# Analysis of regional CO<sub>2</sub> contributions at the high Alpine observatory Jungfraujoch by means of atmospheric transport simulations and $\delta^{13}C$

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- 10 Abstract. Understanding of regional greenhouse gas emissions into the atmosphere is a prerequisite to mitigate climate change. In this study, we investigated the regional contributions of carbon dioxide (CO<sub>2</sub>) at the location of the high Alpine observatory Jungfraujoch ("JFJ", Switzerland, 3580 m a.s.l.). To this purpose, we combined receptor-oriented atmospheric transport simulations for CO<sub>2</sub> concentration in the period of 2009–2017 with stable carbon isotope (δ<sup>13</sup>C-CO<sub>2</sub>) information. We applied two Lagrangian particle dispersion models driven by output from two different numerical weather prediction systems (FLEXPART-COSMO and STILT-ECMWF) in order to
- simulate CO<sub>2</sub> concentration at JFJ based on regional CO<sub>2</sub> fluxes, to estimate atmospheric  $\delta^{13}$ C-CO<sub>2</sub>, and to obtain model-based estimates of the mixed source signatures ( $\delta^{13}$ C<sub>m</sub>). Anthropogenic fluxes were taken from a fuel typespecific version of the EDGAR v4.3 inventory, while ecosystem fluxes were based on the Vegetation Photosynthesis and Respiration Model (VPRM). The simulations of CO<sub>2</sub>,  $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{13}$ C<sub>m</sub> were then compared to observations
- 20 performed by quantum cascade laser absorption spectroscopy. The models captured around 40 % of the regional CO<sub>2</sub> variability above or below the large-scale background, and up to 35 % of the regional variability in  $\delta^{13}$ C-CO<sub>2</sub>. This is according to expectations considering the complex Alpine topography, the low intensity of regional signals at JFJ, and the challenging measurements. Best agreement between simulations and observations in terms of short-term variability and intensity of the signals for CO<sub>2</sub> and  $\delta^{13}$ C-CO<sub>2</sub> was found between late autumn and early spring.
- 25 The agreement was inferior in the early autumn periods and during summer. This may be associated with the atmospheric transport representation in the models. In addition, the net ecosystem exchange fluxes are a possible source of error, either through inaccuracies in their representation in VPRM for the (Alpine) vegetation or through a day (uptake) vs. night (respiration) transport discrimination to JFJ. Furthermore, the simulations suggest that JFJ is subject to relatively small regional anthropogenic contributions, due to its remote location (elevated and far from
- 30 major anthropogenic sources), and the limited planetary boundary layer-influence during winter. Instead, the station is primarily exposed to summer-time ecosystem CO<sub>2</sub> contributions, which are dominated by rather nearby sources (within 100 km). Even during winter, simulated gross ecosystem respiration accounted for approximately 50 % of all contributions to the CO<sub>2</sub> concentrations above the largescale background. The model-based monthly mean  $\delta^{13}C_m$ ranged from -22 ‰ in winter to -28 ‰ in summer and reached the most depleted values of -35 ‰ at higher fractions
- of natural gas combustion, and the most enriched values of -17 to -12 ‰ when impacted by cement production emissions. Observation-based  $\delta^{13}C_m$  values were derived independently from the simulations by a moving Keelingplot approach. While model-based estimates spread in a narrow range, observation-based  $\delta^{13}C_m$  exhibited a larger scatter and were limited to a smaller number of data points due to the stringent analysis prerequisites .

### **1. Introduction**

- 40 Reliable regional quantification of greenhouse gas (GHG) emissions into the atmosphere is a prerequisite to determine the effectiveness of mitigation strategies to limit global warming. Carbon dioxide (CO<sub>2</sub>) is the prime player in these regards. Its atmospheric concentrations are altered by both anthropogenic and natural (terrestrial ecosystem and oceanic) fluxes (Friedlingstein et al., 2020). Remote sites are ideal to study large-scale and global emissions, but make it more challenging to characterize individual sources and sinks as during transport of air masses the signals and signatures become increasingly diluted and mixed. Thus, remote atmospheric sites typically focus on long-term trends, and, therefore, sporadic events are often discarded in the time series analyses. This leads to loss of potentially insightful information.
- In this study, we focus on the information contained in the regional scale signals at the remote high altitude observatory Jungfraujoch (JFJ), situated in the Swiss Alps. Owing to its particular location in central Western 50 Europe and its altitude of 3580 m above sea level (a.s.l.), it allows for studying background concentrations of air pollutants and GHGs in the lower free troposphere (Herrmann et al., 2015). These background conditions are representative of large spatial or temporal scale variations and not influenced by regional sources or sinks. Furthermore, regional signals transported from different regions within Western Europe and beyond reach the monitoring station intermittently (Henne et al., 2010). Thus JFJ offers both aspects: i) insight into the atmospheric background, and ii) an opportunity for studying GHGs and pollutants sources and sinks in the planetary boundary 55 layer (PBL) on a regional scale. The latter is challenged, however, by low signal-to-background ratios, and requires high-precision instrumentation. In comparison to a typical low altitude site, the regional signal measured at JFJ is integrated over a larger concentration footprint (source area). This allows for a greater coverage per measurement, but also leads to a higher degree of mixing of various sources and sinks. Atmospheric backward transport 60 simulations can provide information about the history (location backward in time) of the sampled air mass and a quantitative relationship between atmospheric concentrations and sources or sinks (source/sink-receptor relationships) to combat this challenge. Although atmospheric transport and concentration simulations are particularly demanding for complex topography, observations at JFJ have been successfully combined with highresolution transport simulations in previous inverse modelling studies to allocate and quantify emissions of CH<sub>4</sub> 65 (Henne et al., 2016) and halocarbons (Keller et al., 2011; Brunner et al., 2017; Vollmer et al., 2021).

The same task, however, is more challenging for  $CO_2$ , because of the strong contribution of natural processes in addition to anthropogenic sources, the interplay between signals from sources and sinks, and the large temporal variability and broad distribution, especially of the natural fluxes. In this case, multi-tracer approaches are useful tools, as they allow for separation of different processes based on composition characteristics. Some of their benefits and limitations are briefly revoked in the following:

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• Carbon monoxide (CO), which is co-emitted during combustion processes, was used to identify combustion-related CO<sub>2</sub> signals (Levin and Karstens (2007), Vogel et al. (2010), Vardag et al. (2015) or Oney et al. (2017)). However, this method suffers from variable CO/CO<sub>2</sub> emission ratios and atmospheric production and loss of CO. The approach is most promising when all sources/sinks in the footprint area are well characterised, yet remains challenging for sites with low signal-to-background ratios.

- Other promising tracers are isotopes, as isotope composition measurements can provide valuable information on the sources and sinks contributing to the regional signal. Today, sufficiently precise instrumentation is available that allows to measure the stable isotope composition at high precision and temporal resolution for several natural GHGs (see Tuzson et al. (2008b) for CO<sub>2</sub>, Ever et al. (2016) for CH<sub>4</sub> and Waechter et al. (2008) for N<sub>2</sub>O). Applying these or similar techniques, for instance, Röckmann et al. (2016), Hoheisel et al. (2019), Menoud et al. (2020), Xueref-Remy et al. (2020) and Zazzeri et al. (2015 and 2017) derived observation-based isotope source signature estimates from measurements conducted to study near-source or regional-scale CH<sub>4</sub> plumes. Harris et al. (2017a and 2017b) and Yu et al. (2020) presented similar analyses for N<sub>2</sub>O. These studies took advantage of double-isotope constraints, i.e.,  $\delta^{13}$ C-CH<sub>4</sub> and  $\delta^2$ H-CH<sub>4</sub> for CH<sub>4</sub>, and  $\delta^{15}$ N-N<sub>2</sub>O and  $\delta^{18}$ O-N<sub>2</sub>O for N<sub>2</sub>O and provided very promising results, although the availability of long-term data sets is still very limited.
- The stable carbon isotope of CO<sub>2</sub>,  $\delta^{13}$ C-CO<sub>2</sub>, can be an attractive tracer for CO<sub>2</sub> sources and sinks. So far it has been largely employed for analysis of long-term atmospheric background trends (Keeling et al., 1979; Graven et al., 2017), in global ecosystem studies (Ballantyne et al., 2011; Keeling et al., 2017; Van Der Velde et al., 2018), or to characterise emissions close to a source. Traditionally, the near-source  $\delta^{13}$ C-CO<sub>2</sub> studies focus on ecosystem processes in areas with limited anthropogenic influence (Pataki et al., 2003), or on anthropogenic emissions under limited ecosystem influences, such as the vehicle tunnel study by Popa et al. (2014). However, the current instrumental capability of high precision  $\delta^{13}$ C-CO<sub>2</sub> observations at high temporal resolution (e.g., Sturm et al. (2013) or Vogel et al. (2013)) opens up new opportunities to 95 disentangle CO<sub>2</sub> in a more complex setting. For instance, Pugliese et al. (2017) and Vardag et al. (2016) recently studied urban air masses, and Ghasemifard et al. (2019) and Tuzson et al. (2011) attempted to characterise specific regional scale CO<sub>2</sub> signals at remote sites. These studies used hourly to daily resolution, and compared observation-based (mixed) isotope source signatures ( $\delta^{13}C_m$ ) with literature information on source-specific signatures ( $\delta^{13}C_s$ ); often, however, reducing the data to few particular 100 pollution events, as this method is applicable only under very stringent conditions (see e.g., Zobitz et al., 2006). These source identification or apportionment studies may successfully use  $\delta^{13}C_s$  to discriminate CO<sub>2</sub> emissions from fuel burning; in particular to distinguish gaseous (-40 ‰ for thermogenesis gas,-60 ‰ for microbial gas) from solid (-20 % to -25 %, for wood/coal) or liquid fuels (-25 % to -32 %, for heating oil, gasoline and diesel)<sup>1</sup>. However, ecosystem processes and their  $\delta^{13}C_s$  add further complexity, as they are 105 highly dependent on plant growth conditions (ambient humidity, CO<sub>2</sub> concentration) and photosynthetic pathway (C3- vs C4-plants), detailed by Hare et al. (2018) and Kohn (2010). CO<sub>2</sub> from C3 plants (which dominate ecosystems globally) carries a mean respiration signature of -27.5 ‰ with a range from -20 ‰ to -37 ‰ under arid, respectively humid, conditions. The smallest <sup>13</sup>C uptake relative to <sup>12</sup>C, i.e. highest fractionation and thus the most depleted  $\delta^{13}C_s$  of -37 %, is observed in tropical forests, and of little 110 relevance for European ecosystems. C4-plants (which includes primarily a few particular crops such as maize, sugar cane, sorghum and various kinds of millet, selected grasses (e.g., clover), and only few trees

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<sup>&</sup>lt;sup>1</sup> All  $\delta^{13}C_s$  values mentioned here are based on Andres et al. (1994), Vardag et al. (2015 and 2016) and Sherwood et al. (2017), and presented based on the Vienna Pee Dee Belemnite (VPDB) reference scale.

and desert shrubs) exhibit distinctly smaller <sup>13</sup>C fractionation during photosynthesis and can be distinguished from C3 plants based on their peculiar  $\delta^{13}C_s$  of about -12.5 %. In Europe C4 plants make up only a small fraction and are mainly present in croplands (maize production). Instead C3 plants dominate 115 the European and global ecosystems (Ballantyne et al., 2011). It is critical to note, that  $\delta^{13}C_s$  for C3 plant respiration and some anthropogenic sources overlap, limiting source apportionment approaches for ecosystem and anthropogenic contributions, which are based only on  $\delta^{13}C_s$ . The stable oxygen isotope ratio of CO<sub>2</sub>,  $\delta^{18}$ O-CO<sub>2</sub>, is, aside of the carbon cycle, subject to the global water cycle (e.g., Welp et al., 2011) due to the isotope exchange between water and CO<sub>2</sub> and thus ambiguous as CO<sub>2</sub> tracer. Instead, the 120 radiocarbon signature may be used to quantify fossil fuel contributions to atmospheric CO<sub>2</sub>, e.g., Levin et al. (2003), Vogel et al. (2010), Turnbull et al. (2015), Berhanu et al. (2017), or Wenger et al. (2019). The  $\Delta^{14}$ C allows primarily for discrimination of fossil versus ecosystem carbon. Once this is accomplished,  $\delta^{13}$ C provides further insight into the partitioning of fuel types among the fossil pool, or of contributions from different photosynthetic pathways among the ecosystem pool. Such dual carbon-isotope approaches making 125 use of co-located  $\delta^{13}C$  and  $\Delta^{14}C$  measurements have already proven successful for carbon source apportionment in few gas- (Meijer et al., 1996; Zondervan and Meijer, 1996) and particle phase studies (Winiger et al., 2019; Andersson et al., 2015). Yet, studies are currently limited to infrequent sampling at few locations, since the involved laboratory analyses are costly, and high frequency, in-situ measurement techniques with sufficient precision for atmospheric  $\Delta^{14}$ C-CO<sub>2</sub> currently unavailable, despite first 130 developments (e.g., Genoud et al., 2019; Galli et al., 2011).

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Despite these promising multi-tracer (CO<sub>2</sub>, CO) and multi-isotope ( $\delta^{13}$ C and  $\Delta^{14}$ C) approaches outlined above, the low signal-to-background ratios at remote sites still remain a challenge as highlighted in previous work by Vardag et al. (2015). Thus, combining measurements in addition with atmospheric simulations is essential for regional CO<sub>2</sub> apportionment. Yet, to date, only few studies have performed hourly-scale regional simulations of CO<sub>2</sub> concentration and/or provide "model-based" atmospheric  $\delta^{13}$ C-CO<sub>2</sub> or mixed isotope source signatures ( $\delta^{13}$ C<sub>m</sub>) for a comparison with observations. The available studies are limited to two ground-based urban locations (Pugliese-Domenikos et al. (2019) and Vardag et al. (2016)), and one rural tall tower location (Wenger et al., 2019).

Here, we address the situation at the high Alpine observatory JFJ. We aim at challenging our understanding of the contribution of CO<sub>2</sub> sources and sinks within the European domain to the regional CO<sub>2</sub> concentration variability at JFJ, and at evaluating model-based δ<sup>13</sup>C-CO<sub>2</sub> and model-based mixed isotope source signatures (δ<sup>13</sup>C<sub>m</sub>) against observations. To this end, we employ long-term regional CO<sub>2</sub> simulations for JFJ for a nine-year period (2009–2017) at 3-hourly time-resolution, using two different atmospheric transport models. We compare the model-based data to atmospheric observations, making use of the unique long-term high-frequency observations of CO<sub>2</sub> and δ<sup>13</sup>C-CO<sub>2</sub> measured by quantum cascade laser absorption spectroscopy (QCLAS) since 2008 (Sturm et al., 2013; Tuzson et al., 2011), and deploy a moving Keeling-plot method to obtain observation-based δ<sup>13</sup>C<sub>m</sub>.

## 2. Methods

### 2.1 Site description

The High Altitude Research Station Jungfraujoch (JFJ) is located at 7°59'20'' E, 46°32'53'' N in the Swiss Alps, at an altitude of 3580 m a.s.l. on a mountain saddle between the peaks of Jungfrau and Mönch (both > 4000 m a.s.l.).

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As part of the Swiss long-term national monitoring network (NABEL), regular measurements of air pollutants and GHGs are performed at JFJ since the 1970s (Buchmann et al., 2016). The station contributes to European (EMEP) and global (Global Atmospheric Watch; GAW) monitoring programmes and was labelled as class 1 station within the European Integrated Carbon Observing System (ICOS) in 2018 (Yver-Kwok et al., 2020).

#### **2.2 Atmospheric Transport Simulations**

- 155 Atmospheric CO<sub>2</sub> concentration simulations were conducted for the period 2009–2017 with two distinct combinations of Lagrangian particle dispersion models (LPDM), meteorological input fields, domain size and spatial resolution (Table 1). Both models were run in a receptor-oriented approach, following 'sampled' air masses backward in time, and as such providing surface source sensitivities ("footprints"). Convoluting these with spatially and temporally resolved CO<sub>2</sub> fluxes allows for quantitative simulations of CO<sub>2</sub> concentrations at the receptor site
- 160 (Seibert and Frank, 2004). Here, we use the fuel type-specific version of the Emissions Database for Global Atmospheric Research (EDGAR v4.3) inventory and the Vegetation Photosynthesis and Respiration Model (VPRM) to account for anthropogenic and ecosystem CO<sub>2</sub> fluxes, respectively. The simulated CO<sub>2</sub> mixing ratios are reported in ppm, and we refer to them as "concentration" for readability. In order to disentangle the influence of the underlying CO<sub>2</sub> fluxes and the transport dynamics on the simulated CO<sub>2</sub> concentrations at JFJ, the influence of
- 165 various parameters such as the domain size, the meteorological input fields, or the LPDM implementation was investigated in dedicated simulations with synthetic  $CO_2$  fluxes in Appendix A1.

LPDM	Meteo. input	Approximate spatial resolution (km <sup>2</sup> )	Domain*	Integration period (days)	Release height (m asl)	Sampling height (m)	Temporal resolution	CO <sub>2</sub> fluxes
FLEX- PART	MeteoSwiss COSMO	$7 \times 7$	WEU	4	3100	50	3-hourly avg.	EDGAR v4.3 (pre-release), VPRM offline (Gerbig and Koch, 2021)
STILT	ECMWF IFS	$\begin{array}{c} 25\times25\\ (10\times10) \end{array}$	EU	10	3100	$0.5  imes h_{ m PBL}$	3-hourly snapshots	EDGAR v4.3 (pre-release) VPRM online (Gerbig, 2021)

Table 1. Overview of atmospheric transport simulation models and their associated parameters.

\* "EU" and "WEU" refers to 33°N-73°N, -15-35°E, and 36.06-57.42°N, -11.92-21.04°E, respectively

### 170 2.2.1 FLEXPART-COSMO

A version of the LPDM FLEXPART (Pisso et al., 2019; Stohl et al., 2005) coupled to output from the regional numerical weather prediction model COSMO (Baldauf et al., 2011) was operated using operational analysis fields generated by MeteoSwiss (see Henne et al., 2016). The model was run in backward mode to calculate source sensitivities for JFJ. Within each 3-hourly interval, 50'000 model particles were initialized continuously at the receptor location and traced back in time for 4 days or until they left the model domain. FLEXPART considers

transport by the mean atmospheric flow as well as turbulent and sub-grid scale convective mixing. COSMO analyses

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were available hourly at a horizontal resolution of approx. 7 km  $\times$  7 km over Western Europe (COSMO-7; 36.06 – 57.42°N, –11.92 – 21.04°E; Figure S1). The horizontal resolution of the model does not resolve the steep topography around JFJ. Hence, a difference between observatory and model altitude exists. In previous studies (e.g., Keller et

180 al., 2011), the optimal release height was determined to be around 3100 m above sea level when using COSMO-7 inputs, which is between the true altitude (3580 m) and the model topography (2650 m) at JFJ. Surface source sensitivities were determined from the location of model particles below a sampling height of 50 m and stored 3-hourly along the backward simulation, allowing for a 3-hourly coupling to temporally variable surface fluxes.

#### 2.2.2 STILT-ECMWF

- 185 The Stochastic Time Inverted Lagrangian Transport (STILT) Model, first described by Lin et al. (2003), was driven by the numerical weather forecast fields from the European Centre for Medium-Range Weather Forecasts (ECMWF), as previously presented by Trusilova et al. (2010) and Kountouris et al. (2018a). The simulations for JFJ were performed at the same release height as with FLEXPART-COSMO (3100 m.a.s.l.), corresponding to 960 m above the model topography. STILT-ECMWF simulations are also routinely performed within the activities of
- 190 the ICOS Carbon Portal (CP), albeit at a release height of 720 m above model ground (2860 m a.s.l.) for the default products for JFJ (<u>https://stilt.icos-cp.eu/worker/</u>). The particles are released instantly on a 3-hourly interval and traced back in time for 10 days or until they leave the European domain (33°N–73°N, 15°W–35°E, Figure S1). The STILT calculations were driven by 3-hourly operational ECMWF-IFS analysis/forecast fields available at a resolution of 0.25° × 0.25° (approx. 25 km × 25 km), whereas STILT output was generated on a finer grid (approx.
- 195  $10 \text{ km} \times 10 \text{ km}$ ). Surface source sensitivities were evaluated by using a variable sampling height ( $0.5 \times h_{PBL}$ ), where  $h_{PBL}$  is the PBL height diagnosed within STILT. Transport and fluxes were coupled at hourly time resolution.

#### 2.3 CO<sub>2</sub> fluxes and boundary conditions for the atmospheric transport simulations

#### 2.3.1. Regional CO<sub>2</sub>

#### A) Anthropogenic Emissions

- Regional anthropogenic CO<sub>2</sub> concentrations for JFJ (CO<sub>2</sub>.anthr) were calculated using emission fluxes based on a pre-release of EDGAR v4.3 (pers. comm. with G. Janssens-Maenhout). The inventory was disaggregated into fuel-type specific categories (Table S1), and provides annual emissions on a 0.1° × 0.1° grid (~10 km × 10 km) (Janssens-Maenhout et al., 2019; Karstens, 2019). Here, we use 14 categories, representing 11 different fossil and biogenic fuel types as well as 3 non-fuel categories from cement and other production processes (Table 2). The CO<sub>2</sub>.anthr comprises CO<sub>2</sub> from fuel-burning CO<sub>2</sub> (oil, gas, coal, liquid biofuels, biogas, solid biomass), and CO<sub>2</sub> from cement and other industrial production (referred to as CO<sub>2</sub>.cement collectively). We temporally extrapolated the inventory, which was established for the base year 2010, using annual scaling factors per country and category based on data
  - from BP (bp, 2019), see Table S2. Additionally, we applied seasonal, weekly, and diurnal time factors for different anthropogenic categories. These are based on MACC-TNO (Kuenen et al., 2014) and available in Table S3.

#### 210 B) Ecosystem Fluxes

Regional ecosystem  $CO_2$  fluxes were based on the VPRM (Mahadevan et al., 2008). Underlying parameters are specific for seven vegetation types (VT) including: 1) evergreen forest, 2) deciduous forest, 3) mixed forest, 4)

shrubland, 5) savanna, 6) cropland, 7) grassland. The VTs are based on the settings typically used within the ICOS Carbon Portal, although, for instance, category 5 (savanna) is irrelevant within the domain boundaries used for JFJ.

- An additional category "others" includes primarily water bodies and urban spaces for which VPRM does not estimate CO<sub>2</sub> fluxes and, hence, was excluded from the final analysis. The VT maps underlying VPRM are based on the synergetic land cover product (SYNMAP, Jung et al., 2006). A map showing the dominant category per grid as used in our study is provided in Figure S2. Note that oceanic sources and sinks (including oceanic biomass), as well as human or animal respiration (see e.g., Ciais et al., 2020) and wildfire related emissions were not included,
- and are expected to be a minor contribution to the regional signal at JFJ. With FLEXPART-COSMO, we use an offline version of VPRM (Gerbig and Koch, 2021) based on the same ECMWF meteorological analysis as in STILT-ECMWF. Although the fluxes are generated based on the individual VTs, ecosystem respiration (CO<sub>2</sub>.resp), ecosystem uptake (also referred to as gross ecosystem exchange, and thus abbreviated CO<sub>2</sub>.gee), and net ecosystem exchange (CO<sub>2</sub>.nee = CO<sub>2</sub>.gee – CO<sub>2</sub>.resp) are provided only as a total over all VTs. The STILT-ECMWF is coupled
- online with VPRM and allows extracting CO<sub>2</sub> concentration contributions at JFJ for CO<sub>2</sub>.nee, CO<sub>2</sub>.gee and CO<sub>2</sub>.resp for the individual VTs separately. The *online* VPRM parametrisation initially presented by Kountouris et al. (2018b) was updated for our study (Gerbig, 2021). A dedicated evaluation of the online compared to the offline implementation with STILT-ECMWF for at JFJ yielded comparable results for CO<sub>2</sub>.nee, CO<sub>2</sub>.gee and CO<sub>2</sub>.resp.

#### 2.3.2 Background CO<sub>2</sub>

We use the Jena CarboScope (JCS) global atmospheric CO<sub>2</sub> product for the determination of the CO<sub>2</sub> boundary conditions. These simulations are based on optimized fluxes (Rödenbeck, 2005) and available at <u>http://www.bgc-jena.mpg.de/CarboScope/</u>. We used three-dimensional CarboScope fields (version/experiment: s04oc\_v4.3) with a temporal resolution of 6 hours and interpolated concentrations in space and time to the endpoints of model particles. The mean over all model particles of a given release forms the background concentration (denoted f<sub>b</sub> herein) at the time of the release. We observed a higher short-term variability in the simulated background CO<sub>2</sub> concentration for

FLEXPART-COSMO compared to STILT-ECMWF, which is a consequence of the smaller domain size, in

- 2.3.3 Total CO<sub>2</sub>
- The sum of CO<sub>2</sub>.anthr and CO<sub>2</sub>.nee concentrations provides the regional contribution to the CO<sub>2</sub> concentration at JFJ (i.e., CO<sub>2</sub>.regional). Together with the simulation-specific background for either FLEXPART-COSMO or STILT-ECMWF this yields the total CO<sub>2</sub> concentration (i.e., CO<sub>2</sub>.total) at JFJ.

particular towards Eastern Europe, and shorter backward-integration time (4 days versus 10 days).

## 2.4 Model-based $\delta^{13}$ C-CO<sub>2</sub> estimation

The stable carbon isotope ratio of CO<sub>2</sub> is referred to as  $\delta^{13}$ C-CO<sub>2</sub>, or  $\delta^{13}$ C in short. The estimation of the mixed  $\delta^{13}$ C-CO<sub>2</sub> source signature ( $\delta^{13}$ C<sub>m</sub>) and ambient  $\delta^{13}$ C-CO<sub>2</sub> isotope ratios ( $\delta^{13}$ C<sub>a</sub>) is based on the CO<sub>2</sub> concentration simulations. All  $\delta^{13}$ C-CO<sub>2</sub> estimates are given in permille (‰) relative to the Vienna Pee Dee Belemnite (VPDB)

simulations. All  $\delta^{13}$ C-CO<sub>2</sub> estimates are given in permille (‰) relative to the Vienna Pee Dee Belemnite (VPDB) reference standard. Further information on stable isotope expressions and definitions are available in Coplen (2011).

#### **2.4.1** Mixed source signature $(\delta^{13}C_m)$

The absolute values of simulated CO<sub>2</sub> concentrations per source and sink category *i*,  $|f_{s,i}|$ , were weighted with category-specific source signatures,  $\delta^{13}C_{s,i}$ , to retrieve a mixed source signature,  $\delta^{13}C_m$  according to Eq. (1) using the  $\delta^{13}C_s$  literature-based assumptions summarized in Table 2 and Table 3. The simulated anthropogenic CO<sub>2</sub> data were disaggregated based on fuel type (Table 2) rather than sectorial processes, because  $\delta^{13}C_s$  can best be attributed as a function of fuel type. For ecosystem fluxes, a seasonal cycle in  $\delta^{13}C_s$  was assumed (Table 3). Following the reasoning of Vardag et al. (2016), the CO<sub>2</sub>.gee was treated as source, i.e., its absolute value, was considered, along with the  $\delta^{13}C_s$ , using a reversed sign in Eq. (1).

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<b>Table 2.</b> Fuel type-specific $\delta^{13}C_s$ assigned to the simulated anthr	copogenic CO <sub>2</sub> categories.
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CO <sub>2</sub> .anthr	$\delta^{13}C_s, \infty$
CO <sub>2</sub> .fuel	
gas, natural	-44.0
gas, derived	-44.0
coal, hard	-24.1
coal, brown	-24.1
coal, peat	-24.1
oil, heavy	-26.5
oil, light	-26.5
oil, mixed	-26.5
bio, gas	-60.0
bio, solid	-24.1
bio, liquid	-26.5
CO <sub>2</sub> .cement	
cement	-0

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Assumptions for fossil and cement sources are based on Andres et al. (1994). Gaseous fuels are characterised by a large range (-15 to -85 ‰) as reviewed by Sherwood et al. (2017), with a mean of -44 ‰. The biogas signature is based on measurements of  $\delta^{13}$ C-CH<sub>4</sub> released by cows, a biogas production plant, and waste-water treatment (Hoheisel et al., 2019; Levin et al., 1993). The values are in line with microbial  $\delta^{13}$ C-CH<sub>4</sub> reviewed by Sherwood et al. (2017). CO<sub>2</sub>.cement includes industrial emissions from cement production (NMM) alongside two minor contributors (CHE, IRO), as detailed in Table S1.

**Table 3.** Assumptions for ecosystem  $\delta^{13}$ Cs, based on Ballantyne et al. (2010 and 2011) and Vardag et al. (2016).

Months	$\delta^{13}C_s, \infty$	$\delta^{13}C_s, \infty$
	CO <sub>2</sub> .resp	CO <sub>2</sub> .gee
January	-27	-25
February	-26	-24
March	-25	-23
April	-24	-22
May	-23	-21
June	-22	-20
July	-22	-20
August	-23	-21
September	-24	-22
October	-25	-23
November	-26	-24
December	-27	-25

$$\delta^{13} C_m = \frac{\sum_{n=1}^{l} (|f_{s,i}| \times \delta^{13} C_{s,i})}{\sum_{n=1}^{i} (|f_{s,i}|)}$$
(1)

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#### 2.4.2 $\delta^{13}$ C-CO<sub>2</sub> background estimate ( $\delta^{13}$ C<sub>b</sub>)

The Jena CarboScope (JCS) CO<sub>2</sub> background concentration simulation for JFJ serves as  $f_b$ . The  $\delta^{13}$ C-CO<sub>2</sub> background value,  $\delta^{13}$ C<sub>b</sub>, is estimated thereof throughscaling  $f_b$  by using a relationship between observations of CO<sub>2</sub> and  $\delta^{13}$ C-CO<sub>2</sub> in background air (flask samples as detailed in section 2.6), derived following the strategy by Vardag et al. (2016) by applying yearly linear regression fits between measurements of CO<sub>2</sub> concentration and  $\delta^{13}$ C-CO<sub>2</sub> under free troposphere conditions at JFJ (method A). The obtained  $\delta^{13}$ C<sub>b</sub> is provided in Figure S3.. In addition to method A we also obtained estimates for  $\delta^{13}$ C<sub>b</sub> based on a moving linear regression over a 12 months window (method B). Alternatively, we tested the ratio of  $\delta^{13}$ C-CO<sub>2</sub> and CO<sub>2</sub> in background air as scaling factor, using monthly data averaged over 2009–2017 (method C), and daily ratios (method D). The daily ratios were obtained from QCLAS measurements at 5-6 AM, as the early morning is considered as background condition for JFJ. Results are available in Figure S4.

#### 2.4.3 Atmospheric $\delta^{13}$ C-CO<sub>2</sub> estimates ( $\delta^{13}$ C<sub>a</sub>)

The mixed source signature,  $\delta^{13}C_m$ , derived in Eq. (1) was combined with the background estimates ( $f_b$ ,  $\delta^{13}C_b$ ) in order to derive estimates of atmospheric  $\delta^{13}C$ -CO<sub>2</sub> isotope ratios at JFJ,  $\delta^{13}C_a$ , following Eq. (2). Note that, contrary to Eq. (1), CO<sub>2</sub>.gee is considered as effective sink in Eq. (2), which is further detailed in Vardag et al. (2016).

$$\delta^{13}C_a = \frac{(f_b \times \delta^{13}C_b) + (\sum_{n=1}^{i} (f_{s,i}) \times \delta^{13}C_m)}{f_b + \sum_{n=1}^{i} (f_{s,i})}$$
(2)

#### 2.5 Observation-based $\delta^{13}$ C-CO<sub>2</sub> estimation

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Observation-based mixed source signature,  $\delta^{13}C_m$ , were derived using a moving Keeling-plot approach following the example of Vardag et al. (2016) and using JFJ specific fitting and filtering criteria, as detailed in section 3.2.3.

#### 2.6 Observations

The CO<sub>2</sub> concentrations and δ<sup>13</sup>C-CO<sub>2</sub> isotope ratios were continuously measured at JFJ by quantum cascade laser absorption spectroscopy (QCLAS) during the period 2009–2017. The custom-built QCLAS instrument (Nelson et al., 2008; Tuzson et al., 2008b, 2008a, 2011; Sturm et al., 2013) provides high-precision data for the three main CO<sub>2</sub> isotopologues (<sup>12</sup>C<sup>16</sup>O<sub>2</sub>, <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O), and therefore, it allows simultaneous determination of the CO<sub>2</sub> concentration and the δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> values at 1 s time resolution. The CO<sub>2</sub> dry air mole fractions (µmol mol<sup>-1</sup>) are reported in units of parts per million (ppm) on the World Meteorological Organization (WMO) CO<sub>2</sub> X2007 scale, while the isotope ratio values are given in ‰, relative to the Vienna Pee Dee Belemnite (VPDB) reference standard. The instrument was configured as described in Tuzson et al. (2011) during 2009–2011.
295 Hardware and calibration strategy were revised during an upgrade in 2012, as described in Sturm et al. (2013) to

improve long-term precision, stability, and SI-traceability. Furthermore, the instrument participated in the

WMO/IAEA Round Robin 6 Comparison Experiment to assess the instrument capability to maintain the link to the WMO recommended level under field operation (NOAA, 2015). Stable operating conditions guarantee a precision of 0.02 ‰ for  $\delta^{13}$ C-CO<sub>2</sub> and 0.01 ppm for CO<sub>2</sub> at an optimum averaging time of 10 min. During 2016–2017,

- 300 laboratory temperature instabilities adversely affected instrument performance, causing lower data coverage. CO<sub>2</sub> concentrations were in addition determined at 1 min time resolution by a commercial cavity ring-down spectrometer (CRDS, G2401, Picarro Inc., USA) since 2010, likewise linked to the WMO CO2 X2007 scale. These data are available as ICOS product (Emmenegger et al., 2020). The mean difference  $(1\sigma)$  between the 10 min averaged CRDS and OCLAS data is  $0.1\pm0.4$  ppm for the entire observation period. Besides the in-situ measurements, air
  - 305 samples were collected in triplicate every second Friday at around 7 AM local time, i.e., at a time when the JFJ site predominantly experiences lower free troposphere conditions (Herrmann et al., 2015). CO<sub>2</sub> concentration,  $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{18}$ O-CO<sub>2</sub> in the flask samples were analysed at Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena as described in Van Der Laan-Luijkx et al. (2013). The flask data, which defined by the sampling time correspond primarily to background conditions at JFJ, are used to construct  $\delta^{13}C_b$ . A comparison of flask sample measurements
  - 310 with the QCLAS measurements for 2009–2017 indicates very good agreement, typically within  $\pm 0.2$  ppm for CO<sub>2</sub> and  $\pm 0.1$  % for  $\delta^{13}$ C-CO<sub>2</sub>, as well as no apparent systematic bias as function of time or signal intensity. It should be noted that the data and sample collection for in-situ measurements (QCLAS) and offline samples (flasks) was not primarily designed to assess an inter-comparison between the two measurements systems. In particular, uncertainties exist regarding the accurate matching of time stamps. Therefore, the real agreement of the
- 315 measurements is likely even better.

#### 2.7 Time-series Analysis

Time series analysis was performed using R programming language, v3.6.1 (R Core Team, 2019), deploying available R packages (<u>https://cran.r-project.org</u>) as well as custom developed scripts. While FLEXPART-COSMO simulations provide 3-hourly averages, STILT-ECMWF provides instantaneous snapshots every 3<sup>rd</sup> hours. STILT-ECMWF simulations were interpolated between the 3-hourly nodes for comparison with 3-hourly averages of

320 ECMWF simulations were interpolated between the 3-hourly nodes for comparison with 3-hourly averages of observational data. For comparing the observations with the LPDM model output, we use 3-hourly and monthly averages of the QCLAS measurements. Furthermore, a common JCS-based background is subtracted from the measurements. The STILT-ECMWF JCS-based background is preferred as common background for this particular assessment over the FLEXPART-COSMO background owing to the higher short-term variations in the latter (compare Figure S3a). The background-subtracted data set is referred to as "regional observations".

### **3. Results and Discussion**

#### 3.1 Regional CO<sub>2</sub> simulations at JFJ

#### 3.1.1 Monthly time-scale

#### A) Planetary boundary layer influence at JFJ

- 330 Air mass transport dynamics determine the exposure of the receptor site JFJ to air masses from the planetary boundary layer (PBL). Thus, together with the source or sink strength in the footprint region, they drive the regional contributions to the  $CO_2$  concentrations, and are discussed upfront. Previous analyses of tracers (e.g., radon and  $CO/NO_{y}$ ) by Herrmann et al. (2015) suggested that, compared to winter (December–February), the PBL-influence at JFJ is enhanced by 1.5 to 2.5-fold in April and August/September, and by 3 to 4-fold from May–July. To isolate 335 the influence of seasonally varying transport, we performed dedicated simulations where  $CO_2$  fluxes were assumed constant in space and time (see Appendix A1). This analysis revealed a 2 to 3-fold larger simulated PBL-influence in summer compared to winter for both models. Diurnal variations were most pronounced in summer, indicating a 1.4-fold larger PBL-influence during the afternoon and evening (maximum at ~16:00 h, UTC+1) compared to the morning (minimum at ~10:00 h, UTC+1). A larger PBL-influence in May and September for STILT-ECMWF 340 compared to FLEXPART-COSMO appears to be a peculiarity of using ECMWF fields and may reflect the lesswell resolved transport in complex terrain in the coarser resolution data from ECMWF. Additional differences appear related to the smaller domain size and shorter backward integration used for FLEXPART-COSMO, which are directly associated with smaller integrated surface CO<sub>2</sub> fluxes. The findings for STILT-ECMWF and FLEXPART-COSMO from the transport dynamics analysis (Appendix A1) appear to explain some of the mismatch
- in the simulated  $CO_2$  observed between the simulations in Figure 1 (see 3.1.1 B).

#### B) Regional CO<sub>2</sub> concentration observations and simulations

Simulated CO<sub>2</sub>.regional for 2009–2017 is compared with the respective regional CO<sub>2</sub> concentration observations in Figure 1 (multi-annual monthly means of 3-hourly). The CO<sub>2</sub>.regional observations show a minimum in June and a maximum in October and November, both with an amplitude of about 1.8 ppm. Subpanels present the corresponding simulated anthropogenic (CO<sub>2</sub>.anthr) and ecosystem components (CO<sub>2</sub>.nee, CO<sub>2</sub>.gee, CO<sub>2</sub>.resp).



**Figure 1.** Multi-annual monthly means of 3-hourly regional CO<sub>2</sub> simulations compared to observations (2009–2017). CO<sub>2</sub>.regional (**a**), and its components CO<sub>2</sub>.anthr (**c**), and net ecosystem exchange (CO<sub>2</sub>.nee) (**d**). The difference between simulations (sim) and observations (obs) are presented in **b**). CO<sub>2</sub>.nee is composed of **e**) gross ecosystem respiration (CO<sub>2</sub>.resp) and **f**) gross ecosystem exchange (CO<sub>2</sub>.gee), i.e. gross uptake. Error bars represent 1SD of the multi annual means and reflect the year-to-year variability for 2009–2017.

While CO<sub>2</sub>.anthr and CO<sub>2</sub>.nee together constitute CO<sub>2</sub>.regional, the sum of ecosystem components CO<sub>2</sub>.gee and CO<sub>2</sub>.resp results in CO<sub>2</sub>.nee. The minimum in June as observed in the measurements is well represented by the
models, though the amplitude is overestimated. The October/November maximum is delayed in both models by about one month. A local minimum in December/January is seen in observations and models. The winter minimum in the regional signal reflects the limited influence of PBL air masses at JFJ during this period of the year, and coincides with a minimum in CO<sub>2</sub>.anthr (Figure 1c) and ecosystem CO<sub>2</sub> (Figure 1d-f). The models thus appear to represent the processes contributing to the seasonal variability of the regional CO<sub>2</sub> signal at JFJ quite realistically.
Noteworthy, the seasonal trends of the regional signal, in particular the local winter minimum, differ from those in the large-scale CO<sub>2</sub> background concentrations, which show a minimum in August, two months later than the regional signal, and only one maximum in March/April, as shown by Sturm et al. (2013).

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Regarding CO<sub>2</sub>.anthr (Figure 1c), we conclude that the reduced transport of PBL air to JFJ during December/January outweighs a maximum in anthropogenic surface emission fluxes related to enhanced fuel use for heating during the cold season. Instead, CO<sub>2</sub>.anthr simulations reach a maximum at JFJ in spring (April/May) in both models, resulting from still relatively large anthropogenic surface emissions and generally more unstable atmospheric conditions due to rising surface temperatures and sustained colder temperatures aloft. The STILT-ECMWF simulations comprise a second CO<sub>2</sub>.anthr maximum in autumn (September), which is in line with the simulated PBL-influence (Appendix A1).

375 Given that ecosystem contributions quantitatively dominate the regional contributions to  $CO_2$  concentrations during summer, we reiterate that the  $CO_2$ .nee simulations depend on the parameterization of

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ecosystem respiration and uptake fluxes in VPRM. The parameterization accounts for environmental factors such as temperature, radiation, and through MODIS derived enhanced vegetation index (EVI) and land surface water index (LSWI) also for soil moisture (Mahadevan et al., 2008). Warmer temperatures generally lead to enhanced gross ecosystem fluxes (CO<sub>2</sub>.resp and CO<sub>2</sub>.gee) in summer compared to winter. These trends are indeed reflected in the simulations for JFJ (Figure 1d-f). The strong negative regional CO<sub>2</sub>.nee from March to October is a result of only partial compensation of uptake (CO<sub>2</sub>.gee) by respiration (CO<sub>2</sub>.resp). The CO<sub>2</sub>.gee minimum in June does not coincide with the CO<sub>2</sub>.resp maximum in July/August. This may be explained by the fact that respiration is strongly dependent on temperature, and July and August typically show the highest average temperatures in the relevant footprint region. Ecosystem uptake, on the other hand, has a more complex relationship with temperature (drops off when too hot), radiation (actually largest in June), water availability (usually decreasing during the summer), and plant phenology (e.g., Bonan, 2015; Mahadevan et al., 2008).

The simulations qualitatively satisfy our expectations. However, the overestimation of the amplitude in summer and early autumn by the two models merit further discussion of potential contributions to this mismatch, which includes uncertainties in the transport model or in the spatio-temporal flux distribution. A quantitative assessment is available in section 3.2.2 C.

- <u>Transport Dynamics</u>: The fluxes computed by VPRM together with the air mass transport dynamics determine the final seasonality of the ecosystem-related CO<sub>2</sub> contributions at JFJ.
- a. It has been reported by Denning et al. (1999) that the signal from respiration CO<sub>2</sub> is amplified over flat terrain, because respiration dominates at night when the boundary layer is shallow. This observation is referred to as "*rectifier effect*". At JFJ, we likely observe the inverse situation, a "*fair-weather effect*", as warm and sunny afternoons favour PBL-influence at JFJ, while low irradiation periods (nighttime, winter) limit the PBL-influence. Vertical atmospheric transport and photosynthetic activity (uptake) covary and are both largest on sunny days. In contrary, ecosystem respiration is active independently of light condition (day/night) and, to a smaller degree, during colder periods, when PBL-influence is limited at JFJ. Such "*fair-weather effects*" may be inadequately captured in the models, as the vertical export of PBL air in these situations is driven by thermally-induced flow systems in complex terrain (up-slope, up-valley, see Rotach et al., 2014) that cannot be adequately resolved at the present model horizontal resolution.
- b. The simulations for JFJ indicate that a considerable fraction of ecosystem CO<sub>2</sub> originated from fluxes within the last few hours before arrival at JFJ and at distances shorter than 100 km from the site (predominantly north of JFJ). We find that this "nearby" contribution is particularly pronounced in summer, whereas cold season sampled air masses are rather associated with a much wider concentration footprint and are less dominated by those "nearby" vegetation fluxes. In addition, the nearby vegetation fluxes seem artificially enhanced by the limited spatial resolution of the vegetation maps (see also 2c).
  - <u>VPRM</u>: An overestimation of the CO<sub>2</sub>.gee or an underestimation of CO<sub>2</sub>.resp may be associated with harvesting activities and drought stress, which are not well reflected in the current parameterisation of VPRM, as well as the spatial representation of vegetation maps and temperature profiles.

- a. Harvesting usually results in a change of the Enhanced Vegetation Index (EVI) derived from the MODIS observations. While the reduced ecosystem uptake due to harvesting is thus in principle already represented in VPRM, the agricultural biomass left behind after the harvest may lead to increased respiration. VPRM is unlikely to capture this latter process with its simple linear dependence of respiration on temperature.
  - b. Water stress (drought) can lead to altered respiration and uptake fluxes (e.g., Ramonet et al. (2020) or Gharun et al. (2020)), but it is not explicitly included in VPRM.
  - c. Owing to the smoothed topography and vegetation maps in the models, the effective temperatures in alpine vegetation is likely not well represented and, moreover, the temperature-parameterisations in VPRM is not optimized for alpine vegetation. No systematic bias net ecosystem exchange is apparent for ecosystem simulations with STILT-ECMWF for other observational sites in Europe (data available at the ICOS Carbon Portal), suggesting that the discrepancy is predominantly linked to JFJ's location in complex terrain. Indeed, summer discrepancies appear to be comparatively large at JFJ (3580 m a.s.l.) even when considering other mountain stations, such as Monte Cimone (~2000 m a.s.l., Italy) or Puy de Dôme (~1500 m a.s.l., France), which are characterized by lower altitude and less complex topography compared to JFJ.
- An assessment of uncertainties in daily ecosystem fluxes is estimated in Kountouris et al. (2015), based on a comparison with eddy covariance flux observations, to be 2.5 µmol m<sup>-2</sup> s<sup>-1</sup> for VPRM, and typical spatial error correlation of around 100 km corr. length and a temporal correlation of 30 days. To estimate the impact of this uncertainty between eddy covariance data and simulations using VPRM on the simulated CO<sub>2</sub>, however, full propagation of the error would be required, including spatial and temporal correlation. As VPRM is used in many inversion studies, the corresponding error in simulated CO<sub>2</sub> can alternatively be assessed based on the change from prior to posterior model-data mismatch. Based on Table 3 in the Technical Note of Kountouris et al. (2018b), typical numbers for mountain sites such as JFJ are around 4 ppm (prior), which drop to about 1.5 ppm for posterior fluxes (the assumed model-data mismatch error).
- 3) <u>EDGAR</u>: A mismatch between CO<sub>2</sub>.regional simulations and observations may also result from biases in the CO<sub>2</sub>.anthr signal. However, as quantified in see subsection 3.2.2 C, an increase of CO<sub>2</sub>.anthr by a factor of 3 to 4 would be required in order to compensate the summer mismatch. Further, the discrepancy during summer is much larger than that during winter when CO<sub>2</sub>.anthr contributes the largest share, and we consider is thus unlikely that CO<sub>2</sub>.anthr is the main driver of the summer mismatch. As JFJ is also a popular destination for touristic daytrips, local emissions from tourists and the JFJ infrastructure itself cannot be excluded. A recent study by Affolter et al. (2021), however, showed that this effect is expected to be well below the discrepancy between observations and simulations found here.

#### C) Composition of simulated anthropogenic and ecosystem CO<sub>2</sub>

Ecosystem contributions to CO<sub>2</sub> concentrations outweigh the anthropogenic ones at JFJ most of the year if we consider the multi-annual monthly means (Figure 1). For instance, gross respiration contributions to CO<sub>2</sub> concentrations are at their maximum 3-4 fold the anthropogenic ones during summer. However, gross respiration is overcompensated by an up to two fold gross uptake in summer. During the colder period, gross respiration

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dominates the net ecosystem exchange and equals roughly the amounts of anthropogenic CO<sub>2</sub>. While on a global scale monthly ecosystem fluxes indeed outweigh anthropogenic CO<sub>2</sub>, this is not the case for urban areas. For instance, Vardag et al. (2016) suggests that on cold winter days, the  $CO_2$  share in an urban environment in Germany (Heidelberg) is 90–95 % fuel-related, which is 2-fold the CO<sub>2</sub> anthr fraction compared to JFJ. Nevertheless, also in Heidelberg ecosystem contributions can make up 80 % in summer, similar to our simulations for JFJ.

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In Figure 2a/b we present the ecosystem contributions at JFJ split for the considered vegetation types (multiannual monthly means for 2009–2017, available for STILT-ECMWF only). For summer, the largest fractions of simulated CO<sub>2</sub>, resp are related to cropland ( $\sim$ 50 %), followed by forest ( $\sim$ 30 %) and grassland ( $\sim$ 10 %). During winter, the cropland share increases, while the mixed forest share decreases. This may be a result of the above discussed change of footprint area from regional (cropland) in winter to more local (mixed forests) in summer. For  $CO_2$ , gee, it is important to consider that absolute quantities approach zero during the cold season, and relative fractions are most meaningful in summer. The CO<sub>2</sub>, gee generally displays a larger forest share in comparison to the one of  $CO_2$  resp, possibly as air masses travel through forest-rich vegetated areas during the last few hours before reaching JFJ (which corresponds to daytime, when uptake is active). Furthermore, we observe a shift in the relative CO<sub>2</sub>.gee share from cropland to forest from April to September, which is likely the result of vegetation dynamics, considering that crops mature earlier in the year, and forests absorb carbon much longer during the growing season.

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In Figure 2c/d we present the relative fractions of  $CO_2$  anthr. The contributions associated with fossil sources sum up to 90 % of CO<sub>2</sub>.anthr. The CO<sub>2</sub>.anthr is dominated by CO<sub>2</sub> from liquid fuel use, in particular light and heavy oil used for on- and off-road transport as well as domestic heating (~50 %). Further 25 % of CO<sub>2</sub> anthr are related to natural gas, and only 10 % are attributed to solid fossil fuels, including a larger fraction of hard coal and a smaller fraction of brown coal. Solid biomass, such as residential wood burning for domestic heating, contributes 10 % to CO<sub>2</sub> anthr. Non-combustion CO<sub>2</sub> from cement and other industry production amounts to 5 % of CO<sub>2</sub>, anthr at JFJ. Seasonal shifts are observed in the contribution of solid biomass (higher in winter, lower in 475 summer) as well as in relative fractions of light oil (higher in summer) and natural gas (lower in summer). The relative contributions of FLEXPART-COSMO (not shown here) are very similar to the ones of STILT-ECMWF despite the differences in the absolute quantities of CO<sub>2</sub> anthr between the two models (Figure 1), which, as discussed above, are primarily driven by the model's implementation of transport dynamics.



**Figure 2.** Simulated regional contributions to the  $CO_2$  concentrations at JFJ (multi-annual monthly means of 3-hourly simulations, 2009–2017, STILT-ECMWF). a) gross ecosystem respiration per vegetation type ( $CO_2$ .resp), b) gross ecosystem exchange (uptake) per vegetation type ( $CO_2$ .gee), c)  $CO_2$ .anthr and  $CO_2$ .resp, d)  $CO_2$ .anthr per fuel-type. Maps of anthropogenic fluxes and vegetation distribution are provided in Figure S1 and S2.

#### 3.1.2 Regression analysis of hourly-scale CO<sub>2</sub> simulations vs. observations

The model performance was further evaluated by comparing the 3-hourly simulated CO<sub>2</sub> concentration time-series with observations. In Figure 3 we present  $CO_2$  total, which includes background ( $f_b$ ) and regional contributions (CO<sub>2</sub>.regional, i.e., the sum of  $f_{s,i}$ ). In order to derive CO<sub>2</sub>.total, the simulation-specific background (i.e., either FLEXPART-COSMO or STILT-ECMWF) was added to the respective CO<sub>2</sub> regional data. Overall, the simulations

- capture the intensity and timing of individual regional short-term events at the models' 3-hourly time-resolution to a high degree, in addition to the good representation of annual and seasonal trends. We assess the performance separately for the four seasons winter (December–February, or DJF), spring
- (March-May, or MAM), summer (June-August, or JJA) and autumn (September-November, or SON) for the 495  $CO_2$ .regional signal, as summarized in Figure 4, and show a four-year subset for 2012–2015 in addition to the full nine-year observation period (2009–2017). The subset is of interest as it comprises a higher frequency and intensity of regional CO<sub>2</sub> at JFJ, in particular considering the winter of 2012/2013, and aside, measurements by QCLAS had the best performance during 2012–2015. We consider primarily the coefficient of determination,  $r^2$ , regression slope, and bias-corrected root mean square error (BRMS) in the assessment of the short-term variability.
  - 500 The mean bias, labelled Y-X) and provided in Figure 5, is usually smaller than 1 ppm with the exception of summer, when the models exhibit a negative bias of up to 2.5 ppm. Removing this bias before calculating the root mean square error (RMSE) focusses onto the short-term variability. The BRMS ranges from 1.8 to 3.1 ppm CO<sub>2</sub>, with lowest errors observed during winter and autumn, and highest errors in summer. For the 3-hourly data, both models reproduce the regional signal with similar quality. The  $r^2$  is 0.44 for FLEXPART-COSMO and 0.41 for STILT-ECMWF, meaning that the models explain about 40 % of the observed regional CO<sub>2</sub> variability at JFJ. 505 Considering the complex topography and small amplitude of the regional signal, this is a very satisfactory result, and in line with comparable simulations by Henne et al. (2016), which were able to explain a similar fraction of variability in regional CH<sub>4</sub> at JFJ for the year 2012, after simulations optimization with respect to CH<sub>4</sub> emissions.
  - When analysing individual seasons, we find that the summer period is characterised by significantly lower 510  $r^2$  for the 3-hourly data compared to the other seasons, although, aside of above-mentioned negative bias, diurnal profiles in the observations during summer are well represented by the simulations. The slightly better performance for FLEXPART-COSMO compared to STILT-ECMWF in terms of mean bias and  $r^2$  for 3-hourly data may be partly attributed to the higher spatial resolution that potentially allows for a better representation of thermally driven atmospheric transport in mountainous terrain during summer. Note that when adding model-specific JCS 515 background values to the regional simulations,  $r^2$  values are substantially higher (~0.6–0.9, not shown), because a considerable part of variability in CO<sub>2</sub> total derives from seasonal variability and long-term trends.

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The regression slopes represent the factors by which simulation and observation intensities agree with each other. For CO<sub>2</sub>.regional, the intensity agreement (slope, ~0.9–1.5) varies as a function of season and model. Slopes are closest to 1 in autumn/winter, and, as for other regression parameters, larger discrepancies occur in spring/summer. The spring/summer discrepancies are driven by negative excursions from the baseline in analogy to the larger warm season mismatch (discussed in 3.1.1) and higher mean bias. Again, note that we find the slopes for  $CO_2$  total to be closer to 1 (~0.9–1.3, not shown), than those for the  $CO_2$  regional, confirming the appropriate assumptions for the background CO<sub>2</sub> concentrations.



**Figure 3.** Time series of CO<sub>2</sub>.total simulations with **a/c**) FLEXPART-COSMO and **b/d**) STILT-ECMWF compared to hourly observations. **a/b**) 2009–2017 (tick marks indicate January of each year), **c/d**) 2013. (JCS-based background is detailed in Figure S3a.)



Figure 4. Summary of the regression analysis of CO<sub>2</sub>.regional simulations vs. observation (data are based on 3-hourly time resolution; error bars = 95 % confidence interval). The parameters (slope, r<sup>2</sup> and bias corrected RMSE, i.e., BRMS) are presented for FLEXPART-COSMO (a-c) and STILT-ECMWF (d-f), including the full observation period, 2009–2017, and a 4-year subset (2012–2015).



**Figure 5.** Heatmaps for CO<sub>2</sub>.*regional* simulations (SIM) using FLEXPART-COSMO (**a**-**e**) and STILT-ECMWF (**f**-**j**), in comparison to regional components of observations (OBS) for 2012–2015, full year and per seasons, on 3-hourly time resolution. The STILT-ECMWF-based JCS background is subtracted from the observations to derive the regional component. The weighted least squares regression takes into account uncertainties in both data sets. (Full page version of this figure is available in SI).

### 540 **3.2 Atmospheric** $\delta^{13}$ C-CO<sub>2</sub>

Simulating regional signals at a high-alpine background site like JFJ is challenging, yet JFJ is one of very few stations that offer continuous high frequency  $\delta^{13}$ C-CO<sub>2</sub> observations over multiple years. Thus, JFJ uniquely allows for combining model-based estimates of atmospheric  $\delta^{13}$ C-CO<sub>2</sub> and of mixed source signatures ( $\delta^{13}$ C<sub>m</sub>) with atmospheric  $\delta^{13}$ C-CO<sub>2</sub> observations and thereof derived ("observation-based")  $\delta^{13}$ C<sub>m</sub> values using a moving Keeling-plot approach.

#### 3.2.1 Atmospheric $\delta^{13}$ C-CO<sub>2</sub> estimates vs. observations

We evaluated the atmospheric  $\delta^{13}$ C-CO<sub>2</sub> isotope ratio estimates ( $\delta^{13}$ C<sub>*a*</sub>), which are derived following Eq. (2) on a 3hourly basis, through comparison with the QCLAS observations during the period 2012–2015 (Figure 6, Table 4). Multi annual monthly means for 2012-2015 are presented in Figure 7.



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**Figure 6.** Time series of model-based and observed atmospheric  $\delta^{13}$ C-CO<sub>2</sub> for the years 2012–2015 (hourly observations). **a**) FLEXPART-COSMO, **b**) STILT-ECMWF; tick marks indicate January of each year. The background,  $\delta^{13}$ C<sub>b</sub>, is presented in further detail in SI (Figure S3b). Data are presented on hourly time resolution. (Zoomed versions of this figure for 2012, 2013, 2014 and 2015 are provided in SI, see Figure S7-S9).



**Figure 7. a)** Multi-annual monthly means of 3-hourly model-based and observed atmospheric  $\delta^{13}$ C-CO<sub>2</sub> for the years 2012–2015. Error bars represent 1SD of the multi annual means and reflect the year-to-year variability for 2012–2015. (b) Difference between simulations (sim) and observations (obs).

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The simulated  $\delta^{13}C_a$  time-series capture the observed variability in  $\delta^{13}C$ -CO<sub>2</sub> at JFJ well, in particular during the transition periods in spring and autumn. For most of the summer, however, the  $\delta^{13}C$ -CO<sub>2</sub> simulations are isotopically heavier than the observations, i.e. they appear more enriched in <sup>13</sup>C. Despite an offset of ~0.15 ‰, which appears related to the background ( $\delta^{13}C_b$ ) assumptions, the diurnal profiles in the observations during summer are well represented by the simulations. Generally, the discrepancy in  $\delta^{13}C$  appears to be larger for STILT-ECMWF compared to FLEXPART-COSMO, and thus the discrepancy in CO<sub>2</sub> concentrations itself likely contributes to the mismatch in  $\delta^{13}C$ -CO<sub>2</sub>, as further assessed in section 3.2.2 C-D, aside of uncertainties associated with assumptions for  $\delta^{13}C_s$  which are discussed in section 3.2.2 A) and  $\delta^{13}C_b$  (discussed in section 3.2.2 B).

570 **Table 4.** Summary of statistics on atmospheric  $\delta^{13}$ C-CO<sub>2</sub> estimates and observations for the period 2012–2015. Values for min., max., median (P<sub>50</sub>) and 25 and 75 percentiles (P<sub>25</sub> and P<sub>75</sub>), mean (avg.) and 1SD are provided (hourly data). (see also Figure S6).

	min	P <sub>25</sub>	P <sub>50</sub>	P <sub>75</sub>	max	avg.	±SD
FLEXPART- COSMO	-9.81	-8.64	-8.51	-8.29	-7.78	-8.47	±0.24
STILT- ECMWF	-9.86	-8.65	-8.52	-8.29	-7.42	-8.47	±0.25
Observation (QCLAS)	-9.81	-8.64	-8.47	-8.29	-7.78	-8.47	±0.24

#### 3.2.2 Sensitivity of $\delta^{13}$ C-CO<sub>2</sub> estimates to different model assumptions

#### 575 A) $\delta^{13}C_s$ assumptions

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The mixed source signature estimates ( $\delta^{13}C_m$ ) as derived in Eq. (1) are presented in Figure 8 on a 3-hourly timescale (monthly data are provided in Figure S5). The estimated average  $\delta^{13}C_m$  is around -24 ‰ and varies seasonally between around -22 ‰ in summer and -28 ‰ in winter, for both, FLEXPART-COSMO and STILT-ECMWF. Extreme values during particular events on 3-hourly time resolution reach -35 ‰ when they are heavily impacted by anthropogenic fuel emissions including a larger fraction of natural gas (~50 % of regional CO<sub>2</sub>), and values between -17 to -12 ‰ when impacted by cement production (~30%). The  $\delta^{13}C_s$  from cement production originates from carbonates, which are characterised by a similar isotope composition as the carbonaceous VPDB reference material itself. Consequently, the  $\delta^{13}C_s$  for cement-related CO<sub>2</sub> is 0 ‰. Although cement-related CO<sub>2</sub> contributions to CO<sub>2</sub>.regional at JFJ are about one order of magnitude smaller than from fuel burning or ecosystem processes, the influence of cement on  $\delta^{13}C_m$  is clearly visible in the model-based data in Figure 8. These cement-related peaks in  $\delta^{13}C_m$  are, however, absent in  $\delta^{13}C_a$  (Figure 6), simply because even the most intense cement signals at around 1-2ppm are much smaller than other CO<sub>2</sub> contributions. Thus, when mixed with the background, the signal is diluted.

The  $\delta^{13}C_s$  values, which are underlying the  $\delta^{13}C_m$ , represent the best available information in the scientific literature. However, while we use static assumptions, these values may vary in reality with air mass source region 590 (footprint) and over time. Further uncertainties may arise from assumed ecosystem  $\delta^{13}C_s$ . For instance, C4 plants are not explicitly represented in our model as a dedicated vegetation type with known spatial distribution. Yet, their contribution to average ecosystem  $\delta^{13}C_s$  is captured in the data of Ballantyne et al. (2010 and 2011), which are underlying the assumptions in Table 3, as these are derived from ambient measurements in mixed C3/C4 ecosystems representative for the Northern Hemisphere. In the footprint region of JFJ, C4 plants are mainly present in cropland 595 due to maize production. For the year 2017, EUROSTAT reports that the grain maize production made up around 21 % of the overall grain and cereal production by weight, within EU-28. Of all cropland, roughly 35 % on a land surface basis is assigned to grain and cereals. Applying a simple "back-of-the-envelope" calculation, this equates to  $\sim$ 7 % C4-related CO<sub>2</sub> fluxes within the European Union, as a yearly average. Because maize production is primarily relevant during the spring and summer, the fraction would be enhanced for this period of the year. Replacing 7 % 600 of the C3-related CO<sub>2</sub> with C4-related CO<sub>2</sub> would marginally change the source signature of crops (< 1 ‰, and that of the overall ecosystem signal by even less); however, generally  $\delta^{13}C_m$  would become more enriched and thus the discrepancy between model and observations larger. Reducing a potential C4-related CO<sub>2</sub> fraction instead would make  $\delta^{13}C_m$  less enriched and thus bring the simulations data into slightly better agreement with observations at JFJ. Indeed, the ecosystem assumptions for the Northern Hemisphere are based on data collected in the USA and might 605 be characterised by a higher C4 fraction than the footprint region for JFJ.

Vardag et al. (2016) report a measurement-based mean source signature ( $\delta^{13}C_m$ ) of -26 ‰ in summer and about -32 ‰ in winter for Heidelberg, which is isotopically lighter when compared to the simulated  $\delta^{13}C_m$  for JFJ (-22 ‰ in summer, -28 ‰ in winter). The winter differences between Heidelberg and JFJ is reasonable as it may derive from larger ecosystem contributions at JFJ (50 %) compared to Heidelberg (5 %). The summer differences, however, may, aside from summer overestimations of CO<sub>2</sub>.regional at JFJ, result from uncertainties in the assumption for the ecosystem  $\delta^{13}C_s$  including the uncertainty of the C4-related CO<sub>2</sub> fraction. Indeed, also Vardag

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et al. (2016) suggest that the assumption of  $\delta^{13}C_s = -23 \ \%$  for ecosystem CO<sub>2</sub> by Ballantyne et al. (2011) is too enriched for August and September in Heidelberg, and a more depleted assumption (through adjusting the seasonality in  $\delta^{13}C_s$ ) would result in improved agreement between model-based  $\delta^{13}C$ -CO<sub>2</sub> and observations at JFJ.



**Figure 8.** Time series **a**) model-based  $\delta^{13}C_m$  (Eq. (1)), **b-c**) model-based  $\delta^{13}C_m$  for ecosystem-, fuel- and cementrelated CO<sub>2</sub>: **b**) FLEXPART-COSMO, **c**) STILT-ECMWF; hourly data are used; tick marks indicate January of each year. (see also Figure S5)

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#### B) $\delta^{13}C_b$ assumptions

The background ( $\delta^{13}C_b$  see Figure 6, Figure 7, and SI), as estimated by the baseline CO<sub>2</sub> taken from the JCS assimilation system and the empirical  $\delta^{13}C/CO_2$  relationship based on yearly linear regression fits (method A), tracks the evolution of the observed  $\delta^{13}C-CO_2$  values outside of the peaks closely and varies seasonally. Yet, inconsistencies are apparent from the use of the yearly regression fits. Assuming a more depleted  $\delta^{13}C_b$  during the second half of the year, for instance, by -0.15 ‰ during late summer (August) and early autumn (September), and assuming a more enriched  $\delta^{13}C_b$  during the first half of the year, for instance by +0.05 to +0.10 ‰ from January to March, would reduce the discrepancies between observations and simulations. Indeed, the moving fit (method B, see Figure S4b) improves the transitioning between years. However, the use of multi-annual monthly ratios in

630 method C introduces discontinuities when transitioning between months, and the daily ratios (method D) introduce higher scatter and data gaps (see Figure S4c-d).

### C) Sensitivity to $CO_2$ concentrations

2015, thereby removing the model bias.

Based on the discussion in section 3.1.1 we defined five scenarios, which aim to bring the simulated summer-time  $CO_2$ .regional concentrations into better agreement with the observations. In each scenario, we adjust one or a combination of  $CO_2$  sources/sinks by a single scaling factor for the whole summer period (JJA) for the years 2012–

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- Scenario 1 (sc1): through increasing CO<sub>2</sub>.anthr we simulate a bias in the anthropogenic emission fluxes or a wrong seasonal factor for CO<sub>2</sub>.anthr during summer.
- Scenario 2 (sc2): through reducing both CO<sub>2</sub>.resp and CO<sub>2</sub>.gee we attempt to represent a general VPRM parameterisation or vegetation map representation issue.
  - Scenario 3 (sc3): through reducing CO<sub>2</sub>.gee we consider its potential overestimation by general VPRM parameterisation or vegetation map representation issue in analogy to sc2; specific only to CO<sub>2</sub>.gee.
  - Scenario 4 (sc4): through increasing CO<sub>2</sub>.resp we consider its potential overestimation by general VPRM parameterisation or vegetation map representation issue in analogy to sc2; specific only to CO<sub>2</sub>.resp.
    - Scenario 5 (sc5): through modifying all signals at equal amounts (CO<sub>2</sub>.anthr, CO<sub>2</sub>.resp, CO<sub>2</sub>.gee) we attempt to represent a pure transport issue (i.e., overrepresentation of PBL-influence).

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Scaling factors for each scenarios were derived by weighted least squares regression and presented in Table 5. The largest scaling factors of ~3-4 are found for CO<sub>2</sub>.anthr, followed by CO<sub>2</sub>.resp (~2), indicating that CO<sub>2</sub>.anthr or CO<sub>2</sub>.resp would need to be substantially increased in order to reduce the bias between model and observations. Instead, a reduction (scaling factor ~0.7-0.8) would be required if only CO<sub>2</sub>.gee was considered, and likewise a reduction in both, CO<sub>2</sub>.resp and CO<sub>2</sub>.gee (scaling factor ~0.7-0.8) in order to achieve a reduced CO<sub>2</sub>.nee would lead to a reduced bias between model and observations.

Table 5.	Scaling	factors	based	on	the	weighted	least	squares	regression	fitting	slope	<i>b</i> ,	and	intercept	i a	(in
parenthes	is), used	to minir	nize th	e Co	$O_2 m$	nodel bias	for JJ.	A, 2012-	-2015.							

	FLEXPART-	STILT-	CO <sub>2</sub>
	COSMO	ECMWF	component
base			
sc1	3.14	3.73	× CO2.anthr
(anthr)	(a = 0.02)	(a = -0.11)	
sc2	0.80	0.72	× CO <sub>2</sub> .resp
(nee)	(a = 1.04)	(a = 1.22)	× CO <sub>2</sub> .gee
sc3	0.79	0.74	× CO <sub>2</sub> .gee
(gee)	(a = 0.45)	(a = 0.49)	
sc4	2.08	1.98	× CO2.resp
(resp)	(a = -0.88)	(a = -0.56)	
sc5 (trans)	0.82 (a = 1.29)	0.74 (a = 1.54)	× CO <sub>2</sub> .anthr × CO <sub>2</sub> .resp × CO <sub>2</sub> .gee

#### D) Regression analysis for hourly $\delta^{13}$ C-CO<sub>2</sub>

We further evaluate the effect of CO<sub>2</sub> adjustments (Table 5) on the estimated regional δ<sup>13</sup>C-CO<sub>2</sub> at JFJ in comparison to the observations. First, however, we discuss the regression analysis for the base scenario (Fehler! Verweisquelle konnte nicht gefunden werden.) To obtain an estimate for regional δ<sup>13</sup>C-CO<sub>2</sub> a δ<sup>13</sup>C-CO<sub>2</sub> background needs to be subtracted from the total signal. Here, we used background method A, following strategy used previously by Vardag et al., 2016). A higher short-term variability was observed for the δ<sup>13</sup>C<sub>b</sub> from FLEXPART-COSMO compared to STILT-ECMWF (Figure S3b). Consequently we used only the STILT-ECMWF-based δ<sup>13</sup>C<sub>b</sub> for further calculations of regional components (i.e., for the

subtraction of background values from total signal).

Based on this particular  $\delta^{13}C_b$  assumption, the regional estimates agree with the regional observations intensity within a factor of 0.7–1, depending on season. The BRMS is between 0.12 and 0.14 ‰. Similar to CO<sub>2</sub>, 670 for spring, autumn, and winter the models capture the short-term variability in  $\delta^{13}$ C-CO<sub>2</sub> better than in summer. Overall, the  $r^2$  values are lower than for CO<sub>2</sub> (max.  $r^2 = 0.35$  for FLEXPART-COSMO and 0.28 for STILT-ECMWF compared to about 0.4 for CO<sub>2</sub>), which is not surprising given the uncertainties in the measurements as well as in the simulations, where, for instance, fixed source signatures were assumed. Despite the fact that model-based  $\delta^{13}$ C-CO<sub>2</sub> includes uncertainties of both, CO<sub>2</sub> simulation (used to construct  $\delta^{13}C_m$ ),  $\delta^{13}C_s$  and  $\delta^{13}C_b$ , the relative performance decreased by only 20-30 %. These results at JFJ were achieved with very low regional CO<sub>2</sub> signals, 675 which, compared to the background ( $\Delta CO_2$ ), reached at maximum 30 ppm. Instead, the previously conducted urban studies benefitted from much more pronounced  $\Delta CO_2$  reaching up to ~150 ppm for both, Heidelberg (Vardag et al., 2016) and Downsview (Pugliese-Domenikos et al., 2019). However, they were limited regarding either the length of the observation period (few months in Downsview), and/or the stringent data filtering (e.g., Vardag et al. (2016) 680 discarded 85 % of the data and biased the urban data sets towards night-time observations, Pugliese-Domenikos et al., 2019 discarded 80% of the data for their isotopic mass balance approach). Contrary, the tall tower study in rural England was challenged by a low signal-to-background ratio ( $\Delta CO_2$  reaching around 20 ppm), and isotope measurements were performed at low (weekly) time-resolution, although simulations are provided on hourly-scale (Wenger et al., 2019). In comparison to the results from JFJ, Pugliese-Domenikos et al. (2019) reported an r = 0.58685  $(r^2 = 0.3)$ , a root mean square error (RMSE) of 1.05 ‰ and a mean bias of 0.04 ‰ for a single month (January) for  $\delta^{13}$ C-CO<sub>2</sub>. Wenger et al. (2019) do not provide any regression parameters for their model-observation comparisons; however, they observed large uncertainties in the  $\delta^{13}$ C-CO<sub>2</sub> estimation using a Monte Carlo approach. They related a part of their uncertainty for the  $\delta^{13}$ C-CO<sub>2</sub> estimates to the influence of ecosystem processes and the dominance of

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A representative set of results of the regression analysis for further scenarios as defined in 3.2.2 C is summarized in the SI in Table S4. Overall, we find that modifications in sc 1 (CO<sub>2</sub>.anthr) do not lead to an improvement in the agreement between regional  $\delta^{13}$ C-CO<sub>2</sub> observations and simulations on 3-hourly resolution. Sc 5 (transport) results only in small improvements with regards to the BRMS. While the other scenarios neither result in major adjustments, for sc 3 (CO<sub>2</sub>.gee) and sc 4 (CO<sub>2</sub>.resp) we observe small model improvements with slightly

ecosystem fluxes on the regional CO<sub>2</sub> observations and simulations at the rural tall tower site. Overall, the JFJ

results are very well in line with previous findings despite the more remote location and correspondingly smaller

magnitudes of regional signals at JFJ.

increased  $r^2$ , slightly reduced BRMS and a smaller bias (Y-X). Note, that the remaining bias depends on the fitting intercept assumptions of the scaling factor. These results indicate that the  $\delta^{13}$ C simulation can be influenced through reasonable modification of CO<sub>2</sub> contributions. Discrepancies between observed and simulated  $\delta^{13}$ C-CO<sub>2</sub> are thus not exclusively related to uncertainties in source signature ( $\delta^{13}$ C<sub>s</sub>) or background ( $\delta^{13}$ C<sub>b</sub>) assumptions. However, an optimization of  $\delta^{13}$ C<sub>b</sub> mentioned in 3.2.2 B might result in an improved agreement between  $\delta^{13}$ C simulation and observation for the base scenario itself, as we found indications for improved performance in the regression analysis, when using  $\delta^{13}$ C<sub>b</sub> derived using moving linear fits (background method B) compared to yearly fits (method A).



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**Figure 9**. Summary of the regression analysis of  $\delta^{13}$ C-CO<sub>2</sub> estimation vs. observation (data are based on 3-hourly time resolution; error bars = 95 % confidence interval). Performance parameters (slope, r<sup>2</sup> and bias corrected RMSE (i.e., BRMS)) are presented for the 4-year subset of the observation period (2012–2015) for FLEXPART-COSMO (**a-c**) and STILT-ECMWF (**d-f**), across all year ("ALL"), and per season (DJF, MAM, JJA, SON).



**Figure 10.** Heatmaps of model-based regional  $\delta^{13}$ C-CO<sub>2</sub> (SIM) vs. observation (OBS) (3-hourly data), for FLEXPART-COSMO (**a-e**) and STILT-ECMWF (**f-j**), during 2012-2015, for the full year (grey), and per season (DJF (blue), MAM (green), JJA (orange), SON (red)). Uncertainties in x- and y-axes are taken into account in the weighted least squares regression applied here. (Full page version of this figure is available in SI).

#### 3.2.3 Observation-based source signature estimates

Observation-based  $\delta^{13}C_m$  values are accessible independently from simulations through a "Keeling"- or "Miller-Tans" plot approach. However, this approach can be applied only after strict pre-selection of conditions under which 720 the underlying hypotheses are fulfilled. Detailed descriptions of pre-requisites and limitations of this method are available in detail elsewhere (Keeling, 1958; Keeling, 1961; Miller and Tans, 2003; Pataki et al., 2003; Zobitz et al., 2006; Ballantyne et al., 2011; Vardag et al., 2016). In brief, previous  $\delta^{13}C_s$  studies have been successful in deriving observation-based  $\delta^{13}C_m$  primarily under the following conditions: First, when measurements were taken close to a well-defined source location and using instrumentation with high precision (e.g., Pugliese et al., 2017). Second, when a pronounced regional signal (referred to as  $\Delta CO_2$  and computed as the difference between the  $CO_2$ 725 concentration at the site and background) with stable source composition was observed during stable background conditions and the regional ecosystem contribution to the observed  $\Delta CO_2$  was comparatively low (e.g., Vardag et al., 2016). Such constrains substantially limit the number of regional events that can be effectively characterised at a given location. Intensities below  $\Delta CO_2 = 5$  ppm, even at high precisions of 0.03 ‰ for  $\delta^{13}C$ -CO<sub>2</sub> and low CO<sub>2</sub> 730 errors of 0.1 ppm, lead to significant fitting errors as assessed by Zobitz et al. (2006). Intensity-based filtering criteria have, therefore, been applied in previous studies (e.g.  $\Delta CO_2 \ge 5$  ppm by Vardag et al. (2016),  $\Delta CO_2 \ge 20$ ppm by Smale et al. (2019),  $\Delta CO_2 \ge 30$  ppm by Pugliese-Domenikos et al. (2019), or  $\Delta CO_2 \ge 75$  ppm by Pataki et al. (2003)), while at JFJ  $\Delta CO_2$  reaches 30 ppm only during the most intense events. Most studies also focus on periods when photosynthetic uptake does not disturb the analysis, consequently biasing the data set to night-time. 735 Since a classical day-/night splitting to filter ecosystem uptake is not applicable at JFJ as the received air masses are composed of integrated fluxes over day and night, such observation-based approaches are expected to be valid mainly during the cold period. However the PBL-influence at JFJ is at a minimum during the cold season. For instance, regional CO<sub>2</sub> intensities at JFJ are at the maximum 30 ppm above the background for the 10 min averaged QCLAS data, and on average occur with an intensity of  $\geq 5$  ppm on 35 days per year during the cold period (range: 740 20–50 times). This includes events reaching  $\geq$ 10 ppm on 10 days per year (range: 2–20) and events reaching  $\geq$  15

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ppm on only 1–6 days per year. Intensities and frequencies, however, are even lower, when hourly averaged data are considered. These conditions make Keeling/Miller-Tans methods to derive observation-based  $\delta^{13}C_m$  particularly challenging at JFJ.

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The high-precision of the  $\delta^{13}$ C-CO<sub>2</sub> measurements and the high time-resolution available from the QCLAS instrument allow to compensate the low  $\Delta CO_2$  and to limit fitting uncertainties to some extent. This enables us to perform a moving Keeling-plot in analogy to Vardag et al. (2016). We used a 5 hour window to conduct the fit on hourly averaged  $\delta^{13}$ C-CO<sub>2</sub> observations. Only fits with five data points were considered (i.e., no data gaps were allowed). In addition, we tested splitting the data set into warm (Apr-Sept) and cold season (Oct-Mar), and demanding a minimum change in  $\Delta CO_2$  of 3 ppm within the 5 hour window (with and without requiring a 750 monotonous increase in concentration with time, threshold: 0.1 ppm). Finally, we filtered the resulting observationbased intercept value ( $\delta^{13}C_m$ ) by the fitting error (4, 3, 2 and 1 %).

Figure 11a shows observation-based estimates from two settings: i) results obtained without considering any predefined change in  $\Delta CO_2$  and without filtering by the intercept error (referred to as "all"), and, ii) results obtained under more stringent criteria (minimum  $\Delta CO_2$  change within a 5 h window of 3 ppm, maximum intercept error of 2 % or 1 %). Keeling fit intercepts ( $\delta^{13}C_m$ ) obtained without predefined criteria and without error-based 755 filtering clearly do not provide meaningful data, as  $\delta^{13}C_m$  is physically meaningful only between 0 ‰, corresponding to pure cement production plumes, and, -44 \% corresponding to pure gaseous fuel burning plumes (in a peculiar event, gaseous fuel burning  $CO_2$  may reach -85 ‰). Most values are expected between -12 and -35 ‰ based on the simulated CO<sub>2</sub> composition. Indeed, using predefined fit criteria and error-based filtering yields physically 760 meaningful  $\delta^{13}C_m$  from the observations at JFJ, in line with previous findings by Vardag et al. (2016) and Pugliese-Domenikos et al. (2019). Overall, the observation-based  $\delta^{13}C_m$  derived with a more stringent fitting approach are in good agreement with the trends found in the independently calculated model-based data, which are also shown in Figure 11a and Table 6 as well. Because different combinations of predefined criteria (minimum  $\Delta CO_2$  or seasonbased restrictions) and filtering (based on the intercept error) may be used when deriving observation-based  $\delta^{13}C_m$ , 765 we display three scenarios in Figure 11b-d. Figure 11b highlights the effect of only filtering by intercept errors of 4, 3, 2 and 1 %. Instead, Figure 11c shows the combined effect of requiring a change in  $\Delta CO_2 > 3$  ppm and filtering by intercept errors, and Figure 11d presents data only for the cold period (Oct-Mar), limiting the disturbance of photosynthetic uptake, in addition to requiring a monotonous increase in  $\Delta CO_2$  within the 5 h window (i.e., the most stringent criteria). We may generally conclude that either more stringent intercept error thresholds (such as 1 ‰ for 770 the settings in Figure 11b), or, alternatively, limiting photosynthetic uptake (through demanding monotonous increase, and/or filtering for cold season or night-time) in combination with less stringent intercept errors (e.g., 2-3 % in Figure 11d) appear to yield equally good results at JFJ, as all  $\delta^{13}C_m$  values are  $\leq 0\%$  and  $\geq -85\%$  and thus physically meaningful). The latter approach, however, discards more data. The same conclusion holds true when using 10-min averages instead of hourly data. Note, that we do not expect that model-based  $\delta^{13}C_m$  and observation-775 based  $\delta^{13}C_m$  can be compared directly with each other, as the model-based  $\delta^{13}C_m$  are calculated for 3-hourly

resolution and, most importantly, not restricted to situations when the underlying  $CO_2$  simulations match the  $CO_2$ observations.



Figure 11. Observation-based mixed source signatures, δ<sup>13</sup>C<sub>m</sub>, derived from a moving Keeling approach ("OBS")
in comparison to model-based estimates ("SIM", FLEXPART-COSMO and STILT-ECMWF). a) time-series of δ<sup>13</sup>C<sub>m</sub> (tick marks indicate January of each year). "all" indicates that neither a minimum change in ΔCO<sub>2</sub> was required, nor any filtering applied. Results when requiring a minimum change of 3 ppm in ΔCO<sub>2</sub> within the 5 h window and a fit intercept error (err) < 2 ‰ and < 1 ‰ are provided as green and black markers (open circles represent Oct-Mar, crosses represent Apr-Sept). b-d) δ<sup>13</sup>C<sub>m</sub> hourly moving Keeling as a function of ΔCO<sub>2</sub> for various criteria: b) filtering by intercept err < 4, 3, 2 and 1 ‰, c) demanding a minimum change in CO<sub>2</sub> of 3 ppm within the 5 h window and filtering by intercept err < 4, 3, 2 and 1 ‰.</li>

	min	P <sub>25</sub>	P <sub>50</sub>	P <sub>75</sub>	max	avg.	±SD
FLEXPART- COSMO	-35.95	-26.38	-24.26	-22.08	-17.16	-24.29	±2.39
STILT- ECMWF	-35.26	-26.63	-24.50	-22.11	-12.78	-24.48	±2.57
OBS; 1‰ Figure 11b*	-61.90	-28.82	-25.93	-21.64	-11.95	-25.85	±6.85
OBS, 1‰ Figure 11c*	-38.66	-28.78	-26.09	-22.24	-12.13	-25.70	±4.88
OBS, 2‰ Figure 11d*	-39.99	-29.64	-25.93	-22.52	-14.43	-26.59	±5.56

**Table 6.** Summary statistics of  $\delta^{13}C_m$  in ‰ (2012–2015).

**790**\*Figure 11b (err < 1‰, w/o  $\Delta CO_2$  prerequisite, w/o seasonal filtering)\*Figure 11c (err < 1‰,  $\Delta CO_2 > 3$  ppm, w/o seasonal filtering)\*Figure 11d (err < 2‰,  $\Delta CO_2 > 3$  ppm (m.i.), Oct-Mar)

## 4. Conclusions

Greenhouse gas emissions source/sink identification and quantification at remote, high altitude sites is particularly
challenging for broadly distributed, multi-source and multi-sink compounds such as CO<sub>2</sub>. In addition, atmospheric transport simulations are highly challenged by complex topography. Despite these difficulties, the CO<sub>2</sub> simulations performed at 3-hourly basis for JFJ agree well with the observations during the multi-year period 2009–2017. Using Lagrangian particle dispersion models (LPDM), we were able to capture 40 % of the observed regional CO<sub>2</sub> variability. The results from the model configurations using two different LPDMs driven by output from two
different numerical weather prediction systems, FLEXPART-COSMO and STILT-ECMWF, appear to differ primarily as a function of meteorological inputs and their spatial resolution (COSMO vs ECMWF), aside additional variations observed related to the domain size and backward integration time. The LPDM implementation (FLEXPART or STILT) itself contributes comparatively small differences.

The regional CO<sub>2</sub> simulations suggest that JFJ's high-altitude location predominantly experiences 805 influences from the rather nearby (within 100 km) ecosystem. This is owing to the enhanced PBL-influence in summer, which overlaps with high ecosystem activity. Instead, the peak in anthropogenic fluxes during winter overlaps with substantially suppressed PBL-influence and a larger (regional) footprint. Therefore, through most of the year, the ecosystem CO<sub>2</sub> contributions composed mainly of cropland and mixed forest respiration and uptake, outweigh the anthropogenic ones composed of 90 % fossil emissions and dominated by heavy and light oil, and natural gas. While the simulated composition resembles our hypothesis for JFJ, the extent to which ecosystem 810 contributions outweigh anthropogenic ones is surprisingly large. Indeed, quantitatively, the models perform the  $CO_2$ simulations best during winter and transition periods (spring/autumn). For the summer, the  $CO_2$  simulations poorly reproduce the quantities despite the good qualitative agreement. The atmospheric transport models employed apparently suffer from their relatively coarse spatial resolution, which deteriorates model performance in 815 summer/fair-weather situations, when topography-induced convection is not captured very quantitatively during day-time. Increased model resolution and improved representation of the alpine boundary layer in both, the LPDMs and the driving numerical weather prediction models will be necessary to overcome this shortcoming and to allow for more quantitative conclusions when interpreting observations during the abovementioned conditions. However, also the net ecosystem exchange fluxes themselves are a likely source of error through inaccurate spatial distribution 820 and VPRM parameterisation of respiration and/or uptake fluxes for the (Alpine) vegetation following limited spatial resolutions of vegetation maps and possibly temperature profiles.

The simulations of regional CO<sub>2</sub> concentrations allow retrieving model-based mixed source signatures  $(\delta^{13}C_m)$  and atmospheric  $\delta^{13}C$ -CO<sub>2</sub> at JFJ. The latter agree well with the high frequency observations. The overall  $\delta^{13}C$ -CO<sub>2</sub> correlation (28–35 %) remains only slightly lower than for CO<sub>2</sub> (41–44 %). In analogy to the findings for CO<sub>2</sub>, also  $\delta^{13}C$ -CO<sub>2</sub> shows the lowest agreement between observations and simulations during the summer. We relate this primarily to the poorly reproduced CO<sub>2</sub> quantities in summer, although the assumption of source signatures ( $\delta^{13}C_s$ ) as well as the estimate of the background ( $\delta^{13}C_b$ ) provide additional uncertainties. For instance, our  $\delta^{13}C_s$  estimates do not consider geographic variations in fuel specific  $\delta^{13}C_s$  and ecosystem values are not specific to photosynthetic pathways. Dedicated maps that allow to separate C3 and C4 vegetation in the VPRM model would

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830 allow for even better representing the forward  $\delta^{13}C_m$  of CO<sub>2</sub>. In addition, the simulations would benefit from further optimizations in deriving the background  $\delta^{13}C_b$ .

Observation-based assessment of  $\delta^{13}C_m$  are challenging at JFJ, owing to the low signal-to-background ratios and the integration of fluxes over day and night, which substantially limited the data set. Yet, physically meaningful values were obtained. A further disaggregation of observation-based  $\delta^{13}C_m$  using mass balance approaches and 835 assumptions for the end-members in order to learn more about the CO<sub>2</sub> regional composition for any further comparison to the simulated CO<sub>2</sub> regional composition, was not attempted here, given the small number of observation-based  $\delta^{13}C_m$  values obtained. This may be the focus in future studies. However, we expect that it will remain challenging to disentangle fuel and ecosystem respiration signals from observation-based  $\delta^{13}C_m$  alone, considering that the simulated regional  $CO_2$  fractions at JFJ indicate approximately equal amounts even during the 840 winter, that solid and liquid fuel emissions  $\delta^{13}C_s$  end-member assumptions overlap with C3 plant respiration signatures. Thus, while  $\delta^{13}C_s$  source apportionment approaches prove meaningful among either the anthropogenic or the ecosystem carbon pool, they are of more limited use as a singular tracer when the carbon pools are mixed.

The simulated regional CO<sub>2</sub> composition at JFJ suggests that further analyses would benefit from a multitracer approach, in combination with the herein presented continuous  $CO_2$  and  $\delta^{13}C$  observations. Additional 845 parameters may include CO, atmospheric potential oxygen (APO), and <sup>14</sup>C as combustion or fossil fuel tracer; and carbonyl sulphide (COS) and  $\delta^{18}$ O-CO<sub>2</sub> as ecosystem tracers. Indeed, CO, APO, COS and  $\delta^{18}$ O-CO<sub>2</sub> observations are available at high time-resolution at JFJ and may be investigated in future, although determining their regional and background contributions will remain challenged by the low signal-to-background ratios. The bi-weekly integrated <sup>14</sup>CO<sub>2</sub> data, currently available for JFJ, instead do not allow distinguishing regional from background 850 contributions. Highly time-resolved <sup>14</sup>CO<sub>2</sub> measurements or grab sampling during periods with intense regional CO<sub>2</sub> influences would be highly valuable and is foreseen to be implemented at JFJ as part of the European-wide flask sampling strategy of the ICOS Research Infrastructure. Moreover, specific episodes at JFJ that represent air masses of particular regional CO<sub>2</sub> composition may be identified based (also) on continuous  $\delta^{13}$ C observations in a multitracer manner in future studies.

#### Appendix A. Transport dynamics analysis for JFJ 855

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simulations for JFJ as represented by different models in different configurations for 2009–2017. In order to analyse source sensitivity dependencies on domain size (Western Europe ("small") vs. Europe ("large")), LPDM implementation (FLEXPART vs. STILT) and meteorological input fields and associated spatial resolution (COSMO vs. ECMWF), we used four different combinations of these three parameters (Table A1). The simulations are based on one assumed input field of idealized, positive  $CO_2$  fluxes, which were kept constant in time and space for seven VTs based on the maps underlying the VPRM model. This analysis is designed to study atmospheric transport of chemically passive tracers released rather uniformly over the European continent to the high Alpine site and the obtained signals serve as a measure of PBL-influence of JFJ. It includes the total of the synthetic  $CO_2$ 865 concentration time-series from all seven VTs, alongside sub-groups comprising a) cropland, b) mixed forest, and c) the total of the remaining 5 VTs. Studying the VT subgroups gives insight into the influence of spatial distributions of the sources within the domains under the given assumptions of uniform fluxes. This transport dynamics analysis supports the interpretation of the results presented in Figure 1.

We performed a dedicated set of simulations to characterise the atmospheric transport in backward LPDM

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	Table A1. Model combinations for transport dynamics analysis. E3 and E4 are the model configurations as used
)	for the CO <sub>2</sub> concentration simulation in the main text.

Ref.	LPDM	Weather Fields	Approximate Spatial Resolution (km²)	Domain*	Integration period (d)	Release Height, (m asl)	Sampling Height (m)	Temporal Resolution
E1	FLEXPART	ECMWF	20×20	EU	10	3000 m	100	3-hourly average
E2	FLEXPART	ECMWF	20×20	WEU	10 (cropped)	3000 m	100	3-hourly average
E3	FLEXPART	COSMO7	7×7	WEU	4	3100 m	50	3-hourly average
E4	STILT	ECMWF	25×25	EU	10	3100 m	$0.5  imes h_{ ext{PBL}}$	snapshots every 3 <sup>rd</sup> hour

\* "EU" and "WEU" refers to 33°N-73°N. -15-35°E, and 36.06-57.42°N. -11.92-21.04°E, respectively



Figure A1. Mean monthly PBL-sensitivity (JFJ, 2009–2017) towards i) domain size (E1 vs. E2), ii) meteorological input fields and spatial resolution (E2 vs. E3), iii) LPDM implementation (E1 vs. E4), iv) combinations (E3 vs. E4).



**Figure A2.** Mean diurnal PBL-sensitivity (JFJ, winter (DJF, top) and summer (JJA, bottom) for the period 2009–2017) for **a**) FLEXPART-COSMO ("E3") and **b**) STILT-ECMWF ("E4").

- 880 Figure A1 provides the multi-annual monthly means of the 3-hourly tracer concentrations at JFJ, and highlights the sensitivity towards domain size (E1 vs. E2), meteorological input fields and spatial resolution (E2 vs. E3), LPDM implementation (E1 vs. E4), and combinations of these (E3 vs. E4). Overall, we find that the synthetic CO<sub>2</sub> concentrations simulated at JFJ vary between the different models and configurations, as well as with seasonality and diurnal cycle. The analyses indicate a significant seasonality in the PBL-influence for all four 885 configurations. Higher tracer concentrations are observed during the warm period (April-September) and relatively lower tracer concentrations during the colder period (October-March). This confirms the generally stronger vertical transport during warm (and possibly sunny) days. Further, meteorological input fields and related spatial resolution (ECMWF vs. COSMO, i.e. E2 vs. E3) appear to have a larger influence compared to the LPDM implementation itself (FLEXPART vs. STILT, i.e. E1 vs. E4), and intensity discrepancies between the models used in the main text 890 (E3, E4) are largest in winter, followed by summer, and smallest during transition periods. Concerning the domain size, we find differences between different VT classes, which is owing to their heterogeneous spatial distribution as some VT classes are present predominantly inside (e.g. mixed forest) or outside (e.g. deciduous forests) the smaller domain boundaries; compare Figure S2. The smallest discrepancy was thus found for mixed forest (essentially 0 %), and a larger discrepancy (on average -15 %) was found for cropland, at the artificially assumed spatially and 895 temporally constant fluxes. The influence of the LPDM implementation itself (FLEXPART vs. STILT, i.e. E1 vs. E4) appears to be smaller than that of the meteorological fields and spatial resolution, generating differences mainly during winter periods, when FLEXPART-ECMWF yields a higher relative signal compared to STILT-ECMWF. In Figure A2, we present the PBL-influence on diurnal timescales, with up to 1.4 times higher synthetic  $CO_2$ concentrations at JFJ during the afternoon and evening (maximum around 16:00-20:00 h, UTC+1) compared to the 900 morning (minimum around 10:00 h, UTC+1). This is observed for FLEXPART-COSMO (E3) as well as STILT-ECMWF (E4), and it is particularly pronounced during summer (June-August).
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## **Abbreviations and Definitions**

	$\mathbf{f}_b$	CO <sub>2</sub> concentration in the background, expressed in ppm					
	$\mathbf{f}_s$	Regional contribution to the CO <sub>2</sub> concentration per category, expressed in ppm					
905	CO <sub>2</sub> .regional	Sum of all regional contributions to the CO <sub>2</sub> concentrations (fs)					
	CO <sub>2</sub> .total	Sum of CO <sub>2</sub> , regional and JCS-based CO <sub>2</sub> background (f <sub>b</sub> )					
	CO <sub>2</sub> .anthr	CO2 concentration associated with all anthropogenic (anthr) categories					
	CO <sub>2</sub> .cement	CO <sub>2</sub> concentration associated with cement production					
	CO <sub>2</sub> .fuel	CO <sub>2</sub> concentration associated with all fuel categories					
910	CO <sub>2</sub> .gee	CO <sub>2</sub> concentration associated with gross ecosystem exchange (i.e. ecosystem uptake) (gee)					
	CO <sub>2</sub> .nee	CO <sub>2</sub> concentration associated with net ecosystem exchange (nee)					
	CO <sub>2</sub> .resp	CO2 concentration associated with gross ecosystem respiration (resp)					
	$\delta^{13}C_a$	$\delta^{13}$ C-CO <sub>2</sub> estimate for atmospheric CO <sub>2</sub> at JFJ ‰					
	$\delta^{13}C_b$	$\delta^{13}$ C-CO <sub>2</sub> estimate for the background CO <sub>2</sub> , ‰					
915	$\delta^{13}C_m$	$\delta^{13}$ C-CO <sub>2</sub> mixed source signature for all $\delta^{13}$ C <sub>s</sub> weighted with the CO <sub>2</sub> concentration (f <sub>s</sub> ), ‰					
	$\delta^{13}C_s$	$\delta^{13}$ C-CO <sub>2</sub> source signature, ‰					
	COSMO	Consortium for Small Scale Modelling					
	ECMWF	European Centre for Medium-Range Weather Forecasts					
	EDGAR	Emissions Database for Global Atmospheric Research					
920	FLEXPART	Flexible Particle Model					
	JCS	Jena CarboScope based background estimate					
	LPDM	Lagrangian particle dispersion model					
	MACC-TNO	Monitoring Atmospheric Composition and Climate (provided by TNO)					
	QCLAS	Quantum Cascade Laser Absorption Spectrometer					
925	STILT	Stochastic Time Inverted Lagrangian Transport					
	VPRM	Vegetation and Photosynthesis Respiration Model					

## Data & Code Availability

References to data/code are provide in main text/Supplement. Additional data will be made available online upon manuscript publication and further information may be requested from <u>Lukas.Emmenegger@empa.ch</u>.

## **Author Contributions**

SMP and SH wrote the manuscript with contributions from all authors. LE supervised the project. *Simulations*: UK, SMP, SH and DB prepared the annual scaling factors for the anthropogenic inventory, CG and TK prepared updated VPRM parameters. SH performed the CO<sub>2</sub> simulations with FLEXPART-COSMO. UK performed the CO<sub>2</sub> simulations with STILT-ECMWF. SH, DB, UK, CG, TK and SMP performed the transport dynamics analysis. *Observations*: BT, MST and LE provided the experimental data from QCLAS and CRDS. *Data Analysis*: SMP, SH, MST and DB prepared the data processing routines. SMP performed the model- and observation-based  $\delta^{13}$ C-CO<sub>2</sub> and  $\delta^{13}$ C<sub>m</sub> estimations, and overall data analyses and evaluations.

## **Conflicting Interests**

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

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