Supporting Information for

The isotopic composition of atmospheric nitrous oxide observed at the high-altitude research station Jungfraujoch, Switzerland

Longfei Yu[1*], Eliza Harris[1†], Stephan Henne[1], Sarah Eggleston[1], Martin Steinbacher[1], Lukas Emmenegger[1], Christoph Zellweger[1], Joachim Mohn[1]

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

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

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

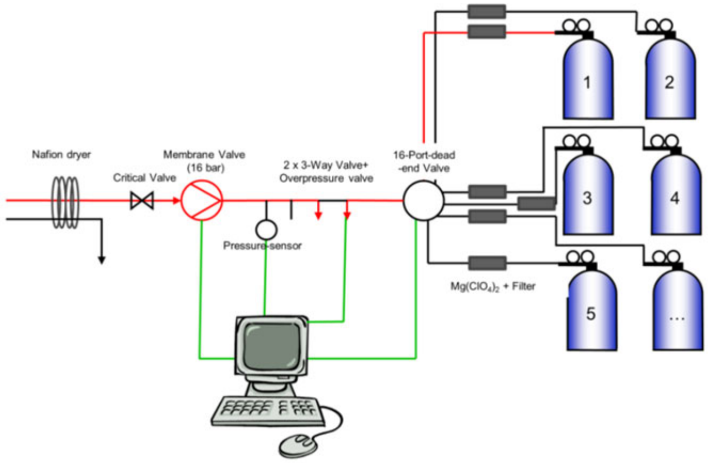

Figure S1 Set-up schematic of the auto-sampler for N_2O isotopic measurements at the Sphinx observatory at Jungfraujoch research station.

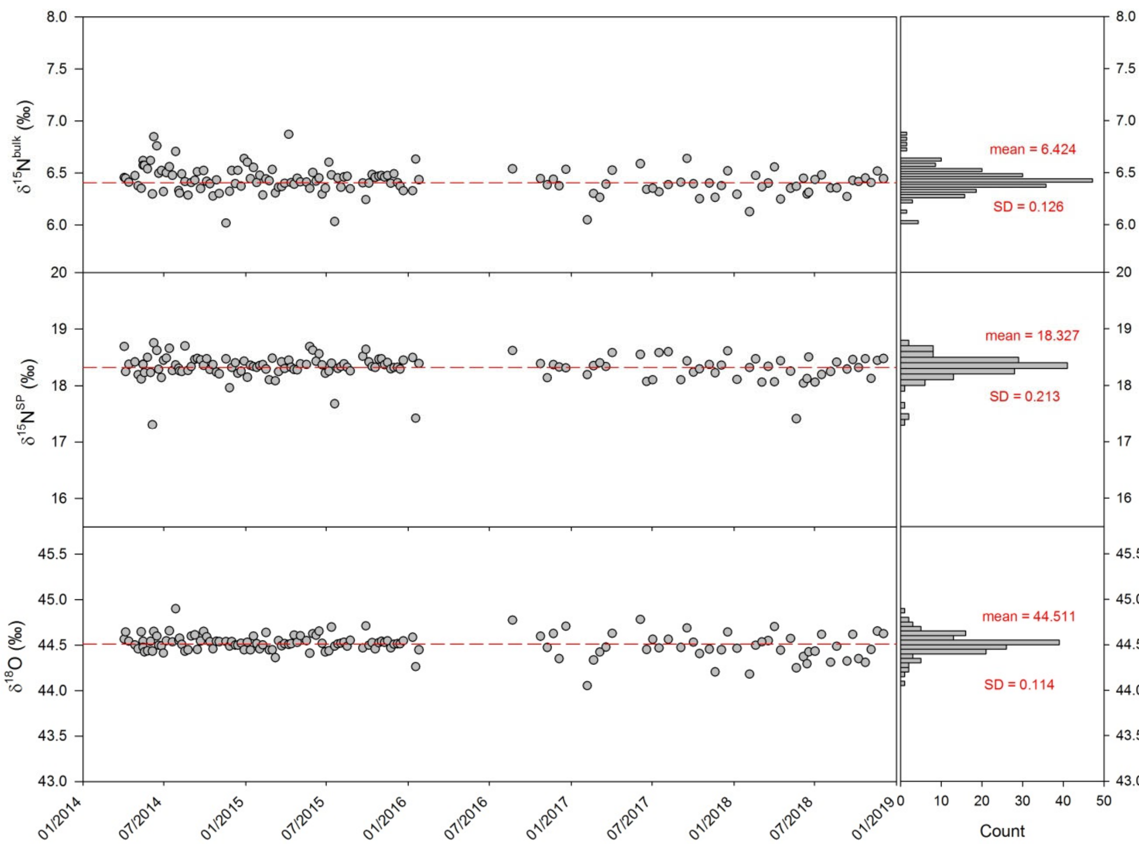

Figure S2 Repeated target gas measurements together with sample measurements; time axis is fit to the same time scale as the sample collection period to show the long-term stability of the isotopic measurements. Target measurements span a period of about four years. Histogram of all target gas measurements are shown on the right side of each figure, with mean and one standard deviation.

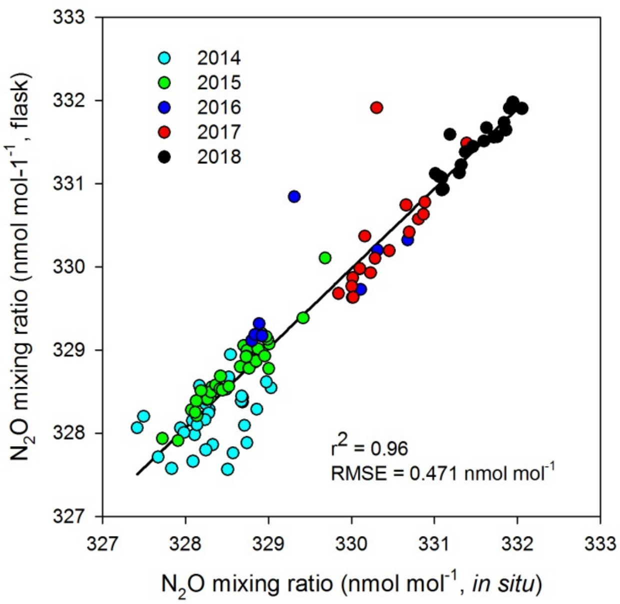

Figure S3 Comparison of *in situ* and discrete measurements of N_2O mixing ratios; *in situ* measurements were 10-minute values averaged over the exact period of discrete sampling time (~ 40 min); *in situ* measurements were performed with GC-ECD method in 2014, and this was replaced with OA-ICOS method from January 2015.

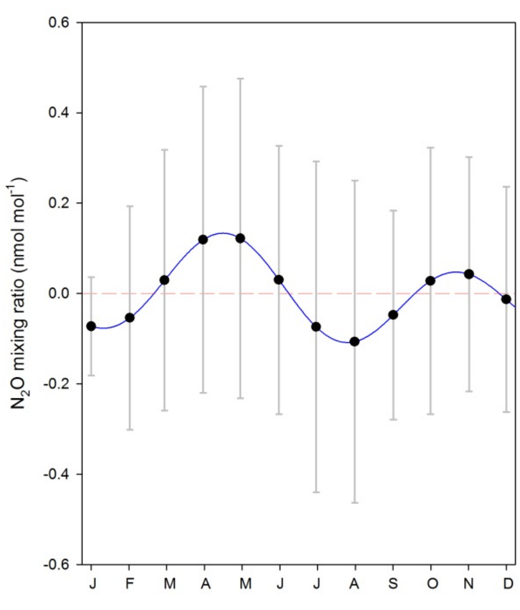

Figure S4 Seasonality of N_2O mixing ratios with discrete measurements; error bars indicate one standard deviation of monthly residuals from the NLS model simulation for time-series.

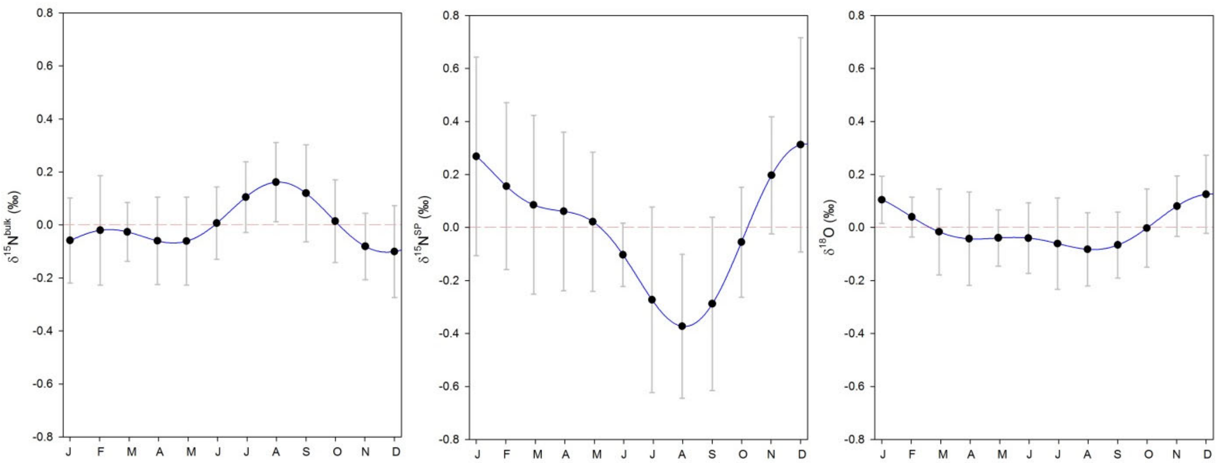

Figure S5 Seasonality of isotopic signatures of atmospheric N_2O (filtered for free troposphere) observed at Jungfraujoch; error bars indicate one standard deviation of monthly residuals from the NLS model simulation for time-series.

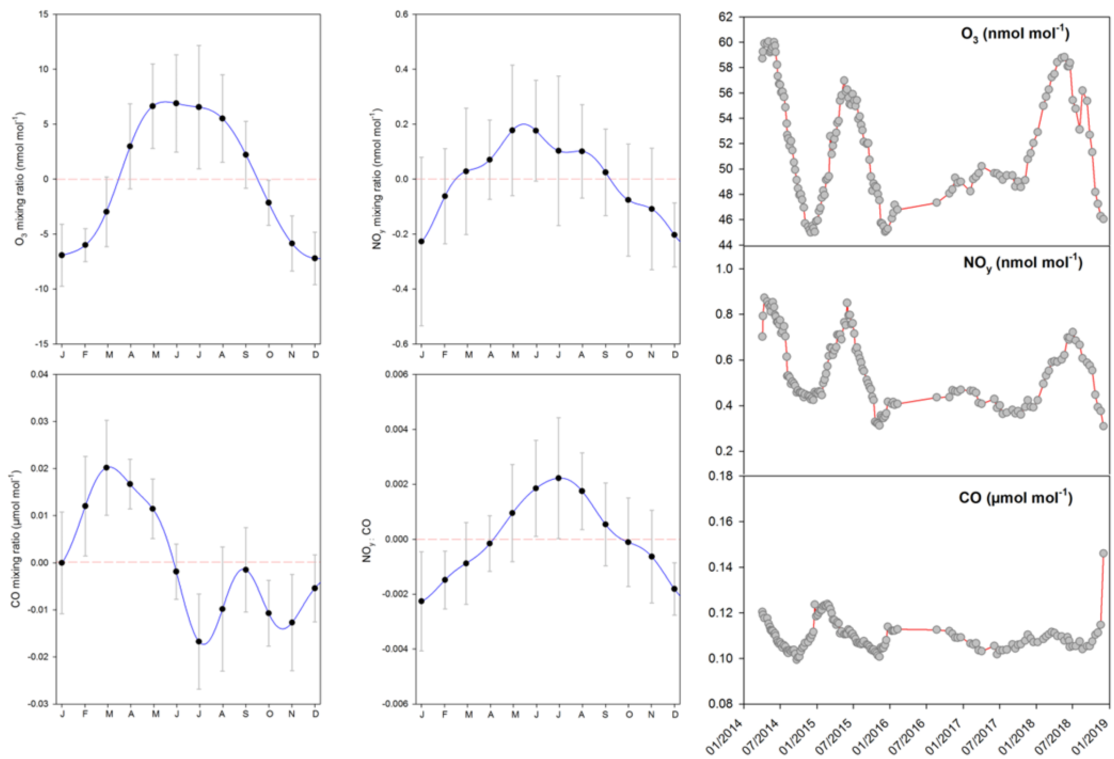

Figure S6 Left and middle: Seasonality of *in situ* measurements of O_3, NO_y and CO mixing ratios and NO_y/CO at Jungfraujoch; error bars represent the one standard deviation of monthly residuals from the NLS model simulation for time-series. 10-minute data were used for seasonality analysis.

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

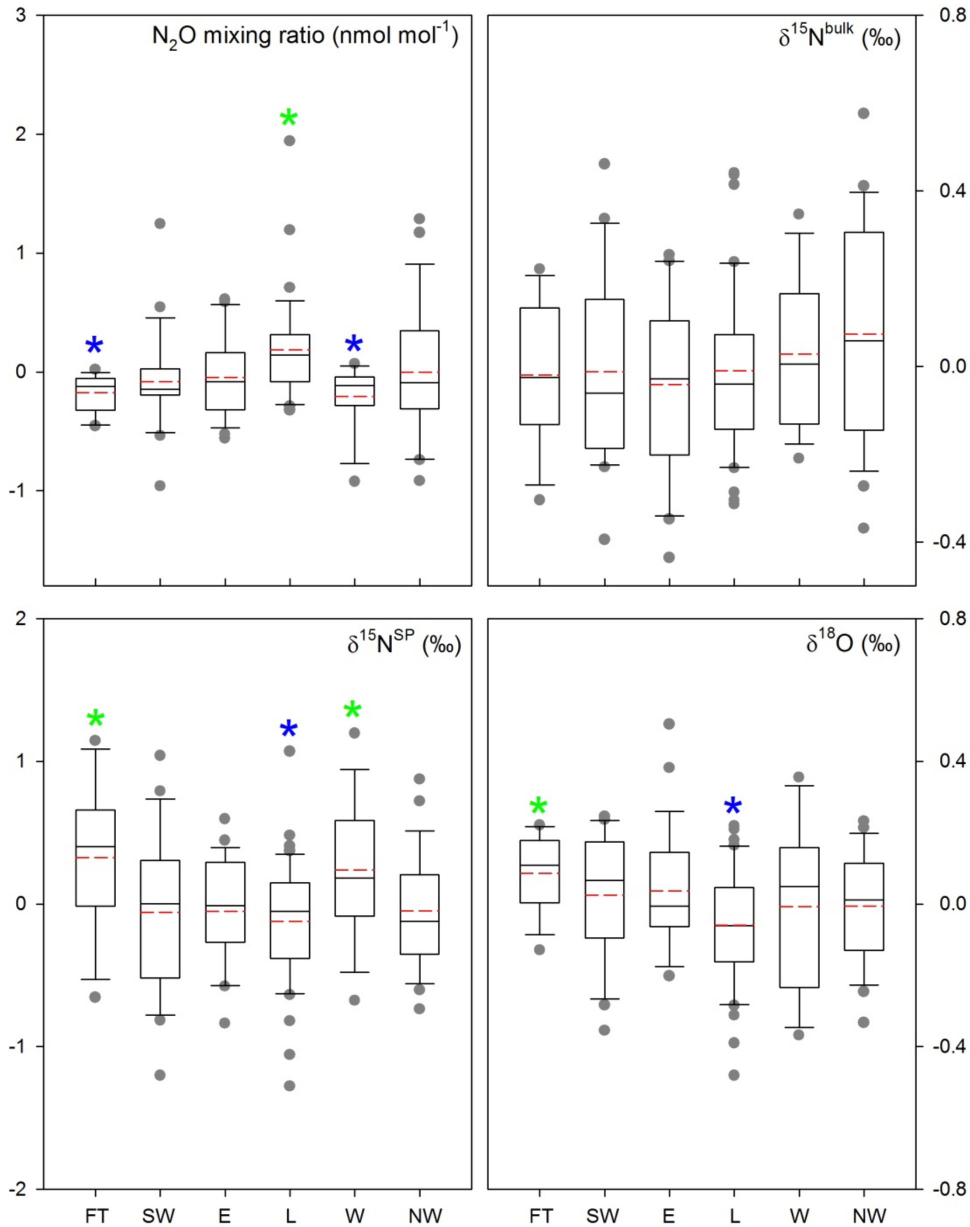

Figure S7 Comparison of N_2O mixing ratios and isotopic signatures (with linear trends removed) for the six air mass footprint clusters used in the present study. Green and blue stars indicate significantly larger and smaller than the others, respectively; red dashed lines indicate mean levels; grey points indicate outliers.

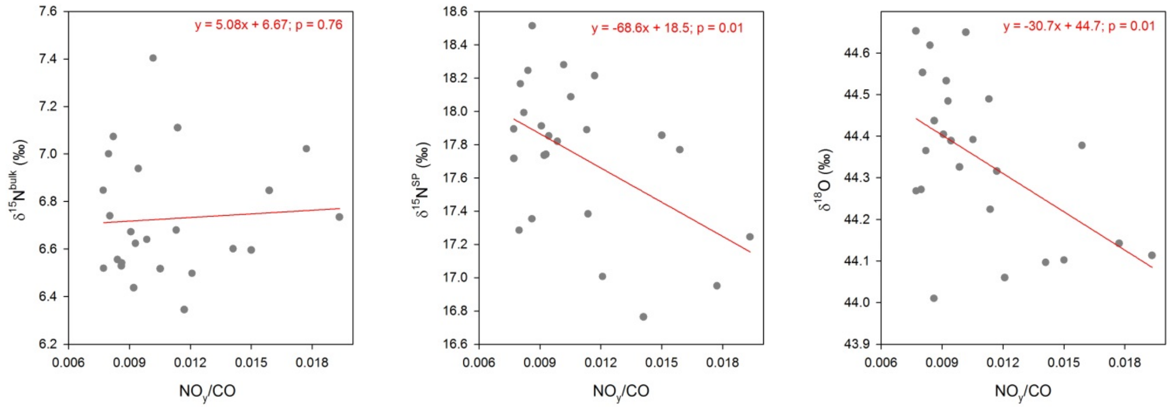

Figure S8 Relationship between the NO_y to CO ratios and isotopic signatures of N_2O; only data points with $NO_y/CO>0.007$ are presented here (which refers to scenarios with strong pollution from local air).

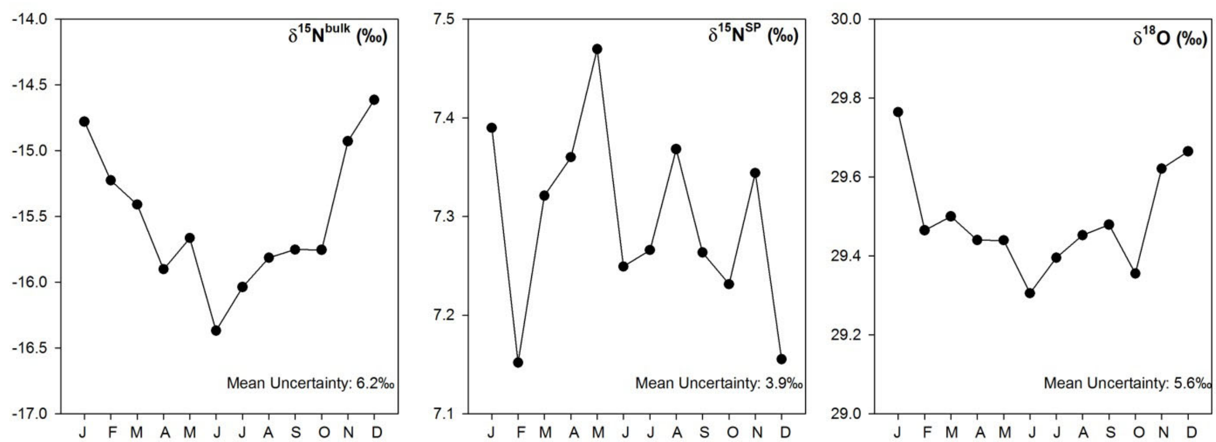

Figure S9 Simulated seasonal variations of isotopic signatures for overall N_2O sources based on the "bottom-up" approach; uncertainties shown in figures are comparable to the ranges of isotopic signatures for variable sources as found in literature.

Table S1 Input variables for simple two-box model (more details in M&M)

Variable	**Description**	**Value**	**Error distribution**	**Ref.**
m_{trop}	Air in the troposphere (mol)	1.5×10^{20}	Constant	2, 4
m_{strat}	Air in the stratosphere (mol)	2.7×10^{19}	Constant	2, 4
TS_{ex}	Troposphere-stratosphere exchange rate (kg a^{-1})	$(4.11 \pm 6.63) \times 10^{17}$	Uniform	2. 4
F_{ocean}	Oceanic N_2O flux (Tg a^{-1})	4±1	Gaussian	4
τ_{PI}	Preindustrial N_2O lifetime (year)	123±10	Gaussian	6
τ_{PD}	Present day N_2O lifetime (year)	116±9	Gaussian	6
c_{PI}	Mixing ratio in the preindustrial troposphere (nmol mol^{-1})	270±7.5	Uniform	1, 2
$\delta^{15}N^{bulk}{}_{PI}$	Mean $\delta^{15}N^{bulk}$ of preindustrial tropospheric N_2O (‰)	8.9±2	Gaussian	5
$\delta^{18}O_{PI}$	Mean $\delta^{18}O$ of preindustrial tropospheric N_2O (‰)	46.1±2	Gaussian	5
$\delta^{15}N^{SP}{}_{PI}$	Mean $\delta^{15}N^{SP}$ of preindustrial tropospheric N_2O (‰)	19.05±2	Gaussian	5
$\delta^{15}N_{ocean}$	Mean $\delta^{15}N^{bulk}$ for oceanic emissions (‰)	5.1±1.9	Uniform	7
$\delta^{18}O_{ocean}$	Mean $\delta^{18}O$ for oceanic emissions (‰)	44.8±3.6	Uniform	7
$\delta^{15}N^{SP}{}_{ocean}$	Mean $\delta^{15}N^{SP}$ for oceanic emissions (‰)	15.8±7.1	Uniform	7
$\delta^{15}N^{bulk}{}_{terr}$	Mean $\delta^{15}N^{bulk}$ for emissions from terrestrial soils (‰)	-16.7±11.2	Uniform	7
$\delta^{18}O_{terr}$	Mean $\delta^{18}O$ for emissions from terrestrial soils (‰)	30.1±9.6	Uniform	7
$\delta^{15}N^{SP}{}_{terr}$	Mean $\delta^{15}N^{SP}$ for emissions from terrestrial soils (‰)	10.1±11.2	Uniform	7

Table S2 An overview of N_2O emission sectors for Swiss Meteotest Inventory and global EDAGR Inventory and available source isotopic signatures (‰)*

Meteotest Category	Meteotest Sources	EDGAR Category[φ]	EDGAR Primary source(s)[φ]	$\delta^{18}O$	$\delta^{15}N^{bulk}$	$\delta^{15}N^{SP}$	References
Orgs	Organic soils	7B, 7C	Indirect soil emissions	29.0±3.7	-17.8±5.7	7.2±3.8	7, 15
IndustrialHeating	Cement production, industrial combustion, furnances, waste incinerator, other industrial	1A1, 1A2	$deNO_x$ use in fossil fuel and MSW incineration plants	35.9±13.1	3.9±2.9	17.6±0.5	9, 10
Transport	Agricultural and construction machinery, road traffic	1A3a, 1A3c, 1A3d, 1A3e, 1A3b	Fuel combustion in non-road transportation	28.6±9.9	-28.7±3.6	4.2±2.4	11
			Fuel combustion for road transportation	40.3±3.7	-7.2±1.2	10.0±4.3	11
Heating	Agricultural, commercial and private heating	1A4	Fuel combustion: other sectors (dominantly household heating)	37±10	5.5±6	3.5±4	9, 12
Refinery	Refineries	1B2a	Refineries	-	-	-	-
IndustryAndUse	Nitric acid production, use in households and hospitals	2 and 3	Nitric acid production (adipic acid, medical, and private (aerosol) use)	29.1±18.8	-8.3±10.6	3.3±5.5	11, 13
Manure	Manure management	4B	Manure management	23.9±3.8	-17.5±6.2	6.5±4.1	14
DirectAgri	Crop residues/soil organic matter, animal waste on pastures, synthetic fertilizer use, manure application	4C, 4D	Direct soil emissions	29.0±3.7	-17.8±5.7	7.2±3.8	7, 15
IndirectAgri	Leaching, other indirect emisions from agri. Soils	4D3	Direct soil emissions	29.0±3.7	-17.8±5.7	7.2±3.8	7, 15
WastBurning	Illegal waste burning	4F	Agricultural waste burning	25±3.0	-1.0±3.0	2.8±3.0	12
Waste	Industrial fermentation, wastewater treatment, sewage sludge burning	6	Waste (wastewater treatment)	31.5±14.1	-11.6±12.7	10.5±5.7	7
IndirectNat	Indirect emissions from (semi-)natural ecosystems	7B, and 7C	Indirect soil emissions	29.0±3.7	-17.8±5.7	7.2±3.8	7, 15

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

[φ] These are the primary sources contributing to N_2O emissions in Switzerland.

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