

Dear Editor,

We thank you again for reviewing our manuscript and your valuable suggestions to improve our manuscript. We also appreciate your opinions on how to use units and symbols. Here, you will find our revised manuscript with a final version and a version with track-change. As you requested, we have revised the typo and have changed the structure. In this round, we accept most suggestions from you except for Fig. S7 (R2). Given that Fig. S7 is only used once in the discussion and was derived from Personal Communication (Henne et al.), we prefer to keep them in the supplementary.

We are happy that this manuscript will finally be accepted for publication. In future, our group will for sure submitted more manuscripts to ACP.

Longfei Yu

On behalf of all co-authors

1 **The isotopic composition of atmospheric nitrous oxide**
2 **observed at the high-altitude research station Jungfrauoch,**
3 **Switzerland**

4 Longfei Yu^{1*}, Eliza Harris^{1†}, Stephan Henne¹, Sarah Eggleston¹, Martin Steinbacher¹, Lukas
5 Emmenegger¹, Christoph Zellweger¹ and Joachim Mohn¹

6 ¹Laboratory for Air Pollution & Environmental Technology, Empa, Swiss Federal Laboratories
7 for Materials Science and Technology, Ueberlandstr. 129, CH-8600 Duebendorf, Switzerland.

8 [†]Current address: Institute of Ecology, University of Innsbruck, Sternwartestrasse 15, A-6020
9 Innsbruck, Austria

10 * Correspondence: L. Yu (longfei.yu@empa.ch)

11 **Abstract**

12 Atmospheric nitrous oxide (N₂O) levels have been continuously growing since preindustrial times.
13 Mitigation requires information about sources and sinks on the regional and global scales. Isotopic
14 composition of N₂O in the atmosphere could contribute valuable constraints. However, isotopic
15 records of N₂O in the unpolluted atmosphere remain too scarce for large-scale N₂O models. Here,
16 we report the results of discrete air samples collected weekly to bi-weekly over a five-year period
17 at the high-altitude research station Jungfraujoch, located in central Switzerland. High-precision
18 N₂O isotopic measurements were made using a recently developed preconcentration-laser
19 spectroscopy technique. The measurements of discrete samples were accompanied by *in situ*
20 continuous measurements of N₂O mixing ratios. Our results indicate a pronounced seasonal pattern
21 with minimum N₂O mixing ratios in late summer, associated with a maximum in $\delta^{15}\text{N}^{\text{bulk}}$ and a
22 minimum in intramolecular ¹⁵N site preference ($\delta^{15}\text{N}^{\text{SP}}$). This pattern is most likely due to
23 stratosphere-troposphere exchange (STE), which delivers N₂O-depleted but ¹⁵N-enriched air from
24 the stratosphere into the troposphere. Variability in $\delta^{15}\text{N}^{\text{SP}}$ induced by changes in STE may be
25 masked by biogeochemical N₂O production processes in late summer, which are possibly
26 dominated by a low- $\delta^{15}\text{N}^{\text{SP}}$ pathway of N₂O production (denitrification), providing an explanation
27 for the observed seasonality of $\delta^{15}\text{N}^{\text{SP}}$. Footprint analyses and atmospheric transport simulations
28 of N₂O for Jungfraujoch suggest that regional emissions from the planetary boundary layer
29 contribute to seasonal variations of atmospheric N₂O isotopic composition at Jungfraujoch, albeit
30 more clearly for $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ than for $\delta^{15}\text{N}^{\text{bulk}}$. With the time-series of five years, we obtained
31 a significant interannual trend for $\delta^{15}\text{N}^{\text{bulk}}$ after deseasonalization ($-0.052\pm 0.012\text{‰ a}^{-1}$), indicating
32 that the atmospheric N₂O increase is due to isotopically depleted N₂O sources. We estimated the
33 average isotopic signature of anthropogenic N₂O sources with a two-box model to be $-8.6\pm 0.6\text{‰}$

34 for $\delta^{15}\text{N}^{\text{bulk}}$, $34.8\pm 3\text{‰}$ for $\delta^{18}\text{O}$ and $10.7\pm 4\text{‰}$ for $\delta^{15}\text{N}^{\text{SP}}$. Our study demonstrates that seasonal
35 variation of N_2O isotopic composition in the background atmosphere is important when
36 determining interannual trends. More frequent, high-precision and inter-laboratory compatible
37 measurements of atmospheric N_2O isotopocules, especially for $\delta^{15}\text{N}^{\text{SP}}$, are needed to better
38 constrain anthropogenic N_2O sources, and thus the contribution of biogeochemical processes to
39 N_2O growth on the global scale.

40 **1 Introduction**

41 Nitrous oxide (N₂O) is a potent greenhouse gas (Fowler et al., 2015) and a strong stratospheric
42 ozone-depleting substance (Ravishankara et al., 2009). For several decades, near-surface
43 atmospheric N₂O mixing ratios have been continuously measured at a series of remote sites, within
44 the networks of the Global Atmosphere Watch Programme (JMA and WMO, 2018), the Advanced
45 Global Atmospheric Gases Experiment (AGAGE) (Prinn et al., 2018), and the National Oceanic
46 and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global
47 Monitoring Division (GMD) (Nevison et al., 2011). These measurements have shown a significant
48 increase in atmospheric N₂O mixing ratio, at a current growth rate of about 0.93 nmol mol⁻¹ a⁻¹
49 (WMO, 2018). On the global scale, given excessive nitrogen (N) fertilizer application, agriculture
50 is known to be the largest and most important anthropogenic source of N₂O (Reay et al., 2012;
51 Tian et al., 2019). However, long-term observations of N₂O in the unpolluted atmosphere have
52 shown seasonal and interannual variabilities as well as interhemispheric differences in N₂O mixing
53 ratios (Nevison et al., 2011; Thompson et al., 2014a, 2014b), which cannot yet be resolved by
54 atmospheric transport models and existing emission inventories. Moreover, regional contributions
55 of N₂O emissions and the strengths of individual N₂O production pathways remain difficult to
56 quantify.

57 Isotopic signatures of atmospheric N₂O can provide important constraints on N₂O sources (Denk
58 et al., 2017) and trends (Kim and Craig, 1993). The ratios of ¹⁵N/¹⁴N and ¹⁸O/¹⁶O in N₂O are often
59 reported in δ notation as $\delta(^{15}\text{N}/^{14}\text{N})$ and $\delta(^{18}\text{O}/^{16}\text{O})$, abbreviated as $\delta^{15}\text{N}^{\text{bulk}}$ (average for ¹⁴N¹⁵N¹⁶O
60 and ¹⁵N¹⁴N¹⁶O) and $\delta^{18}\text{O}$, respectively. A large fraction of N₂O emitted to the atmosphere
61 originates from soil bacterial processes, which usually emit N₂O that is more enriched in light (¹⁴N,
62 ¹⁶O) isotopes than the tropospheric background (Pérez et al., 2001; Snider et al., 2015a; Toyoda et

63 al., 2017). By contrast, N₂O produced in the oceans (Bourbonnais et al., 2017; Fujii et al., 2013)
64 and emitted from fossil fuel combustion (Ogawa and Yoshida, 2005; Toyoda et al., 2008) has
65 higher $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ values which are comparable to the tropospheric background. A recent
66 study has summarized isotopic signatures of anthropogenic N₂O sources divided into the EDGAR
67 (Emissions Database for Global Atmospheric Research) emission categories (Janssens-Maenhout
68 et al., 2019), showing differences in isotopic signatures between agricultural ($\delta^{15}\text{N}^{\text{bulk}} = -17.8$ to -
69 1.0‰ and $\delta^{18}\text{O} = 23.9$ to 29‰) and industrial sources ($\delta^{15}\text{N}^{\text{bulk}} = -28.7$ to 5.5‰ and $\delta^{18}\text{O} = 28.6$
70 to 40.3‰) (Harris et al., 2017). These empirical ranges, together with isotopic mixing models,
71 provide a valuable approach to interpret variability in atmospheric N₂O mixing ratios.

72 A number of studies have analyzed temporal trends in N₂O isotopic composition in the modern
73 atmosphere (Kaiser et al., 2003; Park et al., 2012; Röckmann and Levin, 2005; Toyoda et al., 2013)
74 and in the past from firn and ice cores (Bernard et al., 2006; Ishijima et al., 2007; Prokopiou et al.,
75 2018; Röckmann et al., 2003; Sowers et al., 2002). These isotopic measurements have shown a
76 decrease in both $\delta^{15}\text{N}^{\text{bulk}}$ - and $\delta^{18}\text{O}$ -N₂O associated with an increasing trend in atmospheric N₂O
77 mixing ratios since preindustrial times, indicating that the recent increase of atmospheric N₂O may
78 be due to agricultural emissions (¹⁵N and ¹⁸O depleted). The reported trend since the 1960s seems
79 rather steady (-0.034 ± 0.005 ‰ a⁻¹ for $\delta^{15}\text{N}^{\text{bulk}}$ and -0.016 ± 0.006 a⁻¹ for $\delta^{18}\text{O}$) (Bernard et al.,
80 2006; Ishijima et al., 2007; Park et al., 2012; Prokopiou et al., 2017; Röckmann et al., 2003;
81 Röckmann and Levin, 2005). However, a more recent (1999-2010) study reported a smaller
82 decreasing trend in $\delta^{15}\text{N}^{\text{bulk}}$ and only an insignificant trend in $\delta^{18}\text{O}$ for the Northern Hemisphere
83 (Toyoda et al., 2013). Several hypotheses were proposed to explain the differences in the observed
84 trends: 1) the interhemispheric difference in N₂O emission sources results in inconsistent isotopic
85 signatures among different studies (Thompson et al., 2014b); 2) uncertainties in isotopic

86 measurements and variable sampling schemes (air type, sampling frequency and time) mask the
87 small secular trend of N₂O isotopic composition in the background atmosphere (Toyoda et al.,
88 2013); and/or 3) N₂O source isotopic signatures have changed in recent years, possibly due to
89 shifts in N fertilizer type and climatic forcing (Tian et al., 2019). Hence, further investigation into
90 the global N₂O source inventory and its evolution over time requires more frequent, precise
91 measurements of N₂O isotopocules in the unpolluted atmosphere, particularly in the Northern
92 Hemisphere.

93 Recently, site-specific composition of N₂O isotopomers (site preference: $\delta^{15}\text{N}^{\text{SP}}$), which denotes
94 the difference of ¹⁵N between the central (¹⁴N¹⁵N¹⁶O, α position) and terminal (¹⁵N¹⁴N¹⁶O, β
95 position) N atoms, has been applied to constrain sources contributing to atmospheric N₂O (Toyoda
96 et al., 2013; Yoshida and Toyoda, 2000). $\delta^{15}\text{N}^{\text{SP}}$ of N₂O is particularly effective for distinguishing
97 between the major N₂O production processes, i.e. nitrification and denitrification, generally
98 referred to as aerobic and anaerobic N₂O production, with high and low $\delta^{15}\text{N}^{\text{SP}}$, respectively (Sutka
99 et al., 2006). However, despite the advantages of $\delta^{15}\text{N}^{\text{SP}}$ measurements, existing long-term studies
100 have not yet been able to reach a definitive understanding of the $\delta^{15}\text{N}^{\text{SP}}$ -N₂O trend, showing both
101 positive (Bernard et al., 2006; Park et al., 2012; Röckmann and Levin, 2005) and negative
102 tendencies (Röckmann et al., 2003) over the last four decades. This is probably due to an
103 insufficient analytical precision and poor inter-laboratory agreement, in particular as the
104 aforementioned studies are all based on isotope ratio mass spectrometry (IRMS). To retrieve site-
105 specific isotopic information by IRMS, the N₂O⁺ molecular ions and the NO⁺ fragment ions are
106 analyzed and raw data have to be corrected for rearrangements of central and terminal N and ¹⁷O
107 content (Toyoda et al., 2001). Inappropriate correction algorithms and the limited availability of

108 reference materials (Ostrom et al., 2018) further enlarge the analytical uncertainty (Mohn et al.,
109 2014).

110 Seasonal variability in atmospheric N₂O isotopic composition, which could affect the longer-term
111 trends, is still rarely reported in the literature (Park et al., 2012; Toyoda et al., 2013). Moreover,
112 studies of seasonality of N₂O isotopic composition are limited to the recent past since the air
113 samples derived from firn and ice cores suffer from coarse temporal resolution (< 2 samples per
114 year). Park et al. (2012) studied seasonality of atmospheric N₂O isotopic composition by analyzing
115 a set of archived air samples collected from Cape Grim (Australia) using a sophisticated
116 mathematical modeling approach. They found consistent seasonal patterns in $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{18}\text{O}$ and
117 $\delta^{15}\text{N}^{\text{SP}}$ of atmospheric N₂O, showing highest ¹⁵N/¹⁸O enrichment in June and lowest in December.
118 This pattern was negatively correlated with the seasonality of the N₂O mixing ratios (lowest in
119 April-May and highest in December), which is in agreement with a previous study by Nevison et
120 al. (2011). The negative correlation between isotopic composition and mixing ratios has been
121 explained by stratosphere-troposphere exchange (STE), which transports N₂O-depleted but
122 isotopically enriched stratospheric air (prevailing reduction process) into the lower atmosphere
123 (Yung and Miller, 1997). However, in a more recent study from Hateruma Island (Japan), Toyoda
124 et al. (2013) reported insignificant seasonal patterns in atmospheric N₂O isotopocules (smaller
125 variability than measurement precision), despite their finding of a somewhat similar seasonal
126 pattern in N₂O mixing ratio (minimum in July). Although there are interhemispheric differences
127 in N₂O sources and distinct sampling frequencies in the two studies discussed above (2-3 times
128 per year versus monthly), it is noteworthy that both studies observed significantly larger variability
129 in $\delta^{15}\text{N}^{\text{SP}}$ than in $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$. Whether the fluctuations in $\delta^{15}\text{N}^{\text{SP}}$ are mainly caused by the

130 limited repeatability of the chosen analytical techniques or interplay of processes or mechanisms
131 regulating atmospheric N₂O remains to be tested (Park et al., 2012).

132 With inherent selectiveness, in particular for site-specific isotopic composition, laser spectroscopy
133 provides a new analytical approach for direct, precise measurements of all four N₂O isotopocules
134 (Harris et al., 2014; Mohn et al., 2012). The recent development of quantum cascade laser
135 absorption spectroscopy (QCLAS) coupled with an automated preconcentration unit has been
136 applied to measure N₂O isotopocules in ambient air, with comparable precision for $\delta^{15}\text{N}^{\text{bulk}}$ and
137 $\delta^{18}\text{O}$ and superior precision for $\delta^{15}\text{N}^{\text{SP}}$ relative to IRMS systems (Harris et al., 2017; Mohn et al.,
138 2014). Here, we present results from the application of a preconcentration unit coupled to QCLAS
139 to measure atmospheric N₂O isotopocules in background air collected at the high altitude research
140 station Jungfraujoch, Switzerland. Between April 2014 and December 2018, we collected weekly
141 to bi-weekly air samples for N₂O isotopic analyses, in parallel with online measurement of N₂O
142 mixing ratios. To our knowledge, this work reports the first time-series of background atmospheric
143 N₂O isotopic composition using laser spectroscopy. With this unique dataset, we aim to 1)
144 constrain seasonal patterns of three N₂O isotopic signatures at the Jungfraujoch observatory; 2)
145 determine interannual trends in N₂O isotopocules, especially $\delta^{15}\text{N}^{\text{SP}}$; and 3) interpret the observed
146 patterns in N₂O mixing ratios using temporal trends in N₂O isotopic composition and reported
147 isotopic signatures of anthropogenic sources.

148 **2 Materials and Method**

149 **2.1 Site description**

150 The high altitude research station Jungfraujoch (3580 m above sea level), located on the northern
151 ridge of the Swiss Alps, is a well-established site for studying unpolluted atmosphere over Central
152 Europe (e.g. Buchmann et al., 2016). Although the station is located in the free troposphere most
153 of the time, it is occasionally affected by air recently lifted from the planetary boundary layer
154 (Herrmann et al., 2015; Zellweger et al., 2003). Henne et al. (2010) investigated the
155 representativeness of 35 European monitoring stations and categorized Jungfraujoch as “mostly
156 remote”. The Jungfraujoch station is part of several national and international networks, like the
157 meteorological SwissMetNet network operated by MeteoSwiss, the Swiss National Air Pollution
158 Monitoring Network (NABEL), the Global Atmospheric Watch Programme (GAW) of the World
159 Meteorological Organization (WMO) and the Integrated Carbon Observation Systems (ICOS)
160 Research Infrastructure. This results in an extended set of long-term and continuously available
161 parameters such as meteorological variables (Appenzeller et al., 2008), greenhouse gases (Schibig
162 et al., 2015; Sepúlveda et al., 2014; Yuan et al., 2018), CO₂ isotopic composition (Sturm et al.,
163 2013; Tuzson et al., 2011), ozone-depleting substances and their replacement products (Reimann
164 et al., 2008), atmospheric pollutants (Logan et al., 2012; Pandey Deolal et al., 2012; Zellweger et
165 al., 2009) and aerosol parameters (Bukowiecki et al., 2016).

166 **2.2 *In situ* measurements and discrete air sampling (flasks)**

167 *In situ* observations of N₂O mixing ratios commenced at Jungfraujoch in December 2004. Initially,
168 measurements were made with gas chromatograph (GC) (Agilent 6890N, USA) followed by
169 electron capture detection (ECD). The time resolution of these measurements was 24 to 30 minutes.

170 In late 2014, we implemented a cavity-enhanced off-axis integrated cavity out-put spectroscopy
171 analyzer (OA-ICOS, Los Gatos Research Inc., Mountain View, CA, USA), which measures the
172 atmospheric N₂O mixing ratio continuously. Measurements of N₂O mixing ratios at Jungfraujoch
173 were calibrated with three standard gases (319, 327 and 342 nmol mol⁻¹) and accompanied with
174 measurement of a working standard (331 nmol mol⁻¹) every 160 minutes to account for
175 instrumental drift. In addition, short- (two times every 40 hours) and long-term (every 40 hours)
176 target measurements were included to monitor the data quality. Due to the superior measurement
177 precision compared to the GC-ECD method (Lebague et al., 2016), the OA-ICOS record has
178 become the primary time-series since January 2015. The GC-ECD observations continued until
179 summer 2016 for comparison and quality control.

180 Additional parameters, recorded within the NABEL network and the ICOS infrastructure, were
181 included in the analysis below. These data were carbon monoxide (CO) (measured by cavity ring-
182 down spectroscopy; Model G2401, Picarro Inc., USA), the sum of oxidized nitrogen species (NO_y)
183 (measured by chemiluminescence detection after conversion of NO_y to NO on a heated gold
184 catalyst; CLD 89p, Eco Physics, Switzerland) and O₃ (measured by UV absorption; TEI 49i,
185 Thermo Scientific, USA). Details on measurement methods and calibration strategies can be found
186 in Zellweger et al. (2009) for CO, Pandey Deolal et al. (2012) for NO_y and Logan et al. (2012) for
187 O₃.

188 In conjunction with the online measurements, we deployed an automated sampling system (Fig.
189 S1) to collect pressurized air samples in aluminum cylinders from the same air inlet at the Sphinx
190 observatory of the Jungfraujoch station, for subsequent N₂O mixing ratio and isotopic analyses.
191 The sample collection was conducted weekly from April 2014 to February 2016. After a sampling
192 gap of five months due to a technical failure, we reinitiated a bi-weekly sampling, which continued

193 from August 2016 to December 2018. The sampling system, automated by a customized LabVIEW
194 program (National Instruments Corp., USA), consisted of a Nafion drier (PD-100T-48MSS, Perma
195 Pure LLC, USA), a membrane gas compressor (KNF Neuberger, USA; Type N286 series), a 16-
196 port selector valve (EMT2CSD16MWEPPH, VICI AG, Switzerland), and a rack to accommodate
197 nine 2-L aluminum flasks (Luxfer, Messer Schweiz AG, Switzerland). During sample filling, pre-
198 evacuated flasks were first purged with ambient air five times (1 hour), and then filled to 12000
199 hPa within 40 min, resulting in approximately 24 L (298 K and 1000 hPa) of air per flask for
200 isotopic analysis. Air sample filling generally took place between 2:00 and 3:00 pm local time at
201 each sampling day. Sample flasks were sent back to the laboratory at Empa for analyses every few
202 months. For this study, 142 air samples were collected in flasks and analyzed for N₂O isotopocules.

203 **2.3 Analyses of discrete air samples**

204 Discrete air samples were regularly analyzed in batches but not in chronological order to prevent
205 the imprint of analytical drifts on temporal trends of the samples. N₂O mole fractions were
206 analyzed by QCLAS (CW-QC-TILDAS-76-CS, Aerodyne Research Inc., USA) against NOAA
207 standards on the WMO-X2006A calibration scale (Hall et al., 2007), at a precision around 0.1
208 nmol mol⁻¹ (determined with the average of 1-min data).

209 The four most abundant N₂O isotopocules (¹⁴N¹⁴N¹⁶O, 99.03%; ¹⁴N¹⁵N¹⁶O, 0.36%; ¹⁵N¹⁴N¹⁶O,
210 0.36%; ¹⁴N¹⁴N¹⁸O, 0.20%) were analyzed using a customized QCLAS system (Aerodyne Research,
211 Inc., USA) (Heil et al., 2014) coupled with an automated preconcentration device (Mohn et al.,
212 2010). Before entering the pre-concentration unit, sample air is passed through a Sofnocat 423 trap
213 (Molecular Products Limited, GB) to remove CO, and subsequently through an Ascarite trap
214 (Ascarite: 6 g, 10–35 mesh, Sigma Aldrich, Switzerland, bracketed by Mg(ClO₄)₂, 2 × 1.5 g, Alfa
215 Aesar, Germany) to remove CO₂ and water. Approximately 5.5 L of air with a flow of 250 ml min⁻¹

216 ¹ (at 295 K and 3500 hPa) is then passed through a HayeSep D trap cooled to -145 °C to collect
217 N₂O (Mohn et al., 2010). For N₂O release to the multipath cell of the QCLAS, the HayeSep D trap
218 is quickly heated to 10 °C and flushed with high-purity synthetic air (20.5% of O₂ in N₂) carrier
219 gas at a flow rate of 25 ml min⁻¹ (at 295 K and 3500 hPa). A final cell pressure around 16 hPa is
220 achieved, which results in an N₂O mixing ratio of about 45 μmol mol⁻¹. More instrumental details
221 can be found in previous studies (Harris et al., 2017; Mohn et al., 2010, 2012). Sample tanks were
222 each analyzed twice to yield duplicates for N₂O isotopic results, which left sufficient air for amount
223 fraction analysis as described in the previous paragraph.

224 **2.4 Data analyses**

225 We used 10-minute averages of the continuous *in situ* measurements from the Jungfraujoch station
226 across this study. For a point-to-point comparison of continuous and discrete measurements of
227 N₂O mixing ratio, we aggregated 10-minute averages of *in situ* data for the same period when the
228 discrete sample was filled into the cylinder (40 min).

229 In this study, we report abundances of N₂O isotopocules using δ notation (‰) as below:

$$230 \quad \delta X = \frac{(R_{sample} - R_{standard})}{R_{standard}} \quad (1)$$

231 where X refers to ¹⁵N^α (¹⁴N¹⁵N¹⁶O), ¹⁵N^β (¹⁵N¹⁴N¹⁶O) and ¹⁸O (¹⁴N¹⁴N¹⁸O); R refers to the ratio
232 between the amount fractions of the rare isotopocules as mentioned above and the amount fraction
233 of ¹⁴N¹⁴N¹⁶O; isotope standards refer to atmospheric N₂ for ¹⁵N and Vienna Standard Mean Ocean
234 Water (VSMOW) for ¹⁸O.

235 Hence, the total ¹⁵N content of N₂O and site-specific composition of N₂O isotopomers could be
236 further illustrated as δ¹⁵N^{bulk} and δ¹⁵N^{SP}, respectively, according to the equations below:

237
$$\delta^{15}N^{bulk} = (\delta^{15}N^{\alpha} + \delta^{15}N^{\beta})/2 \quad (2)$$

238
$$\delta^{15}N^{SP} = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta} \quad (3)$$

239 Two standards (CG1 and CG2; in 79.5% N₂ and 20.5% O₂) with distinct isotopic signatures ($\delta^{15}N^{\alpha}$
240 = $16.29 \pm 0.07\text{‰}$ (CG1) and $-51.09 \pm 0.07\text{‰}$ (CG2); $\delta^{15}N^{\beta} = -2.59 \pm 0.06\text{‰}$ and $-48.12 \pm 0.04\text{‰}$;
241 $\delta^{18}O = 39.37 \pm 0.04\text{‰}$ and $30.81 \pm 0.03\text{‰}$) were used for calibrating isotopic composition. The
242 calibration gases CG1 and CG2 were calibrated on the Tokyo Institute of Technology (TIT) scale,
243 based on cross-calibration with primary standards assigned by TIT (Mohn et al., 2012, 2014). In
244 addition, CG1 was measured repeatedly between samples and target gases to account for
245 instrumental drift. Both CG1 and CG2 have N₂O mixing ratios of 45 $\mu\text{mol mol}^{-1}$, similar to the
246 N₂O amount fraction of the samples after preconcentration. However, to correct for possible
247 instrumental dependence on N₂O mixing ratio, CG1 was diluted to N₂O mole fractions of 35-40
248 $\mu\text{mol mol}^{-1}$ within each measurement batch. In general, duplicated isotopic measurements of flask
249 samples yielded values of repeatability of 0.10-0.20‰ for $\delta^{15}N^{bulk}$ and $\delta^{18}O$, and 0.15-0.25‰ for
250 $\delta^{15}N^{SP}$.

251 At the beginning of the project, a batch of three cylinders (50 L water volume, Luxfer, Italy) were
252 filled with pressurized ambient air in Dübendorf with an oil-free, three stage compressor (SA-3,
253 Rix Industries, USA) and used as long-term target gases. The pressurized ambient air target gas
254 was analyzed with identical treatment as Jungfrauoch air samples during every analysis batch, to
255 monitor long-term analytical drift. Standard deviations for repeated target gas measurements
256 throughout the period of Jungfrauoch sample measurements, were 0.13‰ for $\delta^{15}N^{bulk}$, 0.21‰ for
257 $\delta^{15}N^{SP}$, and 0.11‰ for $\delta^{18}O$ (Fig. S2).

258 **2.5 Surface air footprint analysis and simulated regional N₂O enhancement**

259 We analyzed the air mass origin at Jungfraujoch by applying the Lagrangian particle dispersion
260 model (LPDM) FLEX-PART in the backward mode (Stohl et al., 2005). The model was driven by
261 meteorological fields taken from the ECMWF-IFS operational analysis cycle, extracted at a
262 resolution of $1^\circ \times 1^\circ$, 90/137 levels globally, and at higher horizontal resolution of $0.2^\circ \times 0.2^\circ$ for
263 central Europe. We released 50000 virtual air parcels every 3 hours at 3000 m a.s.l. from
264 Jungfraujoch to perform backward dispersion simulations over 10 days, which allowed us to
265 calculate surface source sensitivities (concentration footprints). A release height of 3000 m a.s.l.
266 was previously determined to be an optimum for simulating concentration footprints at
267 Jungfraujoch, given the stated horizontal resolution which results in a considerable smoothing of
268 the complex, alpine orography (Keller et al., 2012). The 3-hourly surface footprints for the whole
269 observation period were used to categorize different transport regimes using the clustering
270 approach outlined in Sturm et al. (2013). This allowed us to distinguish among six different source
271 regions: Free Troposphere (FT), Southwest (SW), East (E), Local (L), West (W) and Northwest
272 (NW).

273 Similar to Henne et al. (2016) for CH_4 and based on spatially resolved N_2O emission inventories
274 (Meteotest for Switzerland; EDGAR for Europe), we used the FLEXPART concentration
275 footprints to calculate time-series of atmospheric mole fraction increases at Jungfraujoch resolved
276 by emission sectors (Henne et al., 2016). The emission inventory by Meteotest consists of 12
277 emission sectors, among which all sectors except “organic soils” are comparable to sectors in the
278 EDGAR inventory (See Table S1) (Janssens-Maenhout et al., 2019). To improve seasonal
279 representation of the emissions in our model, we used a monthly resolved, optimized version of
280 the emission inventory, which was obtained through inverse modeling using the N_2O atmospheric
281 mole fractions observed between March 2017 and September 2018 at the tall tower site

282 Beromuenster on the Swiss plateau (Henne et al., 2019). Therefore, in this study, source
283 contributions to Jungfraujoch were estimated specifically for the period mentioned above.

284 **2.6 Evaluation of seasonal pattern and interannual trend for time-series**

285 To explore seasonality and interannual trends, we fit the time-series of *in situ* measurements of
286 N₂O and O₃ mixing ratios, NO_y-to-CO ratios and isotopic measurements of N₂O with polynomial
287 functions and Fourier series (four harmonics for *in situ* measurements and two harmonics for
288 discrete measurements) (Thoning et al., 1989). Time-series were then decomposed into a linear
289 trend, seasonal variability (per 12 months) and residuals. This fit was conducted with a nonlinear
290 least-squares (NLS) model with R-3.5.3 (R Core Team, 2016). The detrended seasonality was
291 examined by comparing peak-to-peak amplitudes with our analytical precisions and the
292 uncertainty given by the one standard deviation of monthly residuals. To determine interannual
293 trends, a linear regression was applied to both the raw and the deseasonalized datasets. The
294 significance level is set to $p < 0.01$. The interannual trends for N₂O mixing ratios were found to be
295 little affected by seasonality, so growth rates were determined only based on the raw datasets.

296 Although Jungfraujoch is a remote site, episodic influence from the planetary boundary layer can
297 be observed at the station (Pandey Deolal et al., 2012; Zellweger et al., 2003). For evaluating trends
298 of N₂O mixing ratio measurements, we filtered out *in situ* data with significant influence of plenary
299 boundary layer, in order to represent a major air mass footprint from the free troposphere (FT). In
300 addition to the air transport regimes, an alternative filtering criterion for the free troposphere was
301 based on the published mean ranges of NO_y mixing ratios (501-748 pmol mol⁻¹ depending on the
302 season) and NO_y to CO ratios (0.003-0.005 depending on the season) at Jungfraujoch (Zellweger
303 et al., 2003). This criterion is less strict than that given by footprint analyses (Herrmann et al.,

304 2015). After applying this criterion to the isotopic time-series (which led to the exclusion of 32
305 measurement points), we re-evaluated the seasonal and interannual trends in the N₂O isotopic
306 composition. In addition, because of the strong variability observed for isotopic data during the
307 first 1.5 years (until February 2016), we performed an independent evaluation for the time-series
308 starting from August 2016.

309 **2.7 Two-box model simulation**

310 A two-box model representing a well-mixed troposphere and stratosphere was used to estimate the
311 anthropogenic N₂O source strength and isotopic composition from the trends measured at
312 Jungfraujoch, similar to the approaches used by several previous studies (Ishijima et al., 2007;
313 Röckmann et al., 2003; Schilt et al., 2014; Sowers et al., 2002). The input variables used to run the
314 model are given in Table S2. 200 iterations of the model were run using a Monte Carlo-style
315 approach to approximate the uncertainty considering the uncertainty distribution for each input
316 variable as given in Table S2. All variables were set independently within the Monte Carlo
317 approximation except for preindustrial N₂O life time (τ_{PI}), which was fixed to 106% of the present-
318 day N₂O life time τ_{PD} (Prather et al., 2015).

319 Within each iteration of the model, the preindustrial N₂O burden was first described, assuming
320 steady state in the preindustrial era. The preindustrial stratospheric N₂O mixing ratio ($c_{S,PI}$)
321 (270 ± 7.5 nmol mol⁻¹) was taken from Sowers et al. (2002):

$$322 \quad 0 = F_{ex} (c_{PI} - c_{S,PI}) - (M_{PI} + M_{S,PI})/\tau_{PI} \quad (4)$$

323 where F_{ex} refers to the troposphere-stratosphere exchange rate; c_{PI} refers to the preindustrial
324 tropospheric N₂O mixing ratio; and M_{PI} and $M_{S,PI}$ are the masses of N₂O in the troposphere and
325 stratosphere respectively. The preindustrial terrestrial flux in Sowers et al. (2002) (equation 2) was

326 used here assuming no anthropogenic emissions. The delta values for the preindustrial stratosphere
327 and the fractionation factor for the stratospheric sink were taken from equations 6 and 7 from
328 Sowers et al. (2002) assuming steady state and no anthropogenic emissions. The model was run
329 with a yearly time step starting from the preindustrial assuming that anthropogenic emissions
330 began in 1845 (Sowers et al., 2002). For each year of the model run, the anthropogenic flux was
331 calculated according to the exponential increase described by Sowers et al. (2002):

$$332 \quad F_{\text{anth},t} = e^{\alpha(t-t_0)} - 1 \quad (5)$$

333 where t is the current year, $t_0 = 1845$ and α is the growth rate (assumed to be constant). The rates
334 of change for tropospheric and stratospheric N₂O mixing ratios were then retrieved from equations
335 2 and 3 in Sowers et al. (2002), and for the isotopic composition of stratospheric and tropospheric
336 N₂O from equations 6 and 7 in Sowers et al. (2002).

337 The values of the parameters describing the anthropogenic flux were optimized to fit both the trend
338 and the absolute values for the five years of Jungfraujoch isotope data, and the mixing ratio data
339 from the Jungfraujoch flasks and *in situ* data since 2005 (GAW data source). The uncertainties in
340 α and in the anthropogenic source isotopic signatures were approximated by one standard
341 deviation of values derived from repeated model runs.

342 **2.8 Evaluation of the combined effects from STE and soil emission on $\delta^{15}\text{N}^{\text{SP}}$**

343 To evaluate the combined effects of STE and soil emission on the seasonal variability of $\delta^{15}\text{N}^{\text{SP}}$
344 (i.e. August minima), we made a mixing calculation as below:

345 *Soil emission:* Based on the determined seasonality of N₂O mole fraction at Jungfraujoch, the
346 maximum N₂O mole fraction enhancement was approximately 0.2 nmol mol⁻¹ above baseline (Fig.

347 1b). Hence, we assumed N₂O enhancement from soil emission to be close to 0.15 to 0.20 nmol
348 mol⁻¹, which is close to the maximum N₂O enhancement in our observation. The isotopic effect
349 from soil emission can be derived from the difference between soil emission (7.2‰; Table S1) and
350 tropospheric air (18‰, Fig. 2) in δ¹⁵N^{SP}, i.e. -10.8‰.

351 *Mixing with stratospheric air:* The minimum of N₂O mole fraction in August (-0.20 nmol mol⁻¹)
352 is likely to be the result of both N₂O mole fraction enhancement from soil emission and N₂O mole
353 fraction depletion due to STE. Given the assumed N₂O enhancement from soil emission, we
354 estimated the N₂O depletion due to STE as -0.35 to -0.40 nmol mol⁻¹. The isotopic effect due to
355 mixing with stratospheric air can be approximated using the apparent isotopic fractionation ε_{app}
356 (Kaiser et al., 2006), which was derived from the slope of Rayleigh plot with normalized N₂O
357 mole and isotope ratios. For ¹⁵N^{SP}, ε_{app} is calculated from the difference between ¹⁵N/¹⁴N isotope
358 fractionations at the central and terminal N atoms, i.e. α_{ε_{app}} - β_{ε_{app}}. Therefore, for the lower
359 stratosphere, ε_{app}(¹⁵N^{SP}) was calculated to be about -15‰ (see more details in Kaiser et al., 2006).

360 *Overall effect:* Combing the isotope effects and contributions to the change of N₂O mole fraction
361 by the two processes, the net effect is [(-0.35 to -0.40 nmol mol⁻¹) (-15‰) + (0.15 to 0.20 nmol
362 mol⁻¹) (-10.8‰)] / (330 nmol mol⁻¹) ≈ 0.01‰. Such isotope effect is below our analytical
363 precision and too small to be measured in the background atmosphere.

364 2.9 “Bottom-up” estimates of source isotopic signatures

365 To gauge the accuracy of the two-box model, we deployed a “bottom-up” approach as an
366 alternative method of estimating the N₂O source signatures. The isotopic signatures of most N₂O
367 source sectors given in the Meteotest/EDGAR emission inventory are available from the literature,
368 except for the “Refinery” (Table S1). As “Refinery” generally contributes only about 0.02% of the

369 N₂O emission at Jungfraujoch, it was excluded for source isotopic signature estimation. The
370 simulated N₂O emissions by variable sources were categorized according to the EDGAR emission
371 types (Janssens-Maenhout et al., 2019). We then calculated isotopic signatures for the overall
372 source and the anthropogenic sources alone (excluding indirect natural emission) as weighted
373 averages.

374 **3 Results**

375 **3.1 Atmospheric N₂O mixing ratios at Jungfraujoch**

376 We observed a linear growth of atmospheric N₂O at Jungfraujoch during the period 2014-2018
377 (Fig. 1a). A point-to-point comparison of discrete and *in situ* measurements showed good
378 agreement, in particular after the first year (2015-2018), where the data quality of *in situ*
379 measurements was largely improved due to the implementation of the more precise laser
380 spectroscopy method as compared to GC-ECD (Fig. S31b). The improvement in analytical
381 precision for N₂O mixing ratio was due to better temporal coverage by the OA-ICOS instrument,
382 in contrast with the GC analyses which conduct one measurement per 24-30 minutes. The annual
383 growth rates from 2014 to 2018 determined with *in situ* measurements were 0.880 ± 0.001 and
384 0.993 ± 0.001 nmol mol⁻¹ a⁻¹ with and without GC-ECD measurements in 2014, respectively. This
385 difference in N₂O growth rates is probably due to the limited data quality of GC-ECD, although a
386 lower growth rate in 2014 compared to 2015-2018 cannot be excluded. It is noteworthy that the
387 N₂O growth rate determined for 2015 to 2019 at Jungfraujoch is slightly above the global mean
388 growth rate for the recent decade reported by NOAA (0.93 ± 0.03 nmol mol⁻¹ a⁻¹) (WMO, 2018).
389 If we filter the *in situ* dataset to examine only the “free troposphere” periods, we obtain a lower
390 increase (0.858 ± 0.002 nmol mol⁻¹ a⁻¹). By comparison, the absolute growth rate determined from
391 the discrete gas samples was even lower albeit larger uncertainty (0.813 ± 0.027 nmol mol⁻¹ a⁻¹).

392 A significant seasonal pattern was observed for N₂O mixing ratios measured *in situ*, with a
393 maximum in early summer and a minimum in late summer (Fig. 4b1c). For discrete N₂O
394 measurements a similar trend was observed, but the detrended seasonality was not significant (Fig.
395 S3), which might be due to the much lower number of samples (Fig. S4).

396 3.2 Interannual trends of N₂O isotopic composition and anthropogenic source signatures

397 Time-series of $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ for atmospheric N₂O at Jungfraujoch are shown in Figure
398 2. The NLS model simulation accounts well for the variabilities of isotopic time-series. Interannual
399 trends of three isotopic deltas were determined for both raw and deseasonalized datasets by linear
400 regression (Table 43). The deseasonalized interannual trends were slightly smaller than the trends
401 determined with the raw datasets. For the whole dataset, the deseasonalized trend indicates a
402 significant decrease in $\delta^{15}\text{N}^{\text{bulk}}$, of $-0.052\pm 0.012\text{‰ a}^{-1}$. In contrast, deseasonalized time-series of
403 $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ increased, albeit insignificantly, by $0.065\pm 0.027\text{‰ a}^{-1}$ and $0.019\pm 0.011\text{‰ a}^{-1}$,
404 respectively. The trends determined for periods with major air mass footprints from the free
405 troposphere were close to those calculated for the whole dataset, except that $\delta^{15}\text{N}^{\text{SP}}$ trends
406 decreased after filtering out the samples with significant impact from plenary boundary layer. This
407 indicates that N₂O interannual trends observed at Jungfraujoch are of regional relevance, despite
408 the fact that a small impact from local sources can be seen. Because of the observed irregular
409 variability and the change in sampling frequency (though no change in daily sampling time) in our
410 dataset, we separated the time-series into two phases: April 2014-February 2016 (first phase;
411 weekly sampling) and August 2016-December 2018 (second phase; bi-weekly sampling). In the
412 first phase, the rates of increase in $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ were almost one order of magnitude larger than
413 over the whole dataset. This is most likely due to the unexpectedly low $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ in summer
414 2014 followed by a distinct increase in winter 2014-2015, which results in large rates of increase
415 over short periods. Such growth rates were not seen in the second phase, when both $\delta^{15}\text{N}^{\text{SP}}$ and
416 $\delta^{18}\text{O}$ showed small and insignificant variations. $\delta^{15}\text{N}^{\text{bulk}}$ displayed a decreasing interannual trend
417 in both phases; however, the rate of decrease was larger in the second phase ($-0.130\pm 0.045\text{‰ a}^{-1}$).

418 We tuned our two-box model to best match the observed N₂O mixing ratios and isotopic
419 composition at Jungfraujoch. An estimate of anthropogenic emissions and source signatures is
420 given in Table 24. For 2018, annual N₂O emissions were estimated to be 8.6±0.6 Tg N₂O-N a⁻¹
421 equivalents. The average isotopic signatures for anthropogenic sources were -8.6±4‰, 34.8±3‰
422 and 10.7±4‰ for δ¹⁵N^{bulk}, δ¹⁵N^{SP} and δ¹⁸O, respectively, which are clearly lower than those for
423 preindustrial N₂O in the tropospheric background (Table S2; Toyoda et al., 2013).

424 3.3 Seasonal variation of N₂O isotopic composition

425 δ¹⁵N^{SP} of N₂O showed the most pronounced variability among all isotopic time-series (Fig. 2),
426 spanning 2.5‰ for individual flask sample measurements. Seasonal variability was estimated with
427 the NLS model and presented as mean seasonal cycles (Fig. 3). For δ¹⁵N^{SP} a “summer minimum”
428 was found regardless of whether the entire dataset or only the second phase was considered (Fig.
429 3), although seasonal variability of the second time-series was smaller and showed the minimum
430 occurring earlier. The seasonal pattern of δ¹⁵N^{bulk} determined from the whole dataset indicates a
431 significant summer maximum, but this was not seen when only the data from the second phase
432 was taken, as there was no significant seasonal pattern over this period alone. For δ¹⁸O, we
433 observed only small temporal variability and a lack of seasonal pattern. In addition, seasonal
434 variations of time-series filtered for free troposphere were evaluated; these show temporal patterns
435 similar to the whole dataset (Fig. S5).

436 3.4 Air mass origin and *in situ* measurements at Jungfraujoch

437 Back-trajectory simulations indicate six major transport clusters during 2014-2018, as shown in
438 Figure 4a. Four of these transport regimes (SW, E, L and NW) dominate, accounting for about 60-
439 90% coverage of the whole period. By contrast, the free troposphere cluster only represents 10-

440 20% of the data. Averaged monthly contributions of transport clusters are shown in Figure 4b,
441 with more pronounced impact by the L, E and NW regions in summer and stronger contribution
442 by FT and SW in winter. The source patterns of the air masses at Jungfraujoch were generally
443 consistent across the years in the present study. However, an apparent discrepancy was found for
444 discrete sampling times in the last two years (e.g. particularly low contribution from SW) which
445 is most likely due to the low and variable sampling frequency of the discrete sample collection
446 (Fig. 4b).

447 The detrended seasonal variability of *in situ* measurements indicates summer maxima for NO_y
448 mixing ratios as well as NO_y-to-CO ratios at Jungfraujoch (Fig. S6). This likely indicates stronger
449 exchange with the polluted planetary boundary layer in summer (Herrmann et al., 2015; Zellweger
450 et al., 2003), which is consistent with the seasonal pattern of air mass footprint derived from back-
451 trajectory simulations. The late spring-to-summer maxima for O₃ mixing ratios may be attributed
452 to air mixing with stratosphere and/or planetary boundary layer, similar to the findings from a
453 previous study at Jungfraujoch (Tarasova et al., 2009). On the other hand, CO shows a maximum
454 in early spring and decreases in summer when its atmospheric lifetime is shortest. Atmospheric
455 O₃, NO_y and CO measurements during our discrete sampling periods also well represented
456 seasonal variability shown for *in situ* measurements, except for 2016-2017 where there was a five-
457 month sampling gap (Fig. S5).

458 Comparisons of air mass footprints as well as O₃, NO_y and CO mixing ratios between *in situ* and
459 discrete sampling indicate that the discrete sampling covers the main air source regions and
460 variabilities in local pollution/free troposphere fairly well (Figs. 4 and S6). In the second phase
461 (2016-2018), the less frequent sampling impedes evaluation of the seasonal and interannual
462 variabilities.

463 **3.5 Relationship between N₂O isotopic signatures and air mass footprints**

464 We categorized N₂O mixing ratio and isotopic signature time-series into subsets based on the six
465 air mass transport clusters. One-way ANOVA among clusters indicates that N₂O mixing ratios in
466 air masses originating from cluster L were significantly higher and those from clusters FT and W
467 were significantly lower than the others (Fig. 56). In accordance with the pattern found for mixing
468 ratios, $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ were high for cluster FT, and low for cluster L. For $\delta^{15}\text{N}^{\text{bulk}}$, little difference
469 between transport clusters was detected.

470 **4 Discussion**

471 **4.1 Quality assurance of isotopic measurements**

472 This study reports the first results of background N₂O isotopic measurements based on a laser
473 spectroscopic technique. Benefiting from the preconcentration process, we achieved measurement
474 repeatability for a target gas of 0.10-0.20‰ for $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ (Fig. S2), which is comparable
475 to that of IRMS measurements of ambient atmosphere (Park et al., 2012; Prokopiou et al., 2017;
476 Röckmann et al., 2003; Toyoda et al., 2013). The long-term robustness of our technique is adequate
477 for disentangling both seasonal and interannual temporal variability as shown in Figure 2. In
478 particular, our repeatability of target measurements for $\delta^{15}\text{N}^{\text{SP}}$ (0.15-0.25‰) appears to be better
479 than previous studies measuring background atmosphere or firm air (0.8‰, Park et al., 2012; 0.3‰,
480 Prokopiou et al., 2017; 0.3‰, Toyoda et al., 2013).

481 **4.2 Seasonal variabilities of atmospheric N₂O isotopic composition**

482 *In situ* measurements of N₂O mixing ratios showed a clear early summer maximum and late
483 summer minimum (Fig. 1). Such a seasonal pattern was previously found for a number of NOAA
484 and AGAGE sites analyzing long-term N₂O records in the NH (Jiang et al., 2007; Nevison et al.,
485 2011). One explanation of the late-summer minimum is a strong influence of the STE process in
486 this period, which transports N₂O-depleted but isotopically enriched air downward from the
487 stratosphere into the troposphere (Park et al., 2012; Snider et al., 2015b). During the late summer
488 at Jungfraujoch, we find strong enrichment of ¹⁵N in atmospheric N₂O according to the detrended
489 seasonality for the whole dataset (Fig. 3). This is supported by a FLEXPART model simulation of
490 the contribution of upper tropospheric air to Jungfraujoch station, showing highest contributions
491 in August (Fig. S7S4; Henne et al., Personal Communication). At Hateruma Island, Japan, Toyoda

492 et al. (2013) observed a seasonal pattern of atmospheric N₂O mixing ratios which is comparable
493 with our study, but found insignificant variations of isotopic composition. On the other hand, N₂O
494 seasonal variability could be influenced by oceanic emission sources (Jiang et al., 2007; Nevison
495 et al., 2005), complicating the explanations for the observed temporal patterns. For example, in
496 another study looking at archived air from Cape Grim, Australia, Park et al. (2012) detected an
497 April-May minimum and a November-December maximum for N₂O. This is expected for the SH,
498 as STE is most prevalent in April (Nevison et al., 2011). They observed negative correlations of
499 $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{18}\text{O}$ with N₂O mixing ratios, appearing to support the idea that the STE process
500 is responsible for seasonal variabilities in N₂O mixing ratios and isotopic composition at Cape
501 Grim. However, the seasonal cycle for $\delta^{15}\text{N}^{\alpha}$ was much larger than $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$, which could
502 not be explained by STE alone. They suggested that the seasonal patterns of N₂O isotopes at Cape
503 Grim may be due to mixing between oceanic sources (high N₂O with low ¹⁵N and ¹⁸O) and STE
504 (low N₂O with high ¹⁵N and ¹⁸O) (Nevison et al., 2011; Park et al., 2012). However, because we
505 observed a concurrent minimum of $\delta^{15}\text{N}^{\text{SP}}$ and maximum of $\delta^{15}\text{N}^{\text{bulk}}$ in July-August with low N₂O
506 at Jungfraujoch (Fig. 3), additional mechanisms must be considered here.

507 Regional model simulations based on Swiss N₂O emissions derived from the inverse method were
508 used to explore contributions from different sources to the variability in N₂O enhancements at
509 Jungfraujoch. As shown in Figure 6a7a&6b7b, soil emissions, including direct and indirect
510 emissions from agricultural lands and emissions from (semi-)natural areas, account for more than
511 70% of the total N₂O enhancements, while manure and waste management contribute another 20%.

512 Total N₂O enhancements appeared to be highest in May to July (Fig. 6e7c), in accordance with the
513 highest contribution by soil emissions. The early-to-middle summer maximum in the simulated
514 N₂O enhancements is comparable with maximum of N₂O mixing ratios in early summer as

515 observed at Jungfraujoch (Fig. ~~1b~~1c). This underlines the importance of soil emission in
516 accounting for atmospheric N₂O variability (Saikawa et al., 2014). In late summer, the minimum
517 of $\delta^{15}\text{N}^{\text{SP}}$ (Fig. 3) may be then attributed to the influence of soil emitted N₂O, which has lower
518 $\delta^{15}\text{N}^{\text{SP}}$ ($7.2\pm 3.8\text{‰}$; Table ~~S~~1) than the troposphere (Fig. 2). However, the STE process, which
519 resulted in the minimum of N₂O mixing ratio, likely contributes a positive isotope effect in the
520 meanwhile (Kaiser et al., 2006). In order to evaluate the combined effect of STE and soil emission
521 on $\delta^{15}\text{N}^{\text{SP}}$ in late summer, we applied a mixing calculation. Such estimate was made based on the
522 approximated N₂O enhancement/depletion contributed by the two processes and the assumed
523 isotope effects (see more details in M&M). The mixing calculation indicated an overall isotope
524 effect of about 0.01‰, which is extremely small and below our analytic precision. This practice
525 suggests that it is still challenging to build a direct link ~~of~~between N₂O sources/processes and~~with~~
526 the observed isotope signature in the background atmosphere. It is also noteworthy that the $\delta^{15}\text{N}^{\text{SP}}$
527 used in the calculation ($7.2\pm 3.8\text{‰}$) may underestimate the isotope effects of soil emission, given
528 that denitrification, as a major N₂O process in soils, produces N₂O with $\delta^{15}\text{N}^{\text{SP}}$ close to 0‰ (Sutka
529 et al., 2006). Previous field studies have demonstrated that low- $\delta^{15}\text{N}^{\text{SP}}$ N₂O emissions ($\sim 0\text{‰}$), i.e.
530 following the denitrification pathway, predominates during summer periods at Swiss (Wolf et al.,
531 2015) and German (Ibraim et al., 2019) grasslands. By contrast, the influence of biogeochemical
532 processes (nitrification and denitrification) on $\delta^{15}\text{N}^{\text{bulk}}$ is generally smaller than that on $\delta^{15}\text{N}^{\text{SP}}$
533 (Toyoda et al., 2011), and such effect on $\delta^{15}\text{N}^{\text{bulk}}$ are usually overwritten by the wide range of
534 isotopic signatures in soil N substrates (Sutka et al., 2006). Hence, given the distinct $\delta^{15}\text{N}^{\text{bulk}}$
535 maximum and N₂O minimum in late summer during our observation (Figs. 1 and 3), we suggest
536 that the STE process is mainly responsible for the seasonal variability in $\delta^{15}\text{N}^{\text{bulk}}$.

537 The footprint analyses based on air mass residence time revealed a seasonal pattern, with a higher

538 contribution of background air from the FT and SW regions in winter and more pronounced
539 contribution of local planetary boundary layer air from the L, E and NW regions in summer (Fig.
540 4b). The higher frequency of air mass footprints recently in contact with the surface in summer is
541 consistent with inverse modeling results, indicating a larger contribution of soil N₂O emissions in
542 June/July (Fig. 67). For the air mass regime representing the free troposphere, N₂O mixing ratios
543 observed at Jungfraujoch were significantly below the average, while $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ were higher
544 (Fig. 56). By contrast, the local cluster (L) representing a strong impact from the planetary
545 boundary layer had higher N₂O mixing ratios and lower isotopic signatures (except $\delta^{15}\text{N}^{\text{bulk}}$) than
546 the other source regions. In addition, the ratio of NO_y to CO, which is a more straightforward
547 indicator of the free troposphere (Zellweger et al., 2003), show significant negative correlations
548 with $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$, but not with $\delta^{15}\text{N}^{\text{bulk}}$ (Fig. S8). This further suggests that the seasonal
549 variability of $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ observed at Jungfraujoch is most likely influenced by ground-
550 derived emissions, while fluctuations in N₂O mixing ratios and $\delta^{15}\text{N}^{\text{bulk}}$ are possibly driven by STE.
551 Considering the complexity in mechanisms responsible for N₂O isotopic variations, we strongly
552 recommend more field measurements of N₂O isotopic signatures at higher frequency and at
553 different background sites, in order to cover spatial and temporal variability in N₂O sources. For
554 example, in the second phase, we only detected a significant seasonality of $\delta^{15}\text{N}^{\text{SP}}$, with a minimum
555 in July, which is one month earlier than the summer minimum found for the whole dataset (Fig.
556 3). This may be attributed to a difference in source regions, as Northwest regions appeared to be
557 significantly more important during 2017 (second phase). However, due to low sampling
558 frequency, it is challenging to overcome the large uncertainty in seasonality analysis for a two-
559 year period such as the second phase.

560 Based on our bottom-up approach, we simulated isotopic signatures for the overall N₂O sources

561 responsible for the N₂O mixing ratio increase in the atmosphere (Fig. S9). However, the
562 interpretation of simulated versus observed variability in N₂O isotopic composition was difficult,
563 except for the somewhat similar patterns in $\delta^{18}\text{O}$. Our results suggest a limitation in the current
564 knowledge and literature values on isotopic signatures of most N₂O sources. In addition, most N₂O
565 sources may not exhibit a well-defined isotopic signature but a range of values regulated under a
566 number of processes/environmental factors. For example, isotopic signatures of soil-derived N₂O
567 are often determined by an interaction of several soil and climatic factors. It might be possible in
568 the future to model these changes implementing isotopes in ecosystem models, as recently
569 demonstrated by Denk et al. (2019).

570 **4.3 Interannual trends of atmospheric N₂O isotopic composition**

571 Over a period of almost five years, our observations show an interannual increase in N₂O mixing
572 ratio and decrease in $\delta^{15}\text{N}^{\text{bulk}}$ (Fig. 710). This is to be expected, assuming that the atmospheric N₂O
573 increase is primarily attributed to anthropogenic sources, which emit isotopically lighter N₂O
574 relative to the tropospheric background (Table S1) (Rahn and Wahlen, 2000). Compared to several
575 studies on firn air (Ishijima et al., 2007; Röckmann et al., 2003) and surface air (Park et al., 2012;
576 Röckmann and Levin, 2005; Toyoda et al., 2013), the rate of decrease for $\delta^{15}\text{N}^{\text{bulk}}$ at Jungfraujoch
577 is relatively high (-0.05 to -0.06 ‰ a⁻¹, Table 43). Such a discrepancy in the $\delta^{15}\text{N}^{\text{bulk}}$ trend could
578 be due to a large contribution of terrestrial N₂O emission from the European continent to
579 Jungfraujoch (Figs. 46 and 75), as N₂O originating from soil emissions is significantly more
580 isotopically depleted than that of oceanic sources (Snider et al., 2015b). Nevertheless, our
581 observation period is shorter than that of other studies, so the interannual trends determined here
582 are more likely affected by year-to-year variability. Among all reported records, the decrease of
583 $\delta^{15}\text{N}^{\text{bulk}}$ observed at Hateruma Island was the most up-to-date and smallest (-0.020-0.026‰ a⁻¹)

584 (Toyoda et al., 2013). The authors argued that the smaller declining trend for $\delta^{15}\text{N}^{\text{bulk}}$ may be
585 explained by the recent increase in anthropogenic isotopic ratios particularly for agricultural N_2O
586 emissions, although Ishijima et al. (2007) suggested a decline in both $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ in
587 anthropogenic N_2O from 1952-1970 to 1970-2001 based on inverse modeling.

588 For the interannual trends observed at Jungfraujoch, it is noteworthy to point out that our
589 observations covering a rather short period may lead to large uncertainties despite statistical
590 significance. The discrepancy found in the trends between the first and second phases indicates
591 that variability of N_2O isotopic composition is likely to obscure interannual trends over shorter
592 periods (Toyoda et al., 2013). Hence, extended time-series of isotopic measurements are needed
593 to reevaluate, for example, the observed tendency of increase in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}^{\text{SP}}$ at Jungfraujoch
594 (Table 43; only significant during the first phase). For $\delta^{18}\text{O}$ of atmospheric N_2O , a generally
595 declining trend smaller than that of $\delta^{15}\text{N}^{\text{bulk}}$ has been indicated by a number of observations
596 (Bernard et al., 2006; Ishijima et al., 2007; Park et al., 2012; Röckmann et al., 2003; Röckmann
597 and Levin, 2005). This is expected as $\delta^{18}\text{O}$ of anthropogenic N_2O is not much different from that
598 of the natural background, assuming that the oxygen atom in N_2O is largely derived from soil water
599 and ambient oxygen during production (Rahn and Wahlen, 2000).

600 It is still a challenging task to disentangle interannual trends of $\delta^{15}\text{N}^{\text{SP}}\text{-N}_2\text{O}$ in the background
601 atmosphere, due to limitations in analytical repeatability and precision (Harris et al., 2017; Mohn
602 et al., 2014). Past results have reached inconsistent conclusions, showing positive (Bernard et al.,
603 2006; Park et al., 2012; Prokopiou et al., 2017; Röckmann and Levin, 2005) or negative
604 (Röckmann et al., 2003; Toyoda et al., 2013) trends of similar magnitude (Fig. 710). On the one
605 hand, the negative trend in $\delta^{15}\text{N}^{\text{SP}}$ could be explained by the significantly lower $\delta^{15}\text{N}^{\text{SP}}$ from
606 anthropogenic sources (e.g. agricultural sources; Table S1) than of the tropospheric background

607 (near 18‰; Fig. 107). On the other hand, Park et al. (2012) suggested that the increase of $\delta^{15}\text{N}^{\text{SP}}$
608 in the atmospheric N_2O may reflect a global increase in importance of the contribution by
609 nitrification (high- $\delta^{15}\text{N}^{\text{SP}}$ process) to agricultural N_2O emissions. This is based on the assumption
610 that the growth of N_2O emissions is largely due to enhanced fertilizer application which promotes
611 nitrification activity (Pérez et al., 2001; Tian et al., 2019). The observed mean increase rate of 0.02‰
612 a^{-1} for $\delta^{15}\text{N}^{\text{SP}}$ by Park et al. (2012) could then be translated into an increase of 13-23% for the
613 relative amount of nitrification-derived N_2O between 1750 and 2005. However, this should be
614 further evaluated with more frequent sampling (Park et al. (2012) only sampled 1-6 times per year)
615 and tested with isotopic measurements across the NH, where agricultural N_2O emissions are more
616 dominant than in the SH. In addition, the strong seasonal pattern of $\delta^{15}\text{N}^{\text{SP}}$ at Jungfraujoch suggests
617 that seasonal variations of $\delta^{15}\text{N}^{\text{SP}}$ in response to climatic or source factors are crucial and must be
618 taken into consideration for evaluating interannual $\delta^{15}\text{N}^{\text{SP}}$ trends.

619 **4.4 Simulated anthropogenic N_2O sources with the two-box model and comparison with** 620 **other studies**

621 To further evaluate anthropogenic source signatures of N_2O isotopic composition, we applied a
622 two-box model representing a well-mixed troposphere and stratosphere (Röckmann et al., 2003;
623 Schilt et al., 2014; Sowers et al., 2002). The model runs with the whole dataset and the dataset
624 filtered for free-troposphere only (Table 24) exhibit statistically identical results, supporting that
625 our model estimates, with observations at Jungfraujoch, are representative of the background
626 atmosphere. The simulated trends of the N_2O mixing ratios and isotopic composition show a
627 gradual increase in N_2O and decrease in the isotopic signatures (see Fig. 107), which agree with
628 existing observations within the model uncertainty. However, this does not hold for individual
629 studies considered separately. For example, the N_2O mixing ratios observed by Röckmann et al.

630 (2003) and Prokopiou et al. (2017) would lead to a higher preindustrial N₂O compared to our
631 model simulation, which is likely due to the uncertainty in the firm air records (Prokopiou et al.,
632 2017).

633 We compared the anthropogenic isotopic signatures determined by our two-box model with other
634 similar studies in Table 24. Our estimates generally lie within the ranges given in the earlier studies
635 (Ishijima et al., 2007; Park et al., 2012; Prokopiou et al., 2017; Röckmann et al., 2003; Sowers et
636 al., 2002; Toyoda et al., 2013). However, isotopic signatures of N₂O sources estimated for 2018 in
637 this study are higher in $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ (by 4-8‰), and lower in $\delta^{15}\text{N}^{\text{SP}}$ (by 2-7‰) than model
638 estimates for the early 2000s from two other studies from SH (Park et al., 2012; Prokopiou et al.,
639 2017). Such differences in $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ could be related to interhemispheric differences, as
640 the relative contributions of N₂O sources vary between the two hemispheres (Toyoda et al., 2013).
641 Also, more interestingly, this could suggest a shift in the N₂O source isotopic signatures over the
642 last few decades. For example, an increase of $\delta^{15}\text{N}^{\text{bulk}}$ in anthropogenic N₂O sources over time
643 may be attributed to growing contributions of other industrial/waste sources with high $\delta^{15}\text{N}^{\text{bulk}}$
644 (Prokopiou et al., 2017). In addition, if the assumption of increasing $\delta^{15}\text{N}^{\text{bulk}}$ and decreasing $\delta^{15}\text{N}^{\text{SP}}$
645 in anthropogenic N₂O sources over time holds, it points to a recently growing contribution of
646 denitrification relative to nitrification, to the global atmospheric N₂O increase (Sutka et al., 2006;
647 Toyoda et al., 2013). By contrast, Park et al. (2012) and Prokopiou et al. (2017) proposed an
648 increasing importance of nitrification for anthropogenic N₂O emissions based on the increasing
649 $\delta^{15}\text{N}^{\text{SP}}$ trend since 1940. This may suggest that a strong climate change feedback has recently
650 resulted in significant shifts in N₂O source process, hence twisting the isotopic signatures of
651 anthropogenic sources (Griffis et al., 2017; Xu-Ri et al., 2012). Alternatively, the uncertainty in
652 determining N₂O isotopic signatures in the background atmosphere and inter-laboratory

653 comparability may play a role in the observed discrepancy.

654 Given the strong heterogeneity in source contributions to N₂O emissions around the globe
655 (Saikawa et al., 2014), current two- and four-box model estimates based on observations at
656 individual sites or regions are likely to reflect latitudinal or even interhemispheric differences in
657 anthropogenic isotopic signatures. On the other hand, previous discussions of the model
658 sensitivities by Röckmann et al. (2003) and Toyoda et al. (2013) have suggested that anthropogenic
659 isotopic values are most sensitive to the trends in tropospheric isotopic values and the relative
660 difference in tropospheric isotopic values between present and preindustrial times. For example,
661 given the similar parameters used for preindustrial times as our study, Park et al. (2012) observed
662 much lower $\delta^{15}\text{N}^{\text{bulk}}$ in the recent troposphere than in our case, hence resulting in significantly
663 lower $\delta^{15}\text{N}^{\text{bulk}}$ for the anthropogenic source. Furthermore, Park et al. (2012) and Prokopiou et al.
664 (2017) simulated a positive trend in $\delta^{15}\text{N}^{\text{SP}}$ relative to preindustrial times, which in return resulted
665 in a much higher $\delta^{15}\text{N}^{\text{SP}}$ for the anthropogenic sources.

666 Using an alternative bottom-up approach, we estimated the anthropogenic source isotopic
667 signatures based on the N₂O emission inventory simulated for Jungfraujoch and published source
668 isotopic signatures as summarized by Harris et al. (2017) (Table S1). The retrieved anthropogenic
669 isotopic signatures (Table 35) were largely in agreement with the isotopic signature of agricultural
670 soil emissions (Snider et al., 2015b; Wolf et al., 2015), indicating that this source could explain
671 more than 60% of the total N₂O emissions. However, the anthropogenic isotopic signatures
672 estimated by this approach were lower than the results from our two-box model (Table 24). In
673 contrast, another similar bottom-up estimate based on the global N₂O emission inventory (Toyoda
674 et al., 2013) reported anthropogenic isotopic values that agree well with our box-model results.
675 This may be explained by the different isotopic signatures used to describe agricultural N₂O

676 emissions, as those values used for the bottom-up estimates by Toyoda et al. (2013) were
677 significantly lower (Toyoda et al., 2011) than those used in this study (Snider et al., 2015b; Wolf
678 et al., 2015). Such bottom-up estimation suggests that more isotopic measurements of the
679 background atmosphere from different regions, and better constraints on individual anthropogenic
680 (especially agricultural) N₂O isotopic signatures, are necessary for a better representation of N₂O
681 isotopic composition in atmospheric modeling studies.

682 **5 Conclusions**

683 With the recently developed laser spectroscopic technique coupled with a preconcentration device,
684 we achieved good repeatability in measurements of N₂O isotopic composition from the
685 background atmosphere at Jungfraujoch, Switzerland. This time-series covered a period of five
686 years and showed a distinct seasonality, with $\delta^{15}\text{N}^{\text{bulk}}$ maxima and $\delta^{15}\text{N}^{\text{SP}}$ minima in late summer,
687 associated with the lowest N₂O mixing ratios over the year. The seasonal fluctuation of $\delta^{15}\text{N}^{\text{bulk}}$
688 was associated with the stratosphere-troposphere exchange process, in agreement with other
689 monitoring networks (Nevison et al., 2011), while the contrasting depletion of $\delta^{15}\text{N}^{\text{SP}}$ in later
690 summer is possibly a combined result of STE and agricultural emissions, with the latter being more
691 important. The analyses of air mass transport regimes together with the simulation of N₂O
692 enhancements for Jungfraujoch supported our explanations and highlighted that the fluctuation
693 between the free troposphere and local contributions dominated by soil emission drives the
694 seasonality of $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ as observed at Jungfraujoch.

695 We found statistically significant interannual trends for $\delta^{15}\text{N}^{\text{bulk}}$, which is expected as
696 anthropogenic N₂O sources are characterized by low ¹⁵N abundance. For $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$,
697 interannual trends were highly uncertain and possibly masked by their large temporal variabilities.
698 Using a two-box model approach, we simulated the evolution of N₂O isotopic composition from
699 preindustrial times to the present. This model suggests an overall decreasing trend for all isotopic
700 deltas in conjunction with the atmospheric N₂O increase. The anthropogenic source signatures
701 given by the model generally agreed with previous studies. However, these model results are still
702 sensitive to the ranges and trends of the observed N₂O isotopic signatures in the present
703 troposphere. In the future, more extended records of high-precision N₂O isotopic measurements

704 and application of multiple-box modeling approaches (Rigby et al., 2013) are necessary to account
705 for the global N₂O budget and evolution of anthropogenic sources.

706 **Data availability**

707 Data for this study have been deposited in a general data repository
708 (<https://figshare.com/s/077562ab408dd1bd0880>; doi:10.6084/m9.figshare.12032760.v1, 2020).

709 **Author contribution:**

710 LY, EH and JM led and designed this study. LY, EH, SE conducted sample collection at
711 Jungfrauoch; LY and EH analyzed discrete samples at Empa; MS and CZ contributed *in situ*
712 measurements of N₂O, NO_y, CO and O₃ at Jungfrauoch; LY, EH and SH performed data analyses
713 for the time-series and conducted model simulations. LY wrote the main manuscript; EH, SH and
714 JM were involved in the revisions of the manuscript and commenting. SE, MS, LE and CZ were
715 also involved in scientific discussion and commenting on the manuscript.

716 **Competing interests**

717 The authors declare that they have no conflict of interest.

718 **Acknowledgements**

719 We are thankful to the research infrastructure provided by the High Altitude Research Stations
720 Jungfrauoch and Gornergrat. We are grateful to the help from the custodians (Mr. and Mrs. Fischer
721 and Mr. and Mrs. Käser) at the research station of Jungfrauoch. We would like to thank Simon
722 Wyss, Kerstin Zeyer, Patrik Zanchetta and Flurin Dietz for their support with the sample collection
723 as well as laboratory assistance. The NABEL network is operated by Empa in collaboration with
724 the Swiss Federal Office for the Environment. Prof. Sakae Toyoda and Prof. Naohiro Yoshida
725 from Tokyo Institute of Technology are acknowledged for their analyses of the applied reference
726 standards. This study was financially supported by the Swiss National Science Foundation (grant
727 number 200021_163075) and the Swiss contribution to the Integrated Carbon Observation System

728 (ICOS) Research Infrastructure (ICOS-CH). ICOS-CH is funded by the Swiss National Science
729 Foundation and in-house contributions. Longfei Yu was additionally supported by the
730 EMPAPOSTDOCS-II program, which receives funding from the European Union's Horizon 2020
731 research and innovation program under the Marie Skłodowska-Curie grant agreement number
732 754364.

733

734 **References**

- 735 Appenzeller, C., Begert, M., Zenklusen, E. and Scherrer, S. C.: Monitoring climate at Jungfraujoch in the
736 high Swiss Alpine region, *Sci. Total Environ.*, 391(2–3), 262–268, doi:10.1016/j.scitotenv.2007.10.005,
737 2008.
- 738 Bernard, S., Röckmann, T., Kaiser, J., Barnola, J.-M., Fischer, H., Blunier, T. and Chappellaz, J.:
739 Constraints on N₂O budget changes since pre-industrial time from new firn air and ice core isotope
740 measurements, *Atmos. Chem. Phys. Discuss.*, 5(4), 7547–7575, doi:10.5194/acpd-5-7547-2005, 2006.
- 741 Bourbonnais, A., Letscher, R. T., Bange, H. W., Échevin, V., Larkum, J., Mohn, J., Yoshida, N. and
742 Altabet, M. A.: N₂O production and consumption from stable isotopic and concentration data in the
743 Peruvian coastal upwelling system, *Global Biogeochem. Cycles*, 31(4), 678–698,
744 doi:10.1002/2016GB005567, 2017.
- 745 Buchmann, B., Hueglin, C., Reimann, S., Vollmer, M. K., Steinbacher, M. and Emmenegger, L.: Reactive
746 gases, ozone depleting substances and greenhouse gases, in *From weather observations to atmospheric
747 and climate sciences in Switzerland*, edited by S. Willemse and M. Furger, vdf Hochschulverlag AG.,
748 2016.
- 749 Bukowiecki, N., Weingartner, E., Gysel, M., Coen, M. C., Zieger, P., Herrmann, E., Steinbacher, M.,
750 Gäggeler, H. W. and Baltensperger, U.: A review of more than 20 years of aerosol observation at the high
751 altitude research station Jungfraujoch, Switzerland (3580 m asl), *Aerosol Air Qual. Res.*, 16(3), 764–788,
752 doi:10.4209/aaqr.2015.05.0305, 2016.
- 753 Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R. and Zechmeister-Boltenstern, S.: Nitrous
754 oxide emissions from soils: how well do we understand the processes and their controls?, *Philos. Trans.
755 R. Soc. Lond. B. Biol. Sci.*, 368, 20130122, doi:10.1098/rstb.2013.0122, 2013.
- 756 Decock, C. and Six, J.: How reliable is the intramolecular distribution of ¹⁵N in N₂O to source partition
757 N₂O emitted from soil?, *Soil Biol. Biochem.*, 65(2), 114–127, doi:10.1016/j.soilbio.2013.05.012, 2013.
- 758 Denk, T. R. A., Mohn, J., Decock, C., Lewicka-Szczepak, D., Harris, E., Butterbach-Bahl, K., Kiese, R.
759 and Wolf, B.: The nitrogen cycle: A review of isotope effects and isotope modeling approaches, *Soil Biol.
760 Biochem.*, 105, 121–137, doi:10.1016/j.soilbio.2016.11.015, 2017.
- 761 Denk, T. R. A., Kraus, D., Kiese, R., Butterbach-Bahl, K. and Wolf, B.: Constraining N cycling in the
762 ecosystem model LandscapeDNDC with the stable isotope model SIMONE, *Ecology*, 100(5), c02675,
763 doi:10.1002/ecy.2675, 2019.
- 764 Fowler, D., Steadman, C. E., Stevenson, D., Coyle, M., Rees, R. M., Skiba, U. M., Sutton, M. a., Cape, J.
765 N., Dore, a. J., Viero, M., Simpson, D., Zaehle, S., Stocker, B. D., Rinaldi, M., Facchini, M. C.,
766 Flechard, C. R., Nemitz, E., Twigg, M., Erisman, J. W. and Galloway, J. N.: Effects of global change
767 during the 21st century on the nitrogen cycle, *Atmos. Chem. Phys. Discuss.*, 15(2), 1747–1868,
768 doi:10.5194/acpd-15-1747-2015, 2015.
- 769 Fujii, A., Toyoda, S., Yoshida, O., Watanabe, S., Sasaki, K. and Yoshida, N.: Distribution of nitrous
770 oxide dissolved in water masses in the eastern subtropical North Pacific and its origin inferred from
771 isotopomer analysis, *J. Oceanogr.*, 69(2), 147–157, doi:10.1007/s10872-012-0162-4, 2013.
- 772 Griffis, T. J., Chen, Z., Baker, J. M., Wood, J. D., Millet, D. B., Lee, X., Venterea, R. T. and Turner, P.
773 A.: Nitrous oxide emissions are enhanced in a warmer and wetter world, *Proc. Natl. Acad. Sci.*,
774 201704552, doi:10.1073/pnas.1704552114, 2017.
- 775 Hall, B. D., Dutton, G. S. and Elkins, J. W.: The NOAA nitrous oxide standard scale for atmospheric
776 observations, *J. Geophys. Res. Atmos.*, 112(9), 1–9, doi:10.1029/2006JD007954, 2007.

777 ~~Harris, E., Ibraim, E., Henne, S., Hüglin, C., Zellweger, C., Tuzson, B., Emmenegger, L. and Mohn, J.:~~
778 ~~Tracking nitrous oxide emission processes at a suburban site with semicontinuous, in situ measurements~~
779 ~~of isotopic composition, J. Geophys. Res. Atmos., 122, 1850–1870, doi:10.1002/2016JD025906, 2017.~~

780 Harris, E. J., Nelson, D. D., Olsewski, W., Zahniser, M., Potter, E., Mcmanus, B. J., Whitehill, A., Prinn,
781 R. G., Ono, S. and Harris, E.: Development of a spectroscopic technique for continuous online monitoring
782 of oxygen and site-specific nitrogen isotopic com, Anal. Chem., 86(3), 1726–1734, 2014.

783 [Harris, E., Zeyer, K., Kegel, R., Müller, B., Emmenegger, L. and Mohn, J.: Nitrous oxide and methane](#)
784 [emissions and nitrous oxide isotopic composition from waste incineration in Switzerland, Waste Manag.,](#)
785 [35\(x\), 135–140, doi:10.1016/j.wasman.2014.10.016, 2015.](#)

786 ~~Harris, E., Ibraim, E., Henne, S., Hüglin, C., Zellweger, C., Tuzson, B., Emmenegger, L. and Mohn, J.:~~
787 ~~Tracking nitrous oxide emission processes at a suburban site with semicontinuous, in situ measurements~~
788 ~~of isotopic composition, J. Geophys. Res. Atmos., 122, 1850–1870, doi:10.1002/2016JD025906, 2017.~~

789 Heil, J., Wolf, B., Brüggemann, N., Emmenegger, L., Tuzson, B., Vereecken, H. and Mohn, J.: Site-
790 specific ¹⁵N isotopic signatures of abiotically produced N₂O, Geochim. Cosmochim. Acta, 139, 72–82,
791 doi:10.1016/j.gca.2014.04.037, 2014.

792 Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J. and Buchmann, B.: Assessment of parameters
793 describing representativeness of air quality in-situ measurement sites, Atmos. Chem. Phys., 10(8), 3561–
794 3581, doi:10.5194/acp-10-3561-2010, 2010.

795 Henne, S., Brunner, D., Oney, B., Leuenberger, M., Eugster, W., Bamberger, I., Meinhardt, F.,
796 Steinbacher, M. and Emmenegger, L.: Validation of the Swiss methane emission inventory by
797 atmospheric observations and inverse modelling, Atmos. Chem. Phys., 16(6), 3683–3710,
798 doi:10.5194/acp-16-3683-2016, 2016.

799 Henne, S., Mohn, J. and Brunner, D.: Quantification of Swiss nitrous oxide emissions through
800 atmospheric observations and inverse modelling, Final Report, Project of FOEN, 2019.

801 Herrmann, E., Weingartner, E., Henne, S., Vuilleumier, L., Bukowiecki, N., Steinbacher, M., Conen, F.,
802 Coen, M. C., Hammer, E., Juranyi, Z., Baltensperger, U. and Gysel, M.: Analysis of long-term aerosol
803 size distribution data from Jungfraujoch with emphasis on free tropospheric conditions, cloud influence,
804 and air mass transport, J. Geophys. Res. Atmos., 120, 1751–1762, doi:10.1002/2015JD023660, 2015.

805 Ibraim, E., Wolf, B., Harris, E., Gasche, R., Wei, J., Yu, L., Kiese, R., Eggleston, S., Butterbach-Bahl, K.,
806 Zeeman, M., Tuzson, B., Emmenegger, L., Six, J., Henne, S. and Mohn, J.: Attribution of N₂O sources in
807 a grassland soil with laser spectroscopy based isotopocule analysis, Biogeosciences, 16, 3247–3266,
808 doi.org/10.5194/bg-16-3247-2019, 2019.

809 Ishijima, K., Sugawara, S., Kawamura, K., Hashida, G., Morimoto, S., Murayama, S., Aoki, S. and
810 Nakazawa, T.: Temporal variations of the atmospheric nitrous oxide concentration and its $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$
811 for the latter half of the 20th century reconstructed from firn air analyses, J. Geophys. Res. Atmos.,
812 112(3), doi:10.1029/2006JD007208, 2007.

813 Janssens-Maenhout, G., Crippa, M., Guizzardi, D., Muntean, M., Schaaf, E., Dentener, F., Bergamaschi,
814 P., Pagliari, V., Olivier, J., Peters, J., van Aardenne, J., Monni, S., Doering, U., Petrescu, R., Solazzo, E.
815 and Oreggioni, G.: EDGAR v4.3.2 Global Atlas of the three major Greenhouse Gas Emissions for the
816 period 1970-2012, Earth Syst. Sci. Data Discuss., 2010, 1–52, doi:10.5194/essd-2018-164, 2019.

817 Jiang, X., Ku, W. L., Shia, R. L., Li, Q., Elkins, J. W., Prinn, R. G. and Yung, Y. L.: Seasonal cycle of
818 N₂O: Analysis of data, Global Biogeochem. Cycles, 21, GB1006, doi:10.1029/2006GB002691, 2007.

819 JMA and WMO: World Meteorological Organization - Global Atmosphere Watch - World Data Centre
820 for Greenhouse Gases, Data Summary, No. 42, 101 p., [online] Available from:

- 821 <https://gaw.kishou.go.jp/static/publications/summary/sum42/sum42.pdf>, 2018.
- 822 Kaiser, J., Röckmann, T. and Brenninkmeijer, C. A. M.: Complete and accurate mass spectrometric
823 isotope analysis of tropospheric nitrous oxide, *J. Geophys. Res. Atmos.*, 108, 4476,
824 doi:10.1029/2003JD003613, D15, 2003.
- 825 Kaiser, J., Engel, A., Borchers, R. and Röckmann, T.: Probing stratospheric transport and chemistry with
826 new balloon and aircraft observations of the meridional and vertical N₂O isotope distribution, *Atmos.*
827 *Chem. Phys.*, 6(11), 3535–3556, doi:10.5194/acp-6-3535-2006, 2006.
- 828 Keller, C. A., Hill, M., Vollmer, M. K., Henne, S., Brunner, D., Reimann, S., O’Doherty, S., Arduini, J.,
829 Maione, M., Ferenczi, Z., Haszpra, L., Manning, A. J. and Peter, T.: European emissions of halogenated
830 greenhouse gases inferred from atmospheric measurements, *Environ. Sci. Technol.*, 46(1), 217–225,
831 doi:10.1021/es202453j, 2012.
- 832 Kim, K.-R. and Craig, H.: Nitrogen-15 and Oxygen-18 Characteristics of Nitrous Oxide: A Global
833 Perspective, *Science*, 262, 1855–1857, 1993.
- 834 Lebegue, B., Schmidt, M., Ramonet, M., Wastine, B., Yver Kwok, C., Laurent, O., Belviso, S., Guemri,
835 A., Philippon, C., Smith, J. and Conil, S.: Comparison of nitrous oxide (N₂O) analyzers for high-precision
836 measurements of atmospheric mole fractions, *Atmos. Meas. Tech.*, 9(3), 1221–1238, doi:10.5194/amt-9-
837 1221-2016, 2016.
- 838 Logan, J. A., Staehelin, J., Megretskaia, I. A., Cammas, J. P., Thouret, V., Claude, H., De Backer, H.,
839 Steinbacher, M., Scheel, H. E., Stbi, R., Frhlich, M. and Derwent, R.: Changes in ozone over Europe:
840 Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, *J.*
841 *Geophys. Res. Atmos.*, 117(9), 1–23, doi:10.1029/2011JD016952, 2012.
- 842 [Maeda, K., Toyoda, S., Shimojima, R., Osada, T., Hanajima, D., Morioka, R. and Yoshida, N.: Source of](#)
843 [nitrous oxide emissions during the cow manure composting process as revealed by isotopomer analysis of](#)
844 [and amo abundance in betaproteobacterial ammonia-oxidizing bacteria, *Appl. Environ. Microbiol.*,](#)
845 [76\(5\), 1555–1562, doi:10.1128/AEM.01394-09, 2010.](#)
- 846 Mohn, J., Guggenheim, C., Tuzson, B., Vollmer, M. K., Toyoda, S., Yoshida, N. and Emmenegger, L.: A
847 liquid nitrogen-free preconcentration unit for measurements of ambient N₂O isotopomers by QCLAS,
848 *Atmos. Meas. Tech.*, 3(3), 609–618, doi:10.5194/amt-3-609-2010, 2010.
- 849 Mohn, J., Tuzson, B., Manninen, A., Yoshida, N., Toyoda, S., Brand, W. A. and Emmenegger, L.: Site
850 selective real-time measurements of atmospheric N₂O isotopomers by laser spectroscopy, *Atmos. Meas.*
851 *Tech.*, 5(7), 1601–1609, doi:10.5194/amt-5-1601-2012, 2012.
- 852 Mohn, J., Wolf, B., Toyoda, S., Lin, C. T., Liang, M. C., Brüggemann, N., Wissel, H., Steiker, A. E.,
853 Dyckmans, J., Szvec, L., Ostrom, N. E., Casciotti, K. L., Forbes, M., Giesemann, A., Well, R., Doucett,
854 R. R., Yarnes, C. T., Ridley, A. R., Kaiser, J. and Yoshida, N.: Interlaboratory assessment of nitrous
855 oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: Current status and
856 perspectives, *Rapid Commun. Mass Spectrom.*, 28(18), 1995–2007, doi:10.1002/rcm.6982, 2014.
- 857 Nevison, C. D., Keeling, R. F., Weiss, R. F., Popp, B. N., Jin, X., Fraser, P. J., Porter, L. W. and Hess, P.
858 G.: Southern Ocean ventilation inferred from seasonal cycles of atmospheric N₂O and O₂/N₂ at Cape
859 Grim, Tasmania, *Tellus, Ser. B Chem. Phys. Meteorol.*, 57(3), 218–229, doi:10.1111/j.1600-
860 0889.2005.00143.x, 2005.
- 861 Nevison, C. D., Dlugokencky, E., Dutton, G., Elkins, J. W., Fraser, P., Hall, B., Krummel, P. B.,
862 Langenfelds, R. L., O’Doherty, S., Prinn, R. G., Steele, L. P. and Weiss, R. F.: Exploring causes of
863 interannual variability in the seasonal cycles of tropospheric nitrous oxide, *Atmos. Chem. Phys.*, 11(8),
864 3713–3730, doi:10.5194/acp-11-3713-2011, 2011.
- 865 Ogawa, M. and Yoshida, N.: Intramolecular distribution of stable nitrogen and oxygen isotopes of nitrous

866 oxide emitted during coal combustion, *Chemosphere*, 61(6), 877–887,
867 doi:10.1016/j.chemosphere.2005.04.096, 2005a.

868 Ogawa, M. and Yoshida, N.: Nitrous oxide emission from the burning of agricultural residue, *Atmos.*
869 *Environ.*, 39(19), 3421–3429, doi:10.1016/j.atmosenv.2005.01.059, 2005b.

870 Ostrom, N. E., Gandhi, H., Coplen, T. B., Toyoda, S., Böhlke, J. K., Brand, W. A., Casciotti, K. L.,
871 Dyckmans, J., Gieseemann, A., Mohn, J., Well, R., Yu, L. and Yoshida, N.: Preliminary assessment of
872 stable nitrogen and oxygen isotopic composition of USGS51 and USGS52 nitrous oxide reference gases
873 and perspectives on calibration needs, *Rapid Commun. Mass Spectrom.*, 32(15), 1207–1214,
874 doi:10.1002/rcm.8157, 2018.

875 Pandey Deolal, S., Brunner, D., Steinbacher, M., Weers, U. and Staehelin, J.: Long-term in situ
876 measurements of NO_x and NO_y at Jungfraujoch 1998–2009: Time series analysis and evaluation, *Atmos.*
877 *Chem. Phys.*, 12(5), 2551–2566, doi:10.5194/acp-12-2551-2012, 2012.

878 Park, S., Croteau, P., Boering, K. A., Etheridge, D. M., Ferretti, D., Fraser, P. J., Kim, K.-R., Krummel, P.
879 B., Langenfelds, R. L., van Ommen, T. D., Steele, L. P. and Trudinger, C. M.: Trends and seasonal cycles
880 in the isotopic composition of nitrous oxide since 1940, *Nat. Geosci.*, 5(4), 261–265,
881 doi:10.1038/ngeo1421, 2012.

882 Pérez, T., Trumbore, S. E., Tyler, S. C., Matson, P. A., I., O.-M., Rahn, T. and Griffiths, D. W. T.:
883 Identifying the agricultural imprint on the global N₂O budget using stable isotopes, *J. Geophys. Res.*,
884 106, 9869–9878, doi:10.1179/1607845413y.0000000087, 2001.

885 Prather, M. J., Hsu, J., Deluca, N. M., Jackman, C. H., Oman, L. D., Douglass, A. R., Fleming, E. L.,
886 Strahan, S. E., Steenrod, S. D., Søvdde, O. A., Isaksen, I. S. A., Froidevaux, L. and Funke, B.: Measuring
887 and modeling the lifetime of nitrous oxide including its variability Michael, *J. Geophys. Res. Atmos.*,
888 120, 5693–5705, doi:10.1002/2015JD023267.Received, 2015.

889 Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., Dewitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J.,
890 Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M., Lunder, C. R. and Maione, M.:
891 History of chemically and radiatively important atmospheric gases from the Advanced Global
892 Atmospheric Gases Experiment (AGAGE), *Earth Syst. Sci. Data*, 10, 985–1018, 2018.

893 Prokopiou, M., Martinerie, P., Sapart, C. J., Witrant, E., Monteil, G. A., Ishijima, K., Bernard, S., Kaiser,
894 J., Levin, I., Sowers, T., Blunier, T., Etheridge, D., Dlugokencky, E., van de Wal, R. S. W. and
895 Röckmann, T.: Constraining N₂O emissions since 1940 using firn air isotope measurements in both
896 hemispheres, *Atmos. Chem. Phys.*, 2011(June), 1–50, doi:10.5194/acp-2016-487, 2017.

897 Prokopiou, M., Sapart, C. J., Rosen, J., Sperlich, P., Blunier, T., Brook, E., van de Wal, R. S. W. and
898 Röckmann, T.: Changes in the Isotopic Signature of Atmospheric Nitrous Oxide and Its Global Average
899 Source During the Last Three Millennia, *J. Geophys. Res. Atmos.*, 1–17, doi:10.1029/2018JD029008,
900 2018.

901 Rahn, T. and Wahlen, M.: A reassessment of the global isotopic budget of atmospheric nitrous oxide,
902 *Global Biogeochem. Cycles*, 14(2), 537–543, doi:10.1029/1999GB900070, 2000.

903 Ravishankara, A. R., Daniel, J. S. and Portmann, R. W.: Nitrous oxide (N₂O): the dominant ozone-
904 depleting substance emitted in the 21st century., *Science*, 326(5949), 123–5,
905 doi:10.1126/science.1176985, 2009.

906 Reay, D. S., Davidson, E. a., Smith, K. a., Smith, P., Melillo, J. M., Dentener, F. and Crutzen, P. J.:
907 Global agriculture and nitrous oxide emissions, *Nat. Clim. Chang.*, 2(6), 410–416,
908 doi:10.1038/nclimate1458, 2012.

909 Reimann, S., Vollmer, M. K., Folini, D., Steinbacher, M., Hill, M., Buchmann, B., Zander, R. and
910 Mahieu, E.: Observations of long-lived anthropogenic halocarbons at the high-Alpine site of Jungfraujoch

911 (Switzerland) for assessment of trends and European sources, *Sci. Total Environ.*, 391(2–3), 224–231,
912 doi:10.1016/j.scitotenv.2007.10.022, 2008.

913 Rigby, M., Prinn, R. G., O’Doherty, S., Montzka, S. A., McCulloch, A., Harth, C. M., Mühle, J.,
914 Salameh, P. K., Weiss, R. F., Young, D., Simmonds, P. G., Hall, B. D., Dutton, G. S., Nance, D.,
915 Mondeel, D. J., Elkins, J. W., Krummel, P. B., Steele, L. P. and Fraser, P. J.: Re-evaluation of the
916 lifetimes of the major CFCs and CH₃CCl₃ using atmospheric trends, *Atmos. Chem. Phys.*, 13(5), 2691–
917 2702, doi:10.5194/acp-13-2691-2013, 2013.

918 Röckmann, T., Kaiser, J. and Brenninkmeijer, C. A. M.: The isotopic fingerprint of the pre-industrial and
919 the anthropogenic N₂O source, *Atmos. Chem. Phys.*, (3), 315–323, 2003.

920 Röckmann, T. and Levin, I.: High-precision determination of the changing isotopic composition of
921 atmospheric N₂O from 1990 to 2002, *J. Geophys. Res. Atmos.*, 110(21), 1–8,
922 doi:10.1029/2005JD006066, 2005.

923 Saikawa, E., Prinn, R. G., Dlugokencky, E., Ishijima, K., Dutton, G. S., Hall, B. D., Langenfelds, R.,
924 Tohjima, Y., Machida, T., Manizza, M., Rigby, M., O’Doherty, S., Patra, P. K., Harth, C. M., Weiss, R.
925 F., Krummel, P. B., Van Der Schoot, M., Fraser, P. J., Steele, L. P., Aoki, S., Nakazawa, T. and Elkins, J.
926 W.: Global and regional emissions estimates for N₂O, *Atmos. Chem. Phys.*, 14(9), 4617–4641,
927 doi:10.5194/acp-14-4617-2014, 2014.

928 Schibig, M. F., Steinbacher, M., Buchmann, B., Van Der Laan-Luijkx, I. T., Van Der Laan, S., Ranjan, S.
929 and Leuenberger, M. C.: Comparison of continuous in situ CO₂ observations at Jungfraujoch using two
930 different measurement techniques, *Atmos. Meas. Tech.*, 8(1), 57–68, doi:10.5194/amt-8-57-2015, 2015.

931 Schilt, A., Brook, E. J., Bauska, T. K., Baggenstos, D., Fischer, H., Joos, F., Petrenko, V. V., Schaefer,
932 H., Schmitt, J., Severinghaus, J. P., Spahni, R. and Stocker, T. F.: Isotopic constraints on marine and
933 terrestrial N₂O emissions during the last deglaciation, *Nature*, 516(7530), 234–237,
934 doi:10.1038/nature13971, 2014.

935 Sepúlveda, E., Schneider, M., Hase, F., Barthlott, S., Dubravica, D., García, O. E., Gomez-Pelaez, A.,
936 González, Y., Guerra, J.C., Gisi, M., Kohlhepp, R., Dohe, S., Blumenstock, T., Strong, K., Weaver, D.,
937 Palm, N., Sadeghi, A., Deutscher, N. M., Warneke, T., Notholt, J., Jones, N., Griffith, D. W. T., Smale,
938 D., Brailsford, G. W., Robinson, J., Meinhardt, F., Steinbacher, M., Aalto, T. and Worthy, D.:
939 Tropospheric CH₄ signals as observed by NDACC FTIR at globally distributed sites and comparison to
940 GAW surface in situ measurements, *Atmos. Meas. Tech.*, 7(7), 2337–2360, doi:10.5194/amt-7-2337-
941 2014, 2014.

942 Snider, D., Thompson, K., Wagner-Riddle, C., Spoelstra, J. and Dunfield, K.: Molecular techniques and
943 stable isotope ratios at natural abundance give complementary inferences about N₂O production pathways
944 in an agricultural soil following a rainfall event, *Soil Biol. Biochem.*, 88, 197–213,
945 doi:10.1016/j.soilbio.2015.05.021, 2015a.

946 Snider, D. M., Venkiteswaran, J. J., Schiff, S. L. and Spoelstra, J.: From the ground up: Global nitrous
947 oxide sources are constrained by stable isotope values, *PLoS One*, 10(3), 1–19,
948 doi:10.1371/journal.pone.0118954, 2015b.

949 Sowers, T., Rodebaugh, A., Yoshida, N. and Toyoda, S.: Extending records of the isotopic composition of
950 atmospheric N₂O back to 1800 A.D. from air trapped in snow at the South Pole and the Greenland Ice
951 Sheet Project II ice core, *Global Biogeochem. Cycles*, 16(4), 1–10, doi:10.1029/2002GB001911, 2002.

952 Stohl, A., Forster, C., Frank, A., Seibert, P. and Wotawa, G.: Technical note: The Lagrangian particle
953 dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5, 2461–2474,
954 doi:10.3390/atmos9020076, 2005.

955 Sturm, P., Tuzson, B., Henne, S. and Emmenegger, L.: Tracking isotopic signatures of CO₂ at the high

956 altitude site Jungfraujoch with laser spectroscopy: Analytical improvements and representative results,
957 *Atmos. Meas. Tech.*, 6(7), 1659–1671, doi:10.5194/amt-6-1659-2013, 2013.

958 Sutka, R. L., Ostrom, N. E., Ostrom, P. H., Breznak, J. a, Pitt, a J., Li, F. and Gandhi, H.: Distinguishing
959 Nitrous Oxide Production from Nitrification and Denitrification on the Basis of Isotopomer Abundances
960 Distinguishing Nitrous Oxide Production from Nitrification and Denitrification on the Basis of
961 Isotopomer Abundances, *Appl. Environ. Microbiol.*, 72(1), 638–644, doi:10.1128/AEM.72.1.638, 2006.

962 Tarasova, O. A., Senik, I. A., Sosonkin, M. G., Cui, J., Staehelin, J. and Péévot, A. S. H.: Surface ozone
963 at the Caucasian site Kislovodsk High Mountain Station and the Swiss Alpine site Jungfraujoch: Data
964 analysis and trends (1990-2006), *Atmos. Chem. Phys.*, 9(12), 4157–4175, doi:10.5194/acp-9-4157-2009,
965 2009.

966 Team, R. C.: A language and environment for statistical computing. R Foundation for statistical
967 computing, 2015; Vienna, Austria, 2016.

968 [Thiemens, M. H. and Trogler, W. C.: Nylon Production: An Unknown Source of Atmospheric Nitrous](#)
969 [Oxide, *Science*, 251\(4996\), 932–934, doi:10.1126/science.251.4996.932, 1991.](#)

970 Thompson, R. L., Patra, P. K., Ishijima, K., Saikawa, E., Corazza, M., Karstens, U., Wilson, C.,
971 Bergamaschi, P., Dlugokencky, E., Sweeney, C., Prinn, R. G., Weiss, R. F., O’Doherty, S., Fraser, P. J.,
972 Steele, L. P., Krummel, P. B., Saunio, M., Chipperfield, M. and Bousquet, P.: TransCom N₂O model
973 inter-comparison-Part 1: Assessing the influence of transport and surface fluxes on tropospheric N₂O
974 variability, *Atmos. Chem. Phys.*, 14(8), 4349–4368, doi:10.5194/acp-14-4349-2014, 2014a.

975 Thompson, R. L., Ishijima, K., Saikawa, E., Corazza, M., Karstens, U., Patra, P. K., Bergamaschi, P.,
976 Chevallier, F., Dlugokencky, E., Prinn, R. G., Weiss, R. F., O’Doherty, S., Fraser, P. J., Steele, L. P.,
977 Krummel, P. B., Vermeulen, A., Tohjima, Y., Jordan, A., Haszpra, L., Steinbacher, M., Van Der Laan, S.,
978 Aalto, T., Meinhardt, F., Popa, M. E., Moncrieff, J. and Bousquet, P.: TransCom N₂O model inter-
979 comparison - Part 2: Atmospheric inversion estimates of N₂O emissions, *Atmos. Chem. Phys.*, 14(12),
980 6177–6194, doi:10.5194/acp-14-6177-2014, 2014b.

981 Thoning, K. W., Tans, P. P. and Komhyr, W. D.: Atmospheric carbon dioxide at Mauna Loa Observatory:
982 2. Analysis of the NOAA GMCC data, 1974-1985, *J. Geophys. Res.*, 94(D6), 8549–8565,
983 doi:10.1029/jd094id06p08549, 1989.

984 Tian, H., Yang, J., Xu, R., Lu, C., Canadell, J., Davidson, E. A., Jackson, R., Arneeth, A., Chang, J., Ciais,
985 P., Gerber, S., Ito, A., Joos, F., Lienert, S., Messina, P., Olin, S., Pan, S., Peng, C., Saikawa, E.,
986 Thompson, R., Vuichard, N., Winiwarter, W., Zaehle, S. and Zhang, B.: Global soil nitrous oxide
987 emissions since the preindustrial era estimated by an ensemble of terrestrial biosphere models:
988 Magnitude, attribution, and uncertainty, *Glob. Chang. Biol.*, 25(2), 640–659, doi:10.1111/gcb.14514,
989 2019.

990 Toyoda, S., Yoshida, N., Urabe, T., Aoki, S., Nakazawa, T., Sugawara, S. and Honda, H.: Fractionation
991 of N₂O isotopomers in the stratosphere, *J. Geophys. Res.*, 106(D7), 7515, doi:10.1029/2000JD900680,
992 2001.

993 Toyoda, S., Yamamoto, S., Arai, S., Nara, H., Yoshida, N., Kashiwakura, K. and Akiyama, K.:
994 Isotopomeric characterization of N₂O produced, consumed, and emitted by automobiles, *rapid comm*, 22,
995 603–612, doi:10.1002/rcm, 2008.

996 Toyoda, S., Yano, M., Nishimura, S., Akiyama, H., Hayakawa, A., Koba, K., Sudo, S., Yagi, K., Makabe,
997 A., Tobari, Y., Ogawa, N. O., Ohkouchi, N., Yamada, K. and Yoshida, N.: Characterization and
998 production and consumption processes of N₂O emitted from temperate agricultural soils determined via
999 isotopomer ratio analysis, *Global Biogeochem. Cycles*, 25(2), 1–17, doi:10.1029/2009GB003769, 2011.

1000 Toyoda, S., Kuroki, N., Yoshida, N., Ishijima, K., Tohjima, Y. and Machida, T.: Decadal time series of

- 1001 tropospheric abundance of N₂O isotopomers and isotopologues in the Northern Hemisphere obtained by
1002 the long-term observation at Hateruma Island, Japan, *J. Geophys. Res. Atmos.*, 118(8), 3369–3381,
1003 doi:10.1002/jgrd.50221, 2013.
- 1004 Toyoda, S., Yoshida, N. and Koba, K.: Isotopocule analysis of biologically produced nitrous oxide in
1005 various environments, *Mass Spectrom. Rev.*, (36), 135–160, doi:doi:10.1002/mas.21459, 2017.
- 1006 Toyoda, S., Yoshida, N., Morimoto, S., Aoki, S., Nakazawa, T., Sugawara, S., Ishidoya, S., Uematsu, M.,
1007 Inai, Y., Hasebe, F., Ikeda, C., Honda, H. and Ishijima, K.: Vertical distributions of N₂O isotopocules in
1008 the equatorial stratosphere, *Atmos. Chem. Phys.*, (18), 833–844, 2018.
- 1009 Tuzson, B., Henne, S., Brunner, D., Steinbacher, M., Mohn, J., Buchmann, B. and Emmenegger, L.:
1010 Continuous isotopic composition measurements of tropospheric CO₂ at Jungfraujoch (3580 m a.s.l.),
1011 Switzerland: Real-time observation of regional pollution events, *Atmos. Chem. Phys.*, 11(4), 1685–1696,
1012 doi:10.5194/acp-11-1685-2011, 2011.
- 1013 WMO: WMO Greenhouse Gas Bulletin., 2018.
- 1014 Wolf, B., Merbold, L., Decock, C., Tuzson, B., Harris, E., Six, J., Emmenegger, L. and Mohn, J.: First
1015 on-line isotopic characterization of N₂O above intensively managed grassland, *Biogeosciences*, 12(8),
1016 2517–2531, doi:10.5194/bg-12-2517-2015, 2015.
- 1017 Xu-Ri, Prentice, I. C., Spahni, R. and Niu, H. S.: Modelling terrestrial nitrous oxide emissions and
1018 implications for climate feedback, *New Phytol.*, 196(2), 472–488, doi:10.1111/j.1469-8137.2012.04269.x,
1019 2012.
- 1020 Yoshida, N. and Toyoda, S.: Constraining the atmospheric N₂O budget from intramolecular site
1021 preference in N₂O isotopomers, *Nature*, 405(6784), 330–4, doi:10.1038/35012558, 2000.
- 1022 Yuan, Y., Ries, L., Petermeier, H., Steinbacher, M., Gómez-Pelaéz, A. J., Leuenberger, M. C.,
1023 Schumacher, M., Trickl, T., Couret, C., Meinhardt, F. and Menzel, A.: Adaptive selection of diurnal
1024 minimum variation: A statistical strategy to obtain representative atmospheric CO₂ data and its
1025 application to European elevated mountain stations, *Atmos. Meas. Tech.*, 11(3), 1501–1514,
1026 doi:10.5194/amt-11-1501-2018, 2018.
- 1027 Yung, Y. L. and Miller, C. E.: Isotopic fractionation of stratospheric nitrous oxide, *Science*, 278(5344),
1028 1778–1780, doi:10.1126/science.278.5344.1778, 1997.
- 1029 Zellweger, C., Forrer, J., Hofer, P., Nyeki, S., Schwarzenbach, B., Weingartner, E., Ammann, M. and
1030 Baltensperger, U.: Partitioning of reactive nitrogen (NO_x) and dependence on meteorological conditions
1031 in the lower free troposphere, *Atmos. Chem. Phys.*, 3(3), 779–796, doi:10.5194/acp-3-779-2003, 2003.
- 1032 Zellweger, C., Hüglin, C., Klausen, J., Steinbacher, M., Vollmer, M. and Buchmann, B.: Inter-comparison
1033 of four different carbon monoxide measurement techniques and evaluation of the long-term carbon
1034 monoxide time series of Jungfraujoch, *Atmos. Chem. Phys.*, 9(11), 3491–3503, doi:10.5194/acp-9-3491-
1035 2009, 2009.

1036 **Table 1** An overview of N₂O emission sectors for Swiss Meteotest Inventory and global EDAGR Inventory and available source isotopic
 1037 signatures (‰)*

<u>Meteotest Category</u>	<u>Meteotest Sources</u>	<u>EDGAR Category^o</u>	<u>EDGAR Primary source(s)^o</u>	<u>δ¹⁸O</u>	<u>δ¹⁵N^{bulk}</u>	<u>δ⁵N^{SP}</u>	<u>References</u>
<u>Orgs</u>	<u>Organic soils</u>	<u>7B, 7C</u>	<u>Indirect soil emissions</u>	<u>29.0±3.7</u>	<u>-17.8±5.7</u>	<u>7.2±3.8</u>	<u>Snider et al. (2015b), Wolf et al. (2015)</u>
<u>IndustrialHeating</u>	<u>Cement production, industrial combustion, furnaces, waste incinerator, other industrial</u>	<u>1A1, 1A2</u>	<u>deNO_x use in fossil fuel and MSW incineration plants</u>	<u>35.9±13.1</u>	<u>3.9±2.9</u>	<u>17.6±0.5</u>	<u>Ogawa et al. (2005a), Harris et al. (2015)</u>
<u>Transport</u>	<u>Agricultural and construction machinery, road traffic</u>	<u>1A3a, 1A3c, 1A3d, 1A3e, 1A3b</u>	<u>Fuel combustion in non-road transportation</u>	<u>28.6±9.9</u>	<u>-28.7±3.6</u>	<u>4.2±2.4</u>	<u>Toyoda et al., (2008)</u>
			<u>Fuel combustion for road transportation</u>	<u>40.3±3.7</u>	<u>-7.2±1.2</u>	<u>10.0±4.3</u>	<u>Toyoda et al., (2008)</u>
<u>Heating</u>	<u>Agricultural, commercial and private heating</u>	<u>1A4</u>	<u>Fuel combustion: other sectors (dominantly household heating)</u>	<u>37±10</u>	<u>5.5±6</u>	<u>3.5±4</u>	<u>Ogawa et al. (2005a), Ogawa et al. (2005b)</u>
<u>Refinery</u>	<u>Refineries</u>	<u>1B2a</u>	<u>Refineries</u>	<u>=</u>	<u>=</u>	<u>=</u>	<u>=</u>
<u>IndustryAndUse</u>	<u>Nitric acid production, use in households and hospitals</u>	<u>2 and 3</u>	<u>Nitric acid production (adipic acid, medical, and private (aerosol) use)</u>	<u>29.1±18.8</u>	<u>-8.3±10.6</u>	<u>3.3±5.5</u>	<u>Toyoda et al., (2008), Thiemens et al. (1991)</u>
<u>Manure</u>	<u>Manure management</u>	<u>4B</u>	<u>Manure management</u>	<u>23.9±3.8</u>	<u>-17.5±6.2</u>	<u>6.5±4.1</u>	<u>Maeda et al. (2010)</u>
<u>DirectAgri</u>	<u>Crop residues/soil organic matter, animal waste on pastures, synthetic fertilizer use, manure application</u>	<u>4C, 4D</u>	<u>Direct soil emissions</u>	<u>29.0±3.7</u>	<u>-17.8±5.7</u>	<u>7.2±3.8</u>	<u>Snider et al. (2015b), Wolf et al. (2015)</u>
<u>IndirectAgri</u>	<u>Leaching, other indirect emissions from agri. Soils</u>	<u>4D3</u>	<u>Direct soil emissions</u>	<u>29.0±3.7</u>	<u>-17.8±5.7</u>	<u>7.2±3.8</u>	<u>Snider et al. (2015b), Wolf et al. (2015)</u>

<u>WastBurning</u>	<u>Illegal waste burning</u>	<u>4F</u>	<u>Agricultural waste burning</u>	<u>25±3.0</u>	<u>-1.0±3.0</u>	<u>2.8±3.0</u>	<u>Ogawa et al. (2005b)</u>
<u>Waste</u>	<u>Industrial fermentation, wastewater treatment, sewage sludge burning</u>	<u>6</u>	<u>Waste (wastewater treatment)</u>	<u>31.5±14.1</u>	<u>-11.6±12.7</u>	<u>10.5±5.7</u>	<u>Snider et al. (2015b)</u>
<u>IndirectNat</u>	<u>Indirect emissions from (semi-)natural ecosystems</u>	<u>7B, and 7C</u>	<u>Indirect soil emissions</u>	<u>29.0±3.7</u>	<u>-17.8±5.7</u>	<u>7.2±3.8</u>	<u>Snider et al. (2015b), Wolf et al. (2015)</u>

1038 *Isotopic signatures for anthropogenic sources are obtained from the summary by Harris et al. (2017).

1039 ‡ These are the primary sources contributing to N₂O emissions in Switzerland

1040 **Table 2** Input variables for simple two-box model (more details in M&M)

<u>Variable</u>	<u>Description</u>	<u>Value</u>	<u>Error distribution</u>	<u>References</u>
m_{trop}	<u>Air in the troposphere (mol)</u>	<u>1.5×10^{20}</u>	<u>Constant</u>	<u>Röckmann et al. (2003), Schilt et al. (2014)</u>
m_{strat}	<u>Air in the stratosphere (mol)</u>	<u>2.7×10^{19}</u>	<u>Constant</u>	<u>Röckmann et al. (2003), Schilt et al. (2014)</u>
F_{ex}	<u>Troposphere-stratosphere exchange rate (kg a^{-1})</u>	<u>$(5.37 \pm 1.26) \times 10^{17}$</u>	<u>Uniform</u>	<u>Röckmann et al. (2003), Schilt et al. (2014)</u>
F_{ocean}	<u>Oceanic N_2O flux (Tg a^{-1} N equivalents)</u>	<u>4 ± 1</u>	<u>Gaussian</u>	<u>Schilt et al. (2014)</u>
τ_{PI}	<u>Preindustrial N_2O lifetime (year)</u>	<u>123 ± 10</u>	<u>Gaussian</u>	<u>Prather et al. (2015)</u>
τ_{PD}	<u>Present day N_2O lifetime (year)</u>	<u>116 ± 9</u>	<u>Gaussian</u>	<u>Prather et al. (2015)</u>
c_{PI}	<u>Mixing ratio in the preindustrial troposphere (nmol mol^{-1})</u>	<u>270 ± 7.5</u>	<u>Uniform</u>	<u>Sowers et al. (2002), Röckmann et al. (2003)</u>
$\delta^{15}\text{N}_{\text{PI}}^{\text{bulk}}$	<u>Mean $\delta^{15}\text{N}^{\text{bulk}}$ of preindustrial tropospheric N_2O (‰)</u>	<u>8.9 ± 2</u>	<u>Gaussian</u>	<u>Toyoda et al. (2013)</u>
$\delta^{18}\text{O}_{\text{PI}}$	<u>Mean $\delta^{18}\text{O}$ of preindustrial tropospheric N_2O (‰)</u>	<u>46.1 ± 2</u>	<u>Gaussian</u>	<u>Toyoda et al. (2013)</u>
$\delta^{15}\text{N}_{\text{PI}}^{\text{SP}}$	<u>Mean $\delta^{15}\text{N}^{\text{SP}}$ of preindustrial tropospheric N_2O (‰)</u>	<u>19.05 ± 2</u>	<u>Gaussian</u>	<u>Toyoda et al. (2013)</u>
$\delta^{15}\text{N}_{\text{ocean}}$	<u>Mean $\delta^{15}\text{N}^{\text{bulk}}$ for oceanic emissions (‰)</u>	<u>5.1 ± 1.9</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>
$\delta^{18}\text{O}_{\text{ocean}}$	<u>Mean $\delta^{18}\text{O}$ for oceanic emissions (‰)</u>	<u>44.8 ± 3.6</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>
$\delta^{15}\text{N}_{\text{ocean}}^{\text{SP}}$	<u>Mean $\delta^{15}\text{N}^{\text{SP}}$ for oceanic emissions (‰)</u>	<u>15.8 ± 7.1</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>
$\delta^{15}\text{N}_{\text{terr}}^{\text{bulk}}$	<u>Mean $\delta^{15}\text{N}^{\text{bulk}}$ for emissions from terrestrial soils (‰)</u>	<u>-16.7 ± 11.2</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>
$\delta^{18}\text{O}_{\text{terr}}$	<u>Mean $\delta^{18}\text{O}$ for emissions from terrestrial soils (‰)</u>	<u>30.1 ± 9.6</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>
$\delta^{15}\text{N}_{\text{terr}}^{\text{SP}}$	<u>Mean $\delta^{15}\text{N}^{\text{SP}}$ for emissions from terrestrial soils (‰)</u>	<u>10.1 ± 11.2</u>	<u>Uniform</u>	<u>Snider et al. (2015b)</u>

1041

1045 | **Table 1-3** Trends of atmospheric $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ at Jungfraujoch determined using discrete measurements between April 2014 and December 2018. The trends are determined for the whole dataset, the dataset filtered for free troposphere (removing data points with significant influence from plenary boundary layer) and the second-phase dataset with bi-weekly measurements (August 2016 to December 2018).

	$\delta^{15}\text{N}^{\text{bulk}}$ (‰ a ⁻¹)		$\delta^{15}\text{N}^{\text{SP}}$ (‰ a ⁻¹)		$\delta^{18}\text{O}$ (‰ a ⁻¹)	
	Raw	Deseasonalized	Raw	Deseasonalized	Raw	Deseasonalized
Whole dataset	-0.059±0.012*	-0.052±0.012*	0.069±0.029	0.065±0.027	0.020±0.011	0.019±0.011
Free troposphere	-0.060±0.014*	-0.054±0.013*	0.054±0.034	0.036±0.030	0.024±0.013	0.019±0.011
First phase (Apr. 2014-Feb. 2016)	-0.036±0.038	-0.041±0.035	0.449±0.100*	0.314±0.082*	0.238±0.029*	0.207±0.026*
Second phase (Aug. 2016-Dec. 2018)	-0.105±0.049	-0.130±0.045*	0.028±0.067	-0.007±0.066	-0.007±0.042	-0.001±0.040

* Indicate significance of linear regression.

Table 2-4 Results of the two-box model simulations and selected literature values for comparison.

	This study		RMSE ^o	Sowers et al. (2002) ^a	Röckmann et al. (2003) ^b	Ishijima et al. (2007) ^c	Toyoda et al. (2013) ^d	Park et al. (2012) ^e	Prokopiou et al. (2017) ^f
Air sample age	NH [†] 2014-2018	NH(FT ⁿ) 2014-2018		FA [†] , IC [†] 1785-1995	FA NA	FA 1960-2001	NH 1999-2010	SH [†] , FA 1940-2005	FA 1940-2008
α^*	0.0154±0.004	0.0154±0.004	0.65 nmol mol ⁻¹	0.0111 to 0.0128	NA	NA	NA	NA	NA
$F_{\text{anth},2018}$ (Tg N a ⁻¹)	8.6±0.6	8.5±0.6	NA [†]	4.2 to 5.7	6.9	NA	5.5	6.6	5.4±1.7
$\delta^{15}\text{N}^{\text{bulk-anth}}$ (‰)	-8.6±4	-8.5±4	0.23	-7 to -13	-11.4	-11.6	-9.84	-15.6±1.2	-18.2±2.6
$\delta^{18}\text{O}^{\text{-anth}}$ (‰)	34.8±3	34.3±3	0.22	17 to 26	31.7	NA	35.95	32.0±1.3	27.2±2.6
$\delta^{15}\text{N}^{\text{SP-anth}}$ (‰)	10.7±4	10.7±4	0.50	NA	11.3	NA	8.52	13.1±9.4	18.0±8.6

1050 [†] NH and SH: surface atmosphere from the Northern and Southern Hemisphere, respectively; FA: firm air; IC: ice core air; NA: not available.

ⁿ FT: Jungfraujoch dataset filtered for free troposphere (based on NO_y:CO).

* “Value” is the dimensionless constant α describing the exponential increase in the anthropogenic flux

^o RMSE refers to root mean square error. It is in nmol mol⁻¹ for α , referring to the present day tropospheric mixing ratio for N₂O. For source isotopic values, RMSE is in the unit of ‰. Simulations with the whole dataset and the dataset filtered for free troposphere yielded the same RMSE.

1055 ^a Estimates are for 1995.

^b Estimates are for 1998; isotopic signatures of anthropogenic sources were calculated assuming modern tropospheric values to be the same as this study.

^c Estimate is for 2000, for $\delta^{18}\text{O}$ calibration is not comparable.

1060 ^d Estimates are for 2012 using the “Base” scenario.

^e Estimates are for 2005.

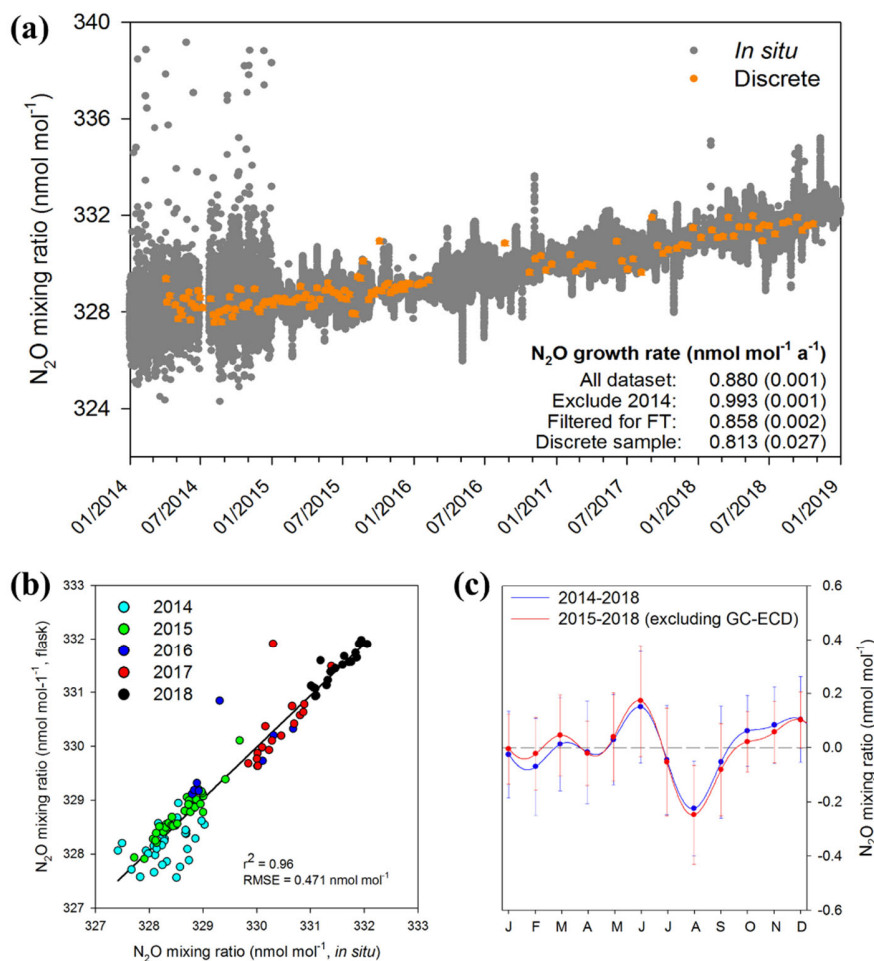
^f $\mathcal{J}_{\text{anth}}$ values are averaged values for the period of 1940-2008.

Table 3-5 Isotopic signatures for the overall, anthropogenic and major N₂O sources contributing to N₂O variations at Jungfrauoch. Source signatures were estimated based on a “bottom-up” approach, with literature-derived isotopic signatures and fluxes for variable sources under the Swiss Meteotest emission inventory.

	Emission inventory (%)	$\delta^{15}\text{N}^{\text{bulk}}$ (‰)	$\delta^{15}\text{N}^{\text{SP}}$ (‰)	$\delta^{18}\text{O}$ (‰)	Reference
Overall source	100	-15.8 (6.2)	7.3 (3.9)	29.4 (5.5)	-
Anthropogenic source	89.4	-15.6 (6.3)	7.4 (4.0)	29.5 (5.7)	-
Agricultural emission	61.5	-17.8 (5.7)	7.2 (3.8)	29.0 (3.7)	Snider et al. (2015) Wolf et al. (2015)
Manure management	7.4	-17.5 (6.2)	6.5 (4.1)	23.9 (3.8)	Maeda et al. (2010)
Waste *	7.2	-11.5 (12.6)	10.4 (5.7)	31.3 (14.0)	Ogawa and Yoshida (2005) Snider et al. (2015)
Natural emission	10.9	-17.8 (5.7)	7.2 (3.8)	29.0 (3.7)	Snider et al. (2015) Wolf et al. (2015)

* “Waste” sources consist of both wastewater treatment and agricultural waste burning (biomass burning).

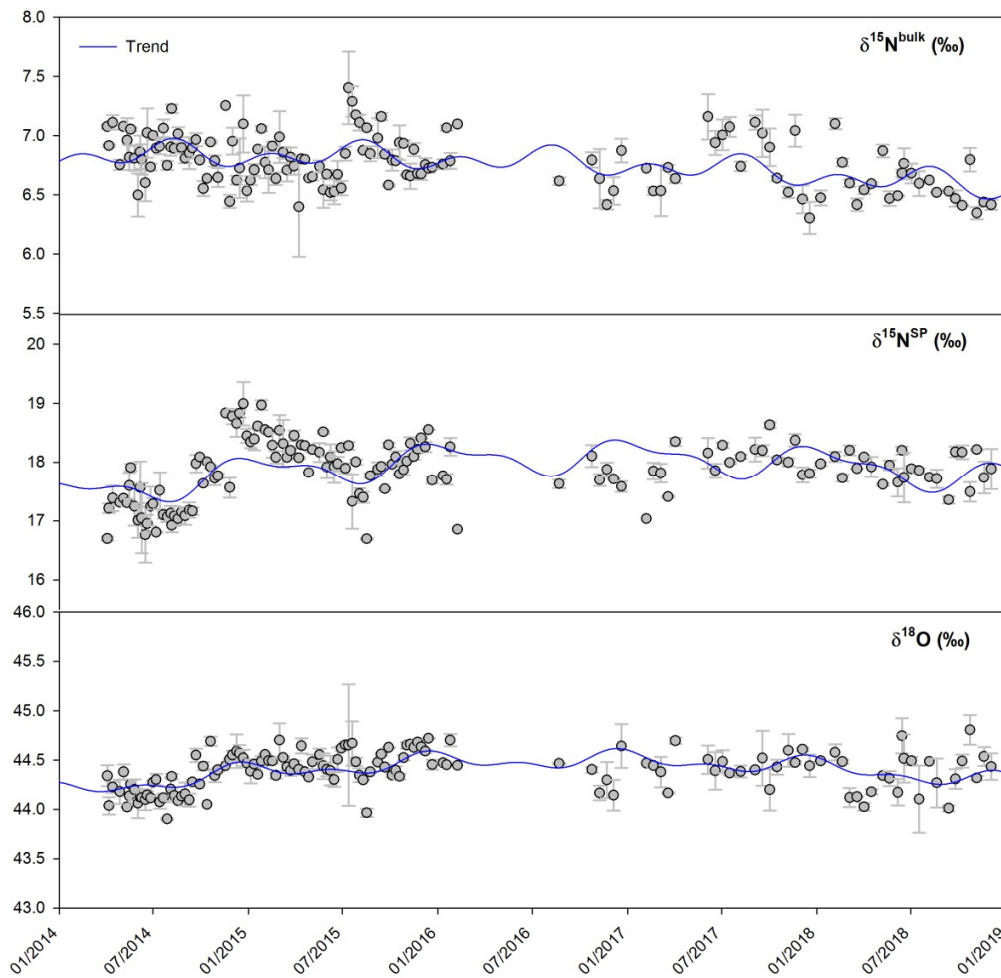
Figures



1070 **Figure 1a** *In situ* (10-min averages) and discrete measurements of N_2O mixing ratios from April 2014 to
 1075 December 2018 at Jungfraujoch. *In situ* N_2O mixing ratio measurements were performed with GC-ECD
 method between April and December 2014. After that, OA-ICOS became the major analytical method for
in situ measurements. Discrete sample points are presented as averages with error bars (one standard
 deviation). Annual N_2O growth rates determined by linear regression are given in the figure (uncertainty
 shown as one standard deviation). A sampling gap exists for discrete samples between February and
 August 2016.

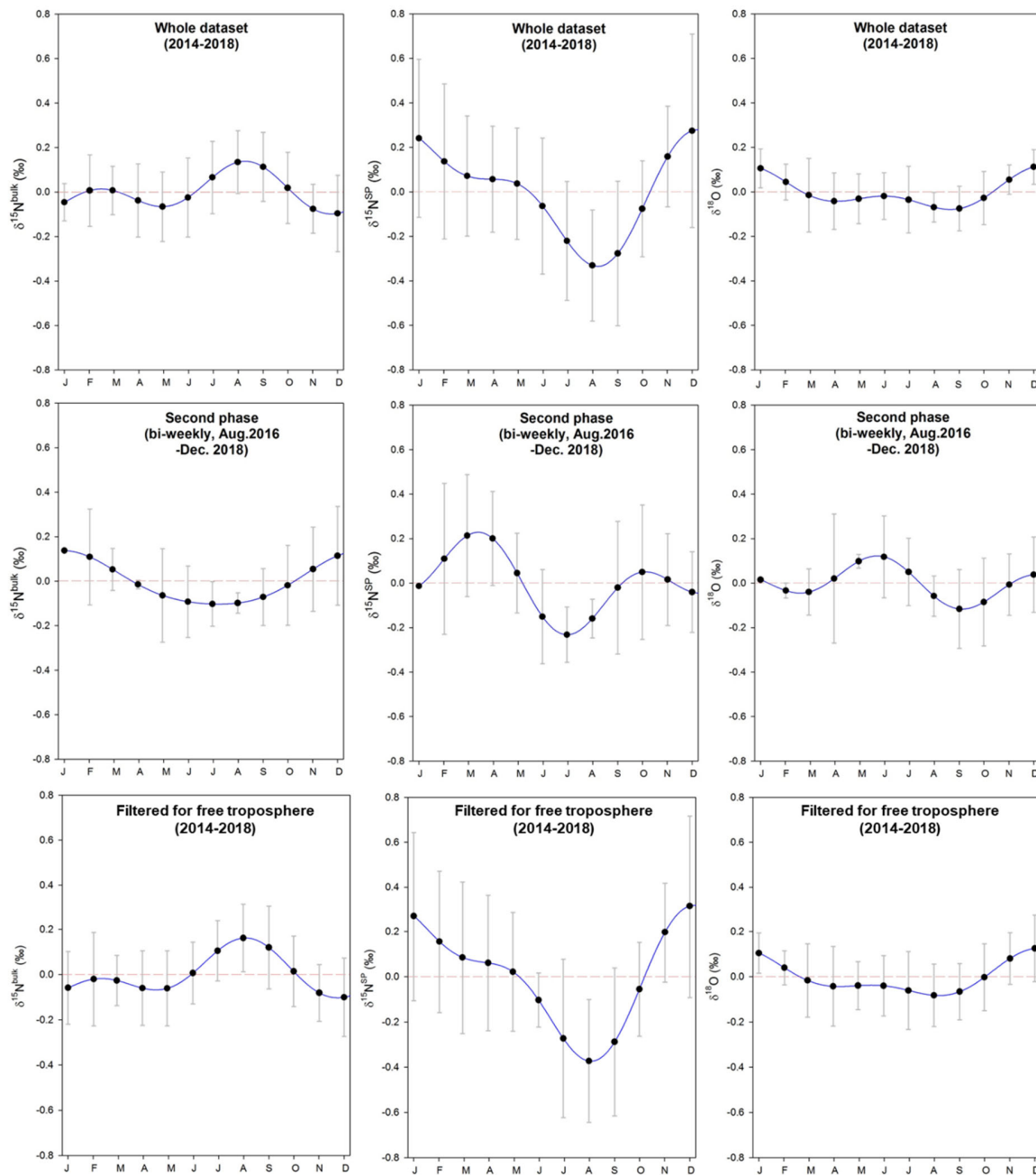
1080 **1b** Comparison of *in situ* and discrete measurements of N_2O mixing ratios; *in situ* measurements were 10-
 minute values averaged over the exact period of discrete sampling time (~ 40 min); *in situ* measurements
 were performed with GC-ECD method in 2014, and this was replaced with OA-ICOS method from
 January 2015.

1b-1c Seasonality of N_2O mixing ratios at Jungfraujoch derived from *in situ* measurements. Datasets
 with/without GC-ECD measurements are compared for seasonality evaluation. The NLS model
 simulation for time-series gives the detrended seasonality, with error bars indicating one standard
 deviation of monthly residuals.



1085

Figure 2 Time-series of isotopic composition of atmospheric N_2O observed at Jungfraujoch from April 2014 to December 2018. Error bars indicate one standard deviation of repeated measurements. Blue lines indicate the simulated trends by the NLS model.



1090 **Figure 3** Seasonality of isotopic signatures of atmospheric N₂O observed at Jungfraujoch. Top panels: seasonality obtained using the whole dataset from April 2014 to December 2018; lower-middle panels: seasonality obtained using bi-weekly data collected between August 2016 and December 2018; lower panels: seasonality obtained using dataset filtered for free troposphere from April 2014 to December 2018. Red dashed lines refer to zero variability. The NLS model simulation for time-series gives the detrended seasonality, with error bars indicating one standard deviation of monthly residuals.

1095

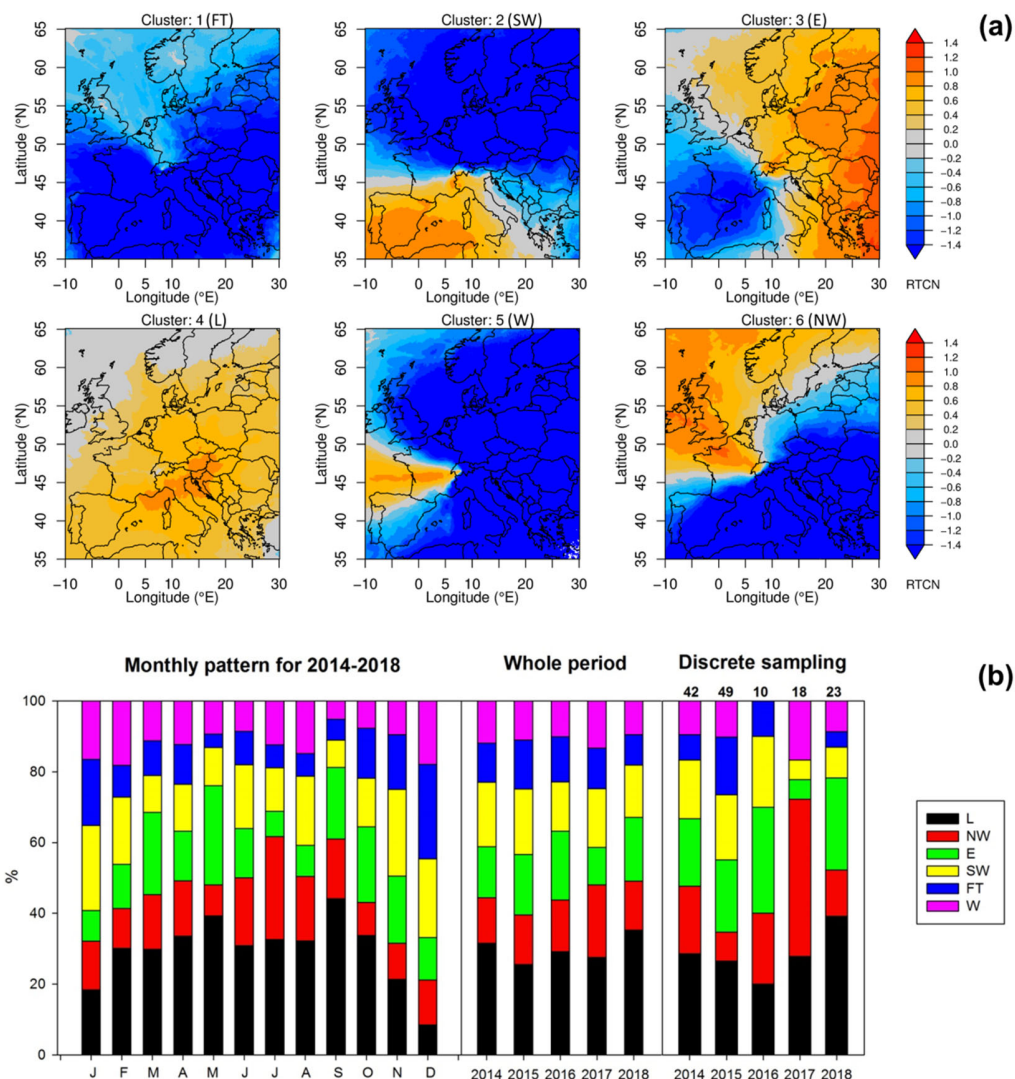


Figure 4a Clusters of air mass transport regimes for Jungfraujoch shown as normalized surface source sensitivities over our sampling period. Cluster abbreviations refer to Free Troposphere (FT), Southwest (SW), East (E), Local (L), West (W) and Northwest (NW). The normalization was done by calculating the difference between cluster average source sensitivity and whole period average source sensitivities, divided by the period average. Orange colors indicate the main source regimes in each cluster, whereas blue colors indicate little to no influence on Jungfraujoch observations. The free tropospheric cluster showed lower than average surface sensitivity everywhere.

4b Cluster frequency of air mass transport regimes (%) shown as a monthly pattern (left) and interannual patterns for the whole periods (middle) and for the periods of discrete sampling (right). Numbers above the right figure indicate the total number of discrete samples per year.

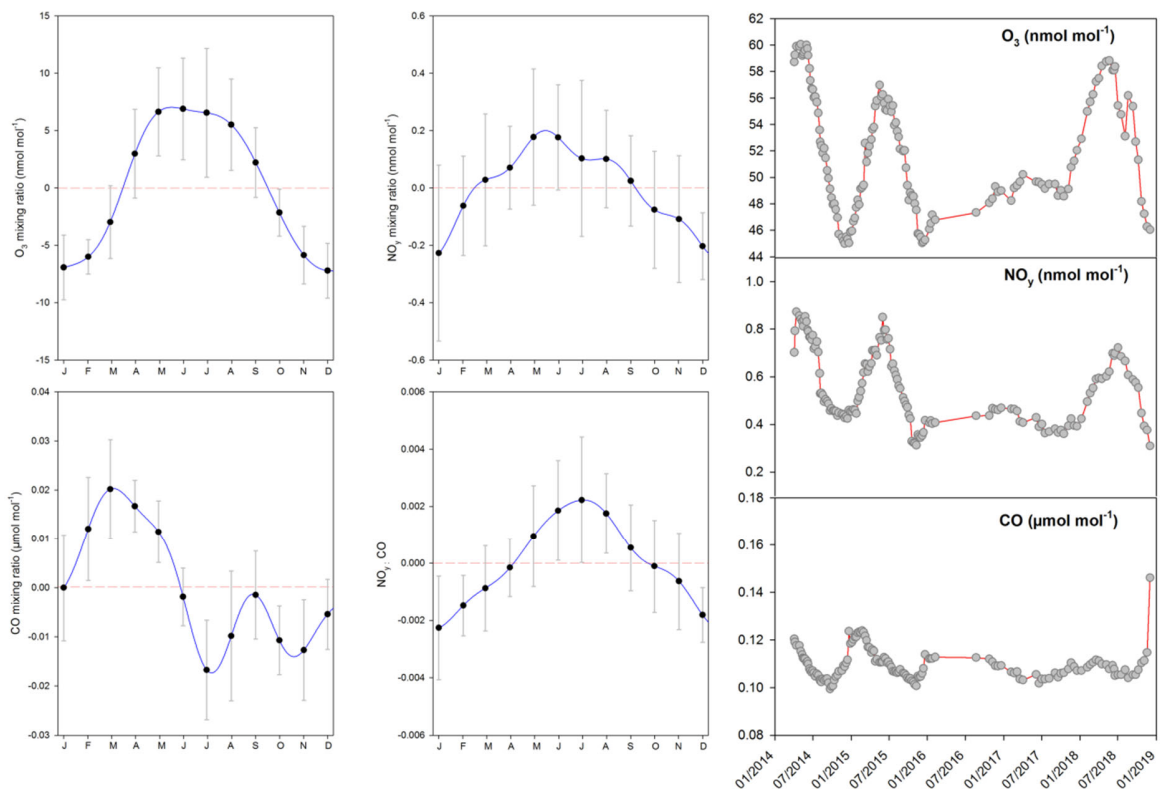


Figure 5 Left and middle: Seasonality of *in situ* measurements of O_3 , NO_y and CO mixing ratios and NO_y/CO at Jungfraujoch; error bars represent the one standard deviation of monthly residuals from the NLS model simulation for time-series. 10-minute data were used for seasonality analysis.

Right: *In situ* measurements of O_3 , NO_y and CO mixing ratios averaged over the exact period of discrete sampling (~40 min).

1110

1115

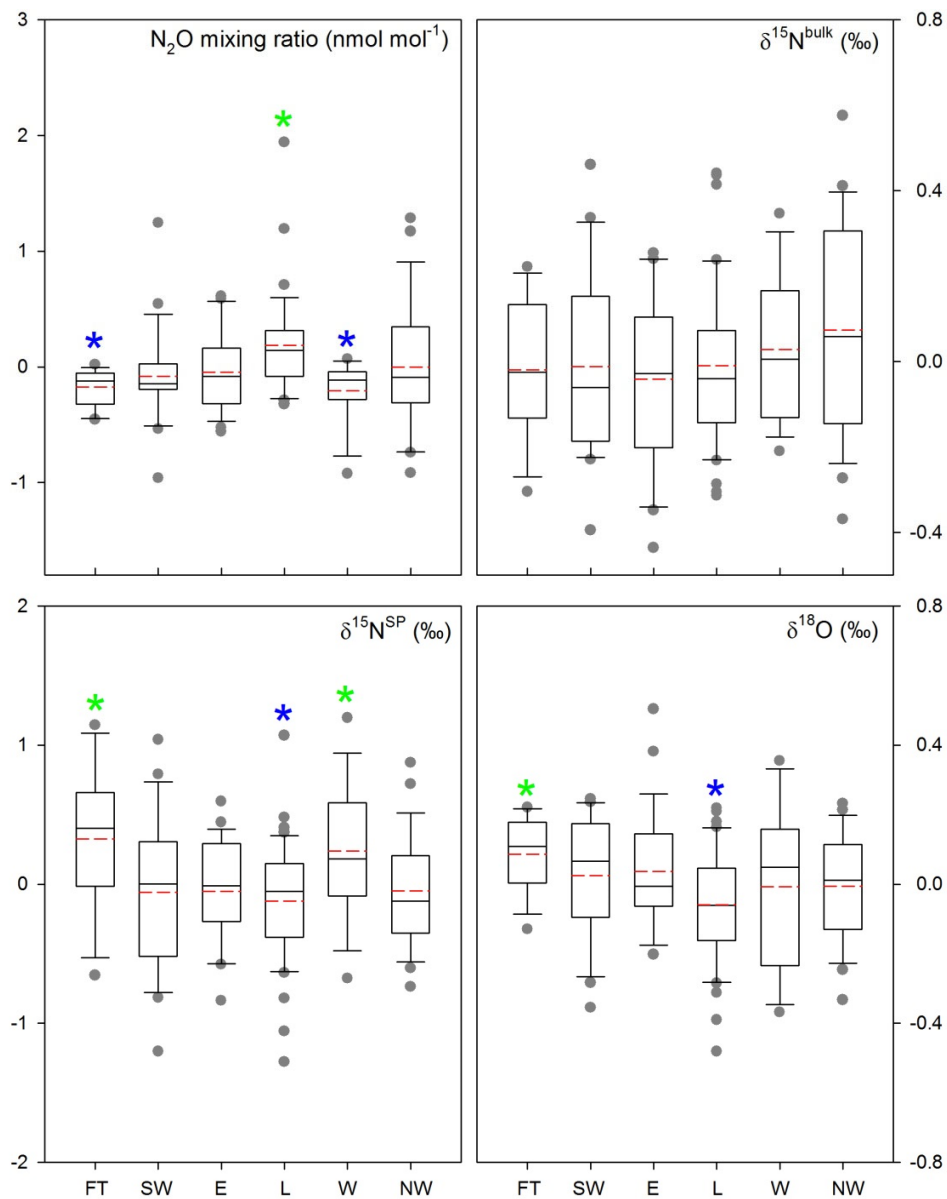


Figure 5-6 Comparison of N_2O mixing ratios and isotopic signatures (with linear trends removed) for the six air mass footprint clusters used in the present study. Green and blue stars indicate significantly larger and smaller values than the others, respectively; red dashed lines indicate mean levels; grey points indicate outliers.

1120

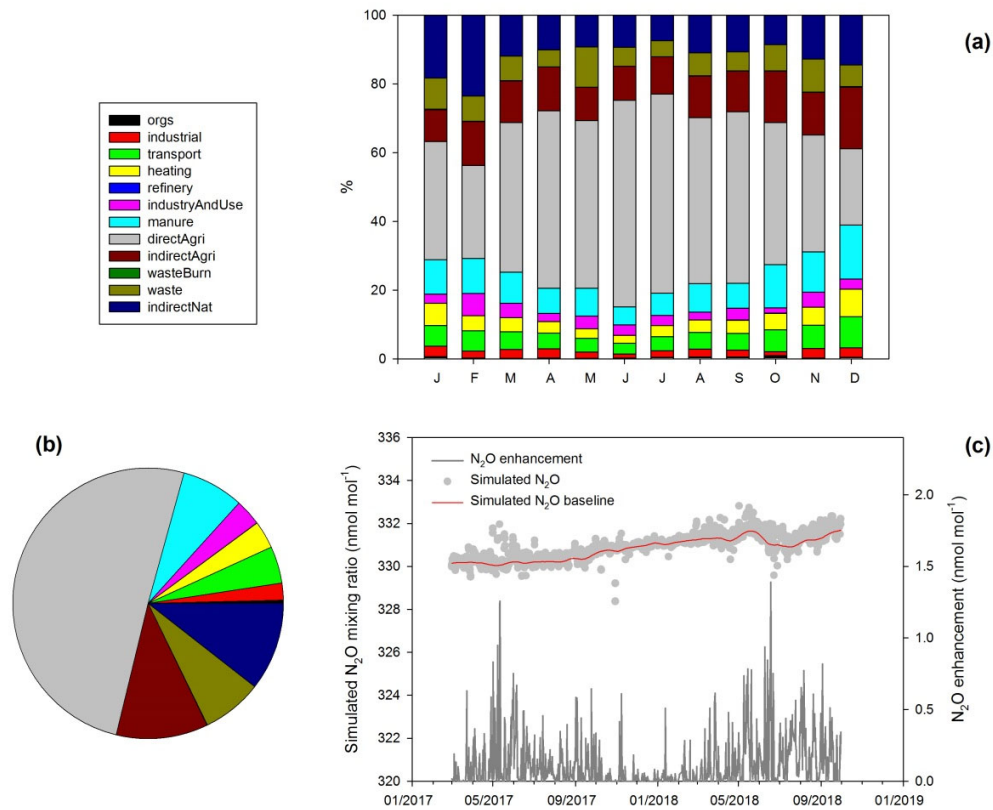
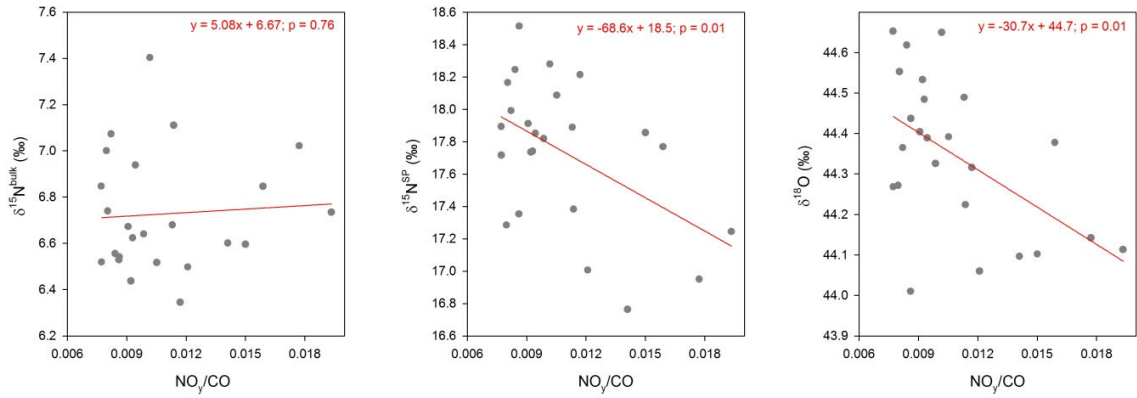


Figure 6a-7a Mean monthly stacked-bar plots of source contributions (%) to atmospheric N₂O at Jungfraujoch derived from inversion modeling.

1125 **6b-7b** Overall contributions of N₂O sources responsible for emission to Jungfraujoch.

6e-7c Simulated 3-hourly N₂O mixing ratios, N₂O mixing ratio baseline and N₂O enhancements in nmol mol⁻¹.



1130

Figure 8 Relationship between the NO_y to CO ratios and isotopic signatures of N_2O ; only data points with $\text{NO}_y/\text{CO} > 0.007$ are presented here (which refers to scenarios with strong pollution from local air).

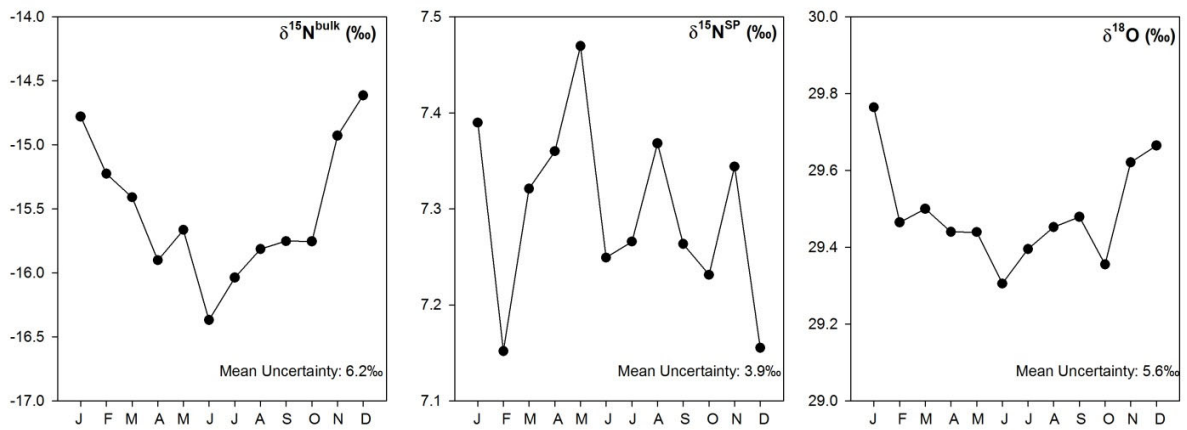
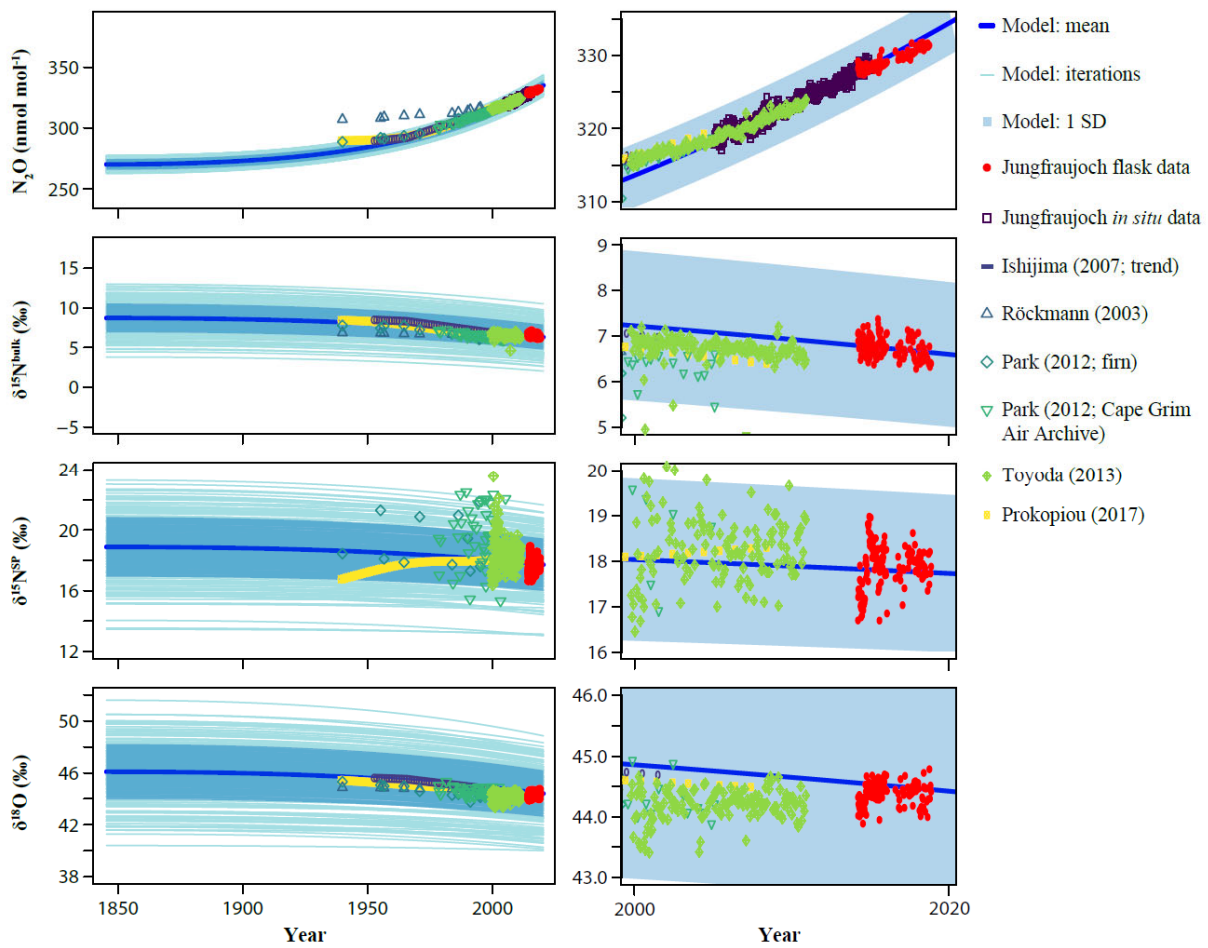


Figure 9 Simulated seasonal variations of isotopic signatures for overall N₂O sources based on the "bottom-up" approach; uncertainties shown in figures are comparable to the ranges of isotopic signatures for variable sources as found in literature.

1135



1140

Figure 7-10 Two-box model results showing the influence of anthropogenic emissions on N_2O mixing ratio and isotopic composition in the troposphere. Left: full time range from the start of the anthropogenic period (1845) to present day; Right: zoom to the last two decades. Isotopic measurements at Jungfraujoch were used as the only constraint of current tropospheric N_2O isotopic composition for the model. See the materials and method as well as the SI for more details and other input parameters. Atmospheric as well as firm air measurements of $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\text{SP}}$ and $\delta^{18}\text{O}$ from the literature are presented for comparison. Blue shaded areas indicate one standard deviation of the model iterations.

1145