brown, T. J., Williamson, G. J., &
1142 Bowman, D. M. J. S. (2015). Climate-induced variations in global wildfire danger from 1979 to
1143 2013. *Nature Communications*, 6(1), 7537. <https://doi.org/10.1038/ncomms8537>
- 1144 Kato, S., Akimoto, H., Röckmann, T., Bräunlich, M., & Brenninkmeijer, C. A. M. (1999). Stable isotopic
1145 compositions of carbon monoxide from biomass burning experiments. *Atmospheric Environment*,
1146 33(27), 4357–4362. [https://doi.org/10.1016/S1352-2310\(99\)00243-5](https://doi.org/10.1016/S1352-2310(99)00243-5)
- 1147 Kato, S., Kajii, Y., Akimoto, H., Bräunlich, M., Röckmann, T., & Brenninkmeijer, C. A. M. (2000).
1148 Observed and modeled seasonal variation of ^{13}C , ^{18}O , and ^{14}C of atmospheric CO at Happono, a
1149 remote site in Japan, and a comparison with other records. *Journal of Geophysical Research:*
1150 *Atmospheres*, 105(D7), 8891–8900. <https://doi.org/10.1029/1999JD901144>
- 1151 Keppler, F., Kalin, R., Harper, D., Mcroberts, C., & Hamilton, J. (2004). Carbon isotope anomaly in the
1152 major plant C1 pool and its global biogeochemical implications. *Biogeosciences Discussions*,
1153 1(2), 123–131. <https://doi.org/10.5194/bg-1-123-2004>



- 1154 Kirago, L., Gustafsson, Ö., Gaita, S., Haslett, S., Gatari, M., Popa, M., Röckmann, T., Zellweger, C.,
1155 Steinbacher, M., Klausen, J., Félix, C., Njiru, D., & Andersson, A. (2023). Sources and long-term
1156 variability of carbon monoxide at Mount Kenya and in Nairobi. *Atmospheric Chemistry and*
1157 *Physics*, 23, 14349–14357. <https://doi.org/10.5194/acp-23-14349-2023>
- 1158 Kirchmeier-Young, M. C., Malinina, E., Barber, Q. E., Garcia Perdomo, K., Curasi, S. R., Liang, Y., Jain,
1159 P., Gillett, N. P., Parisien, M.-A., Cannon, A. J., Lima, A. R., Arora, V. K., Boulanger, Y.,
1160 Melton, J. R., Van Vliet, L., & Zhang, X. (2024). Human driven climate change increased the
1161 likelihood of the 2023 record area burned in Canada. *Npj Climate and Atmospheric Science*, 7(1),
1162 316. <https://doi.org/10.1038/s41612-024-00841-9>
- 1163 Kroopnick, P., & Craig, H. (1972). Atmospheric oxygen: Isotopic composition and solubility
1164 fractionation. *Science (New York, N.Y.)*, 175(4017), 54–55.
1165 <https://doi.org/10.1126/science.175.4017.54>
- 1166 Lan, X., K.W. Thoning, and E.J. Dlugokencky (2022): Trends in globally-averaged CH₄, N₂O, and SF₆
1167 determined from NOAA Global Monitoring Laboratory measurements. Version 2025-01,
1168 <https://doi.org/10.15138/P8XG-AA10>
- 1169 Levy, H. (1971). Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted.
1170 *Science*, 173(3992), 141–143. <https://doi.org/10.1126/science.173.3992.141>
- 1171 Mak, J., & Brenninkmeijer, C. (1994). Compressed Air Sample Technology for Isotopic Analysis of
1172 Atmospheric Carbon Monoxide. *Journal of Atmospheric and Oceanic Technology*, 11(2), 425–
1173 431. [https://doi.org/10.1175/1520-0426\(1994\)011%3C0425:CASTFI%3E2.0.CO;2](https://doi.org/10.1175/1520-0426(1994)011%3C0425:CASTFI%3E2.0.CO;2)
- 1174 Mak, J. E., Kra, G., Sandomenico, T., & Bergamaschi, P. (2003). The seasonally varying isotopic
1175 composition of the sources of carbon monoxide at Barbados, West Indies. *Journal of Geophysical*
1176 *Research: Atmospheres*, 108(D20). <https://doi.org/10.1029/2003JD003419>
- 1177 Mak, J. E., & Kra, G. (1999). The isotopic composition of carbon monoxide at Montauk Point, Long
1178 Island. *Chemosphere - Global Change Science*, 1(1), 205–218. [https://doi.org/10.1016/S1465-9972\(99\)00025-2](https://doi.org/10.1016/S1465-9972(99)00025-2)
- 1179 Muller, J. D., Qubaja, R., Koh, E., Stern, R., Bohak, Y. L., Tatarinov, F., Rotenberg, E., & Yakir, D.
1180 (2025). Leaf carbon monoxide emissions under different drought, heat, and light conditions in the
1181 field. *New Phytologist*, 245(6), 2439–2450. <https://doi.org/10.1111/nph.20424>
- 1182 National Academies of Sciences, Engineering, and Medicine. 2024. A Research Agenda Toward
1183 Atmospheric Methane Removal. Washington, DC: The National Academies Press.
1184 <https://doi.org/10.17226/27157>.
- 1185 Naus, S., Röckmann, T., & Popa, M. E. (2018). The isotopic composition of CO in vehicle exhaust.
1186 *Atmospheric Environment*, 177, 132–142. <https://doi.org/10.1016/j.atmosenv.2018.01.015>
- 1187 Novelli, P., Elkins, J., & Steele, L. (1991). The Development and Evaluation of a Gravimetric Reference
1188 Scale For Measurements of Atmospheric Carbon Monoxide. *Journal of Geophysical Research*,
1189 96, 13109–13121. <https://doi.org/10.1029/91JD01108>
- 1190 Novelli, P., Masarie, K., & Lang, P. (1998). Distributions and recent changes of carbon monoxide in the
1191 lower troposphere. *Journal of Geophysical Research*, 103. <https://doi.org/10.1029/98JD01366>
- 1192 Novelli, P., Steele, L., & Tans, P. (1992). Mixing Ratios of Carbon Monoxide in the Troposphere.
1193 *J. Geophys. Res.*, 97, 20731–20750. <https://doi.org/10.1029/92JD02010>
- 1194 Pathirana, S., Veen, C., Popa, E., & Röckmann, T. (2015). An analytical system for studying the stable
1195 isotopes of carbon monoxide using continuous flow-isotope ratio mass spectrometry (CF-IRMS).
1196 *Atmospheric Measurement Techniques*, 8, 5315–5324. <https://doi.org/10.5194/amt-8-5315-2015>
- 1197 Pelletier, F., Cardille, J. A., Wulder, M. A., White, J. C., & Hermosilla, T. (2024). Revisiting the 2023
1198 wildfire season in Canada. *Science of Remote Sensing*, 10, 100145.
1199 <https://doi.org/10.1016/j.srs.2024.100145>
- 1200 Petron, G., X. Lan, K. Baugh, A.M. Crotwell, M.J. Crotwell, S. DeVogel, M. Madronich, J. Mauss, T.
1201 Mefford, E. Moglia, S. Morris, J.W. Mund, A. Searle, K.W. Thoning, and J. Miller, (2026),
1202 Atmospheric Carbon Monoxide Dry Air Mole Fractions from the NOAA GML Global
1203



- 1204 Greenhouse Gas Reference Network, Carbon Cycle Cooperative Global Air Sampling Network:
1205 1988 - Present, Version: 2026-08-11, <https://doi.org/10.15138/33bv-s284>
- 1206 Popa, E., Vollmer, M., Jordan, A., Brand, W., Pathirana, S., Rothe, M., & Röckmann, T. (2014). Vehicle
1207 emissions of greenhouse gases and related tracers from a tunnel study: CO : CO₂, N₂O : CO₂,
1208 CH₄ : CO₂, O₂ : CO₂ ratios, and the stable isotopes ¹³C and ¹⁸O in CO₂ and CO. *Atmospheric*
1209 *Chemistry and Physics*, 14, 2105–2123. <https://doi.org/10.5194/acp-14-2105-2014>
- 1210 Raymond, N., Bernath, P., Boone, C., & Chipperfield, M. P. (2026). Twenty-One Years of Global
1211 Atmospheric Chlorine Inventories From Atmospheric Chemistry Experiment Fourier Transform
1212 Spectrometer (ACE-FTS) Measurements. *Journal of Geophysical Research: Atmospheres*,
1213 131(5), e2025JD045176. <https://doi.org/10.1029/2025JD045176>
- 1214 Röckmann, T., Brenninkmeijer, C. A. M., Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., &
1215 Crutzen, P. J. (1998). Mass-Independent Oxygen Isotope Fractionation in Atmospheric CO as a
1216 Result of the Reaction CO + OH. *Science*, 281(5376), 544–546.
1217 <https://doi.org/10.1126/science.281.5376.544>
- 1218 Röckmann, T., Jöckel, P., Gros, V., Bräunlich, M., Possnert, G., & Brenninkmeijer, C. (2002). Using
1219 ¹⁴C, ¹³C, ¹⁸O and ¹⁷O isotopic variations to provide insights into the high northern latitude
1220 surface CO inventory. *Atmospheric Chemistry and Physics*, 2(2), 147–159.
1221 <https://doi.org/10.5194/acpd-2-213-2002>
- 1222 Röckmann, T., Kaiser, J., Brenninkmeijer, C. A. M., & Brand, W. A. (2003). Gas
1223 chromatography/isotope-ratio mass spectrometry method for high-precision position-dependent
1224 ¹⁵N and ¹⁸O measurements of atmospheric nitrous oxide. *Rapid Communications in Mass*
1225 *Spectrometry: RCM*, 17(16), 1897–1908. <https://doi.org/10.1002/rcm.1132>
- 1226 Röckmann, T., Herpen, M. van, Brashear, C., Veen, C. van der, Gromov, S., Li, Q., Saiz-Lopez, A.,
1227 Meidan, D., Barreto, A., Prats, N., Mármol, I., Ramos, R., Baños, I., Arrieta, J. M., Zaehle, S.,
1228 Jordan, A., Moossen, H., Timas, H., Young, D., ... Johnson, M. S. (2024). The use of ^{δ13}C in
1229 CO to determine removal of CH₄ by Cl radicals in the atmosphere*. *Environmental Research*
1230 *Letters*, 19(6), 064054. <https://doi.org/10.1088/1748-9326/ad4375>
- 1231 Röckmann, T., & Brenninkmeijer, C. A. M. (1997). CO and CO₂ isotopic composition in Spitsbergen
1232 during the 1995 ARCTOC campaign. *Tellus B: Chemical and Physical Meteorology*, 49(5), 455–
1233 465. <https://doi.org/10.3402/tellusb.v49i5.15985>
- 1234 Rocco, M., Dunne, E., Peltola, M., Barr, N., Williams, J., Colomb, A., Safi, K., Saint-Macary, A.,
1235 Marriner, A., Deppeler, S., Harnwell, J., Law, C., & Sellegri, K. (2021). Oceanic phytoplankton
1236 are a potentially important source of benzenoids to the remote marine atmosphere.
1237 *Communications Earth & Environment*, 2(1), 175. <https://doi.org/10.1038/s43247-021-00253-0>
- 1238 Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblueh, L., Manzini, E., Schlese,
1239 U., & Schulzweida, U. (2006). Sensitivity of Simulated Climate to Horizontal and Vertical
1240 Resolution in the ECHAM5 Atmosphere Model. *Journal of Climate*, 19(16), 3771–3791.
1241 <https://doi.org/10.1175/JCLI3824.1>
- 1242 Rudolph, J., Czuba, E., & Huang, L. (2000). The stable carbon isotope fractionation for reactions of
1243 selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry. *Journal of*
1244 *Geophysical Research: Atmospheres*, 105(D24), 29329–29346.
1245 <https://doi.org/10.1029/2000JD900447>
- 1246 Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., & Harris, G. W. (1995). Carbon kinetic
1247 isotope effect in the reaction of CH₄ with Cl atoms. *Geophysical Research Letters*, 22(10), 1225–
1248 1228. <https://doi.org/10.1029/95GL00881>
- 1249 Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M., & Fischer, H.
1250 (2001). Carbon ¹³C and D kinetic isotope effects in the reactions of CH₄ with O(¹D) and OH:
1251 New laboratory measurements and their implications for the isotopic composition of stratospheric
1252 methane. *Journal of Geophysical Research: Atmospheres*, 106(D19), 23127–23138.
1253 <https://doi.org/10.1029/2000JD000120>



- 1254 Saurer, M., Aellen, K., & Siegwolf, R. (1997). Correlating $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in cellulose of trees. *Plant,*
1255 *Cell & Environment*, 20(12), 1543–1550. <https://doi.org/10.1046/j.1365-3040.1997.d01-53.x>
- 1256 Saurer, M., Prevot, A., Dommen, J., Sandradewi, J., Baltensperger, U., & Siegwolf, R. (2008). The
1257 influence of traffic and wood combustion on the stable isotopic composition of carbon monoxide.
1258 *Atmospheric Chemistry and Physics Discussions*, 8, 19561–19604. [https://doi.org/10.5194/acpd-](https://doi.org/10.5194/acpd-8-19561-2008)
1259 [8-19561-2008](https://doi.org/10.5194/acpd-8-19561-2008)
- 1260 Sharkey, T. D., Loreto, F., Delwiche, C. F., & Treichel, I. W. (1991). Fractionation of Carbon Isotopes
1261 during Biogenesis of Atmospheric Isoprene. *Plant Physiology*, 97(1), 463–466.
1262 <https://doi.org/10.1104/pp.97.1.463>
- 1263 Smiley, W. G. (1965). Note on a reagent for oxidation of carbon monoxide, Nucl. Sci. Abstr, 3, 391.
- 1264 Schütze, M. (1944). Ein neues Oxydationsmittel für die quantitative Überführung von Kohlenoxyd in
1265 Kohlendioxyd. Ein Beitrag zur Chemie des Jodpentoxyds. *Berichte Der Deutschen Chemischen*
1266 *Gesellschaft (A and B Series)*, 77, 484–487. <https://doi.org/10.1002/cber.19440770622>
- 1267 Stevens, C.M., Krout, L., Walling, D., Venters, A., Engelkemeir, A., Ross, L.E. (1972). The isotopic
1268 composition of atmospheric carbon monoxide. *Earth and Planetary Science Letters* 16, 147-165.
1269 [https://doi.org/10.1016/0012-821X\(72\)90183-5](https://doi.org/10.1016/0012-821X(72)90183-5)
- 1270 Stevens, C.M., and Krout, L., Method for the determination of the concentration and of the carbon and
1271 oxygen isotopic composition of atmospheric carbon monoxide, *Int. J. MassSpectrom. Ion Phys.*,8,
1272 265295, 1972. [https://doi.org/10.1016/0020-7381\(72\)83017-1](https://doi.org/10.1016/0020-7381(72)83017-1)
- 1273 Stevens, C. M., Kaplan, L., Gorse, R., Durkee, S., Compton, M., Cohen, S., & Bielling, K. (1980). The
1274 kinetic isotope effect for carbon and oxygen in the reaction $\text{CO} + \text{OH}$. *International Journal of*
1275 *Chemical Kinetics*, 12(12), 935–948. <https://doi.org/10.1002/kin.550121205>
- 1276 Stevens, C., & Wagner, A. (1989). The Role of Isotope Fractionation Effects in Atmospheric Chemistry.
1277 *Zeitschrift Für Naturforschung A*, 44. <https://doi.org/10.1515/zna-1989-0505>
- 1278 Stichler, W., Interlaboratory comparison of new materials for carbon and oxygen ratio measurements,
1279 *Proceedings of a consultants' meeting held in Vienna*, 1 - 3. Dec. 1993. IAEA-TECDOC-825,
1280 IAEA, Vienna, Austria (1995) 67-74. <https://inis.iaea.org/records/8bps0-58578>
- 1281 Szopa, S., V. Naik, B. Adhikary, P. Artaxo, T. Berntsen, W.D. Collins, S. Fuzzi, L. Gallardo, A.
1282 Kiendler-Scharr, Z. Klimont, H. Liao, N. Unger, and P. Zanis, 2021: Short-Lived Climate
1283 Forcers. In *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I*
1284 *to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* [Masson-
1285 Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L.
1286 Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T.
1287 Waterfield, O. Yelekçi, R. Yu, and B. Zhou (eds.)]. Cambridge University Press, Cambridge,
1288 United Kingdom and New York, NY, USA, pp. 817–922, doi:10.1017/9781009157896.008
- 1289 United Nations Environment Programme and Climate and Clean Air Coalition (2021). Global Methane
1290 Assessment: Benefits and Costs of Mitigating Methane Emissions. Nairobi: United Nations
1291 Environment Programme. <https://wedocs.unep.org/handle/20.500.11822/35913>
- 1292 van Asperen, H., Warneke, T., Carioca De Araújo, A., Forsberg, B., José Filgueiras Ferreira, S.,
1293 Röckmann, T., Van Der Veen, C., Bulthuis, S., Ramos De Oliveira, L., De Lima Xavier, T., Da
1294 Mata, J., De Oliveira Sá, M., Ricardo Teixeira, P., Andrews De França E Silva, J., Trumbore, S.,
1295 & Notholt, J. (2024). The emission of CO from tropical rainforest soils. *Biogeosciences*, 21(13),
1296 3183–3199. <https://doi.org/10.5194/bg-21-3183-2024>
- 1297 van der Werf, G.R., Randerson, J.T., van Wees, D. *et al.* Landscape fire emissions from the 5th version of
1298 the Global Fire Emissions Database (GFED5). *Sci Data* 12, 1870 (2025).
1299 <https://doi.org/10.1038/s41597-025-06127-w>
- 1300 van Herpen, M. M. J. W., Li, Q., Saiz-Lopez, A., Liisberg, J. B., Röckmann, T., Cuevas, C. A.,
1301 Fernandez, R. P., Mak, J. E., Mahowald, N. M., Hess, P., Meidan, D., Stuut, J.-B. W., & Johnson,
1302 M. S. (2023). Photocatalytic chlorine atom production on mineral dust–sea spray aerosols over
1303 the North Atlantic. *Proceedings of the National Academy of Sciences*, 120(31), e2303974120.
1304 <https://doi.org/10.1073/pnas.2303974120>



- 1305 van Oldenborgh, G. J., Krikken, F., Lewis, S., Leach, N. J., Lehner, F., Saunders, K. R., van Weele, M.,
1306 Hausteijn, K., Li, S., Wallom, D., Sparrow, S., Arrighi, J., Singh, R. K., van Aalst, M. K., Philip,
1307 S. Y., Vautard, R., & Otto, F. E. L. (2021). Attribution of the Australian bushfire risk to
1308 anthropogenic climate change. *Natural Hazards and Earth System Sciences*, 21(3), 941–960.
1309 <https://doi.org/10.5194/nhess-21-941-2021>
- 1310 Vernooij, R., Ulrike, D., Popa, E., Peng, Y., Shaikat, A., Qiu, C., Winiger, P., van der Veen, C., Eames,
1311 T. C., Ribeiro, N., & van der Werf, G. R. (2022). Stable carbon isotopic composition of biomass
1312 burning emissions – implications for estimating the contribution of C3 and C4 plants.
1313 *Atmospheric Chemistry and Physics*, 22, 2871–2890. <https://doi.org/10.5194/acp-22-2871-2022>
- 1314 Vimont, I., Turnbull, J., Petrenko, V., Place, P., Karion, A., Miles, N., Richardson, S., Gurney, K.,
1315 Patarasuk, R., Sweeney, C., Vaughn, B., & White, J. (2017). Carbon monoxide isotopic
1316 measurements in Indianapolis constrain urban source isotopic signatures and support mobile
1317 fossil fuel emissions as the dominant wintertime CO source. *Elem Sci Anth*, 5, 63.
1318 <https://doi.org/10.1525/elementa.136>
- 1319 Vimont, I. J., Turnbull, J. C., Petrenko, V. V., Place, P. F., Sweeney, C., Miles, N., Richardson, S.,
1320 Vaughn, B. H., & White, J. W. C. (2019). An improved estimate for the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
1321 signatures of carbon monoxide produced from atmospheric oxidation of volatile organic
1322 compounds. *Atmospheric Chemistry & Physics*, 19, 8547–8562. [https://doi.org/10.5194/acp-19-](https://doi.org/10.5194/acp-19-8547-2019)
1323 [8547-2019](https://doi.org/10.5194/acp-19-8547-2019)
- 1324 Wang W, Wang X, Flannigan MD, Guindon L, Swystun T, Castellanos-Acuna D, Wu W, Wang G.
1325 Canadian forests are more conducive to high-severity fires in recent decades. *Science*. 2025 Jan
1326 3;387(6729):91-97. doi: 10.1126/science.ado1006.
- 1327 Wohl, C., Li, Q., Cuevas, C. A., Fernandez, R. P., Yang, M., Saiz-Lopez, A., & Simó, R. (2023). Marine
1328 biogenic emissions of benzene and toluene and their contribution to secondary organic aerosols
1329 over the polar oceans. *Science Advances*, 9(4). <https://doi.org/10.1126/sciadv.add9031>
- 1330 Yamada, K., Hattori, R., Ito, Y., Shibata, H., & Yoshida, N. (2010). Determination of carbon isotope
1331 ratios of methanol and acetaldehyde in air samples by gas chromatography-isotope ratio mass
1332 spectrometry combined with headspace solid-phase microextraction. *Isotopes in Environmental*
1333 *and Health Studies*, 46(3), 392–399. <https://doi.org/10.1080/10256016.2010.505686>
- 1334 Zhang, Q., Wang, Y., Xiao, Q. *et al.* Long-range PM_{2.5} pollution and health impacts from the 2023
1335 Canadian wildfires. *Nature* **645**, 672–678 (2025). <https://doi.org/10.1038/s41586-025-09482-1>
- 1336 Zheng, B., Chevallier, F., Yin, Y., Ciais, P., Fortems-Cheiney, A., Deeter, M. N., Parker, R. J., Wang, Y.,
1337 Worden, H. M., & Zhao, Y. (2019). Global atmospheric carbon monoxide budget 2000–2017
1338 inferred from multi-species atmospheric inversions. *Earth System Science Data*, 11(3), 1411–
1339 1436. <https://doi.org/10.5194/essd-11-1411-2019>