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Source partitioning of atmospheric methane using stable carbon isotope measurements in the Reuss Valley, Switzerland

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ABSTRACT

Measurements of methane (CH_4) mole fractions and $\delta^{13}\text{C}-\text{CH}_4$ that resolve the diel cycle in the agriculturally dominated Reuss Valley, Switzerland, were used to quantify the contributions of different CH_4 sources to the atmospheric CH_4 source mix. Both a nocturnal (NBL) and a diurnal convective boundary layer (CBL) approach were employed. A diel course of CH_4 mole fractions was found with a daytime minimum (background around 1900 ppb) and a nocturnal maximum (up to 3500 ppb). The $\delta^{13}\text{C}$ value in CH_4 only showed small variations during the day (9–21 hours CET, $-45.0 \pm 0.2\text{‰}$ mean $\pm$ SE) when the atmosphere was well mixed, but decreased by $-4.8 \pm 0.1\text{‰}$ during the night. Biogenic emissions dominated in both approaches (ranging from 60 to 94%), but non-biogenic sources were rather important (42.2% and 46.0% with CBL, 5.8% and 40% with NBL approach in 2011 and 2012, respectively, of total emissions). The CH_4 sink, dominated by tropospheric OH oxidation and only to a minor extend by soil surface uptake, was quantified at roughly 4% of local emissions.

KEYWORDS

Agriculture; Greenhouse Gas; Switzerland; Boundary-layer isotope dilution; Nocturnal methane emissions

1. Introduction

Despite being the second-most important greenhouse gas in the atmosphere after carbon dioxide, methane (CH_4), its sources and sinks and their temporal variability are still poorly understood at local to regional spatial scales [1,2]. Here, we aim at identifying the major CH_4 sources in an agriculturally dominated area in Central Europe, and at estimating their respective source strengths.

While a substantial effort is made to reduce uncertainty in global CH_4 budget estimates [3–5], the estimation of regional CH_4 budgets is often impeded by the heterogeneous spatial pattern of different sources and by the unresolved temporal variability of their underlying emissions [6–8]. Direct mole fraction measurements at different spatio-temporal scales are therefore essential for a reliable estimation of regional source distributions and intensities, putting significant constraints on CH_4 budget calculations [2,8]. Particularly top-down approaches [e.g., 9] are generally underconstrained, thus CH_4 budgets remain substantially uncertain, since the small-scale variability is often smoothed out [6]. But also for bottom-up approaches [e.g., 10,11], measurements covering the spatio-temporal variability of CH_4 emissions are scarce. In addition, measurements of atmospheric CH_4 over heterogeneous areas always represent a mixture of different sources, which is rarely partitioned into the

individual contributions resulting in uncertain emission estimates by source sector [4]. Due to their possible cumulative impact on the total CH₄ budget, a separation of individual sources and sinks is needed.

However, based on mole fraction measurements alone, it remains difficult to separate the different components of a CH₄ budget. In regions with diverse CH₄ sources or sinks, combined measurements of CH₄ mole fractions and $\delta^{13}\text{C-CH}_4$ values can improve constraining major CH₄ sources and sinks [12], due to their enrichment or depletion in ¹³C relative to the ambient background value [4,13–16]. Different CH₄ production processes and CH₄ oxidation discriminate against the heavier carbon isotope, and thus the resulting isotopic ratios can be used to differentiate microbial from thermogenic sources and sinks [1,17–19]. Microbially produced CH₄, e.g., from enteric fermentation and manure, is characterized by low $\delta^{13}\text{C-CH}_4$ values (see Table 1). In contrast, thermogenically produced CH₄, e.g., CH₄ contained in fossil fuel and to a lesser extent CH₄ resulting from incomplete combustion at high temperatures, is enriched in ¹³C. Similarly, CH₄ resulting from methanogenic consumption or oxidation via atmospheric radicals leads to enrichment in ¹³C [2,20]. On the global scale, the use of $\delta^{13}\text{C}$ in CH₄ is well established for long-term and present-day emission budgets [4,21–27]. Evaluations of small-scale emission budgets using $\delta^{13}\text{C-CH}_4$ of atmospheric CH₄, however, are often limited to source strength estimations of specific land-use types such as landfills, rice paddies, peatlands or pastures, where source signatures are relatively well known, and problems caused by multiple sources can be avoided [28–31]. Nevertheless, some studies have successfully identified multiple sources of atmospheric CH₄ via $\delta^{13}\text{C-CH}_4$. Rural areas in New Zealand revealed a significant nocturnal decrease in $\delta^{13}\text{C-CH}_4$ resulting from CH₄ emissions from grazing sheep [32]. Urban areas, in contrast, were mainly affected by emissions from landfills, gas leakages, and waste water treatments, whose source position and strength could be assessed through $\delta^{13}\text{C-CH}_4$ in combination with wind direction analysis [1,15,33]. However, the heterogeneous character of source distributions, the low temporal resolution of CH₄ mole fraction measurements, and the complex atmospheric transport processes affected an unequivocal estimation of the regional CH₄ budget.

Our study asks the question “what information on local or regional sources and sinks can be extracted from diel variations of CH₄ mole fraction and associated variations in the

$\delta^{13}\text{C-CH}_4$ values”? Thus, the objectives of our study were: (1) to use $\delta^{13}\text{C-CH}_4$

75 measurements that resolve the diel cycle during two field campaigns within the atmospheric boundary layer over an agriculturally dominated valley in Switzerland, (2) to identify major local or regional sources and sinks using a mixing model, (3) to quantify their night- and daytime contributions to the background CH_4 source mix, and (4) to discuss the resulting implications on the regional CH_4 budget.

80 **2. Materials and methods**

2.1. Study area

The Reuss Valley in central Switzerland is aligned in a south-east to north-west direction and is surrounded by relatively low mountain ranges (up to 760 m a.s.l. vs. ≈ 400 m a.s.l. at the valley bottom). About 57% of its area is used for agriculture, mostly forage production
85 (meadows and maize) with pastures where cattle (mostly meat production) and a occasionally sheep are grazing. Due to soils and climatic limits, other field crops only cover a small share of the agricultural area. About 23% and 18% are forests and urban areas, respectively [34]. Lakes and unproductive areas are of minor importance ($<3\%$). Under fair weather conditions, the wind direction in the Reuss Valley (Figs S1, S2) is dominated by the
90 valley wind system: during the day, when a convective boundary layer (CBL) establishes, the wind trajectories are directed from the lowlands towards the Alpine region (Figs S1c,d and S2c,d). With the development of a stable nocturnal boundary layer (NBL) at night, these winds are replaced by opposite cold air drainage flows [see e.g. 35] (Figs S1e,f and S2e,f). To probe the NBL for the distribution and temporal evolution of CH_4 mole fractions, we
95 used two measurement approaches, (i) a stationary set-up (during 16–18 August 2011 and 24–25 July 2012), using a tethered balloon system, and (ii) a mobile set-up (during 24–25 July 2012 only), using a car. All dates and times are reported in Central European Time CET (UTC + 1 hour), and the time periods represent typical anticyclonic fair weather conditions.

2.2. Stationary set-up

100 The stationary set-up was installed on the valley bottom at the Chamau research station (47°12'37" N, 8°24'38" E at 393 m a.s.l., Fig. 2). The station is mainly used for forage production and its livestock density changes over the year according to the seasonal three-stage farming system [36]. During the winter, the cattle stay at the base farm, i.e., at the Chamau research station of ETH, whereas during the summer months, most of them are
105 moved to higher located alpine grazing pastures. We measured CH₄ mole fractions within the atmospheric boundary layer at 0.2, 0.5, 2, 8 and 10 m a.g.l. using a guy-wired extension mast, and at 25, 50, 100 and 160 m a.g.l. using a tethered balloon system. Five inlet hoses were installed at the different heights up to 10 m a.g.l., and one 200-m hose was carried up with the balloon. Sample air was pulled at a flow rate of $\approx 1 \text{ L min}^{-1}$ through a multi-inlet
110 valve switching unit connected to a fast greenhouse gas analyzer (FGGA, Los Gatos Research Inc., Mountain View, CA, USA), placed at the ground in a weatherproof instrument box and measuring at 1 Hz. Calibration was done in the laboratory by the manufacturer (WMO X2004 CH₄ scale) prior to field deployment.

2.2.1. Air sampling for stable isotope analysis

115 A T-split at the end of the hose connected to the FGGA allowed us to take gas samples for stable carbon isotope analysis in the laboratory (Section 2.4). Air drawn from the different heights was collected in 300 mL glass flasks (Ernst Keller & Co. AG, Basel, Switzerland). At the stationary site, we used three portable automatic Air SAmplers (ASA) with 33 glass flasks per unit [37,38]. Each glass flask was filled for 5 minutes at a flow rate of $\approx 0.7 \text{ L}$
120 min^{-1} . Flasks were evacuated and filled with He at a slight overpressure of 0.3 bar before use. In addition to the standard measurements with the FGGA (see above), during sampling with the ASAs the sample air of the second end of the T-split was drawn through a particle filter (Gelman, Li-COR, USA) and a Li-COR 840 infrared gas analyser (IRGA) to measure CO₂ mole fraction in the sample using a small pump (DC12/8FK, Fürgut GmbH, Tannheim,
125 Germany) as a redundant measure to compare with the corresponding FGGA measurement. For the analyses presented here, however, only the CH₄ mole fractions (measured by the FGGA) were of interest, and the redundant CO₂ measurements were only used for quality control purposes. In-between the T-split and the IRGA a part of the air stream was pushed

with a second pump through a drying column containing magnesium perchlorate and then
130 into one of the glass flasks selected by a multi-port Valco valve (EMT- MA2ST12MWE;
VICI, Schenkon, Switzerland). A slight overpressure inside each flask ascertained that
isotopic contamination was minimised during transport, storage, and analysis on the isotope
ratio mass spectrometer (see Section 2.4). For additional details see Theis *et al.* [37] and
Zeeman *et al.* [38].

135 2.2.2. *Meteorological measurements*

These measurements were complemented with measurements of air temperature,
atmospheric pressure, relative humidity, wind speed, and wind direction using a TS-5A-SEN
meteorological probe (Atmospheric Instrument Research, Inc, Boulder, USA) attached to the
tether line near the hose inlet. The extension mast measurements were complemented with
140 wind direction (Figs S1, S2) as well as wind speed measurements at the top of the mast
(10 m a.g.l.) using a wind monitor (model Young 05103LM, Campbell Scientific Inc.,
Loughborough, UK), and with measurements of air temperature and relative humidity
(HydroClip S3, Rotronic AG, Bassersdorf, Switzerland) at 2 m a.g.l. in 2011 and at 0.2 m
a.g.l. in 2012. Measurements from a permanent weather station at ≈ 100 m distance provided
145 additional longer-term climate data.

2.3. *Mobile set-up*

The mobile set-up consisted of measurements at four predefined sampling locations (Fig. 2,
A–D) in and around the Reuss Valley, covering an altitudinal range from 380 m to 697 m
a.s.l. A fast CH₄ analyzer (FMA DLT-100, Los Gatos Research, CA, USA) installed in a car,
150 and an Airmar weather station (AIRMAR Technology Corporation, Mirford, NH, USA),
mounted on the car's roof measured CH₄ mole fractions at 1 Hz (mean flow rate of
 ≈ 0.5 L min⁻¹), air temperature, relative humidity, air pressure, wind direction and wind
speed at each sampling location. Each time a sampling location was visited ($5 \times$ each in
2012), air samples were collected in an ASA unit (collection time 5 minutes at ≈ 1 L min⁻¹).
155 Note that no similar mobile measurements were carried out in 2011.

2.4. Isotope ratio analysis

We used a PRECON unit (Fig. 1) to pre-concentrate CH₄ in sample air and separate it from other gasses before analysis. The PRECON was connected to a combustion reactor, followed by a PORAPLOT-Q (Agilent, Santa Clara, CA, U.S.A.) gas chromatography column (Fig. 1) from which the resulting gas was guided into an isotope ratio mass spectrometer (IRMS, Delta Plus XL; all Thermo Finnigan, Bremen, Germany). The IRMS was operated as follows: The ASAs containing the glass flasks with the air samples were directly connected to the PRECON. The sample gas was led from the glass flasks in He carrier gas (15 mL min⁻¹) through a glass tube (5 mm diameter) filled with silicagel, trenched in Iodine Pentoxide (I₂O₅), to oxidize CO to CO₂. Subsequently the CO₂ was removed with soda lime followed by Magnesium perchlorate (Mg(ClO₄)₂) to remove water vapor. The gas stream was led via a cryogenic trap – which was continuously submerged in liquid nitrogen (LN₂) to remove any residual CO₂ or H₂O – to the micro combustion reactor, containing oxidized Ni wires, where CH₄ was oxidized to CO₂ at 1040°C. Prior to measurement, the reactor was preconditioned with pure O₂ for 12 hours. The reaction products from the CH₄ oxidation were frozen and trapped in two additional sequentially automated cryogenic traps (LN₂), one filled with Ni wires for quantitative trapping, the other retaining the analyte before transferring to the gas chromatography column (30 m PORAPLOT Q) for further purification and separation of N₂O from CO₂ (Fig. 1). Further details are given in Brand [39]. Using a gas chromatography column after combustion as in our set-up (Fig. 1) is considered the best technical solution to eliminate Kr interference according to Schmitt *et al.* [40], because the CH₄-derived CO₂ is separated from Kr in such a configuration.

We referenced the ¹³C/¹²C ratios of our methane samples to the Vienna Pee Dee Belemnite (V-PDB) standard using the relative deviation $\delta^{13}\text{C-CH}_4$ from that standard,

$$\delta^{13}\text{C-CH}_4 = \frac{(^{13}\text{C-CH}_4/^{12}\text{C-CH}_4)_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}} - 1 . \quad (1)$$

First, we performed a PRECON-IRMS system calibration with a CO₂ calibration gas from OZTEC ($\delta^{13}\text{C-CO}_2 = -40.7\text{‰}$), with all chemical traps and the first cryo trap bypassed and the reactor furnace temperature reduced to 80°C. In the next step we applied a calibration gas mixture of 1% CH₄ in pure N₂ with a $\delta^{13}\text{C-CH}_4$ value of -46.2‰ . Since we had no

access to such high standard calibration gases as described in Sperlich *et al.* [41] we applied
 185 the calibration gas from the Department of Oceanography, Florida State University (USA).
 For calibrating our PRECON-IRMS system we injected 1 mL of this gas mixture in 300 mL
 of synthetic air (20% O₂ and 80% N₂) resulting in a CH₄ mole fraction of ca.
 3000 nmol mol⁻¹ (3 ppm). The precision was $\pm 0.13\text{‰}$ (standard deviation, n=33). Note that
 the use of a CH₄ in synthetic air mixture yielded significantly better precision than a CH₄ in
 190 N₂ mixture, which was $>0.5\text{‰}$. From preliminary experiments with both synthetic air and
 an oxygen-free N₂-CH₄ mixture we deduced that the 20% oxygen in the synthetic air
 contributes largely to a complete conversion of CH₄ to CO₂, preventing any fractionation
 during the conversion process, thereby enhancing reproducibility and precision of the
 measurements. Based on these calibrations, we prepared a working standard, which was
 195 compressed air (Messer Griesheim, Lenzburg, Switzerland) with a CH₄ mole fraction of
 2 ppm and a $\delta^{13}\text{C-CH}_4$ value of -44.5‰ .

2.5. Nighttime source identification

We used a two-component mixing model (also known as the “Keeling plot” approach) to
 identify the source mix leading to a significant increase of atmospheric CH₄ mole fraction,
 200 i.e., excess CH₄, over a specific background [6,15,31,33]:

$$\delta^{13}\text{C}_{\text{source}} = \frac{\delta^{13}\text{C}_{\text{obs}} \cdot c_{\text{obs}} - \delta^{13}\text{C}_{\text{ldbg}} \cdot c_{\text{ldbg}}}{c_{\text{obs}} - c_{\text{ldbg}}}, \quad (2)$$

where c_{ldbg} and $\delta^{13}\text{C-CH}_4_{\text{ldbg}}$ are the CH₄ mole fraction and the $\delta^{13}\text{C-CH}_4$ value of the local
 daytime background, respectively, calculated from daytime observations at Chamau (see
 below). The observed CH₄ mole fraction and its $\delta^{13}\text{C-CH}_4$ value are denoted as c_{obs} and
 $\delta^{13}\text{C-CH}_4_{\text{obs}}$. Depending on the isotopic signature of the additional CH₄, which mixes into
 205 the background air, the $\delta^{13}\text{C-CH}_4_{\text{obs}}$ deviates from $\delta^{13}\text{C-CH}_4_{\text{ldbg}}$. Using equation (2), the
 isotopic signature of the source can be calculated for each flask sample. The derived source
 signal describes an average isotopic signature of several sources, and $\delta^{13}\text{C-CH}_4_{\text{source}}$
 therefore characterizes a source mix. This two-component mixing model is based on three
 assumptions [6,42]: First, it assumes that only two gas components are involved in the
 210 mixing process, that is, the source and the local daytime background. Second, the isotopic

signatures of the components are not changing during the time of sampling. And third, sinks are not present (unless they are defined as negative sources). Although these assumptions are rarely perfectly fulfilled even at night [42], the weak atmospheric mixing and sufficiently large mole fraction ranges observed during the night provide the best possible conditions for such a model application.

For both measurement campaigns (August 2011 and July 2012), we determined the values for $\delta^{13}\text{C-CH}_{4\text{ldbg}}$ and c_{ldbg} from the mean of all profile measurements during well-mixed daytime conditions, when the CH_4 mole fractions at each height simultaneously reached their minima. The local daytime background in 2011 for CH_4 and $\delta^{13}\text{C-CH}_4$ obtained in this way was 1929 ± 6 ppb and $-46.0 \pm 0.7\text{‰}$ (mean $\pm$ standard deviation). For 2012, we obtained a mean CH_4 and $\delta^{13}\text{C-CH}_4$ local daytime background value of 1965 ± 9 ppb and $-45.6 \pm 0.5\text{‰}$. Equation (2) was applied to nighttime isotopic signatures measured between 21:00 and 06:00 CET, and the resulting $\delta^{13}\text{C-CH}_{4\text{source}}$ values were compared to specific $\delta^{13}\text{C-CH}_4$ signatures of CH_4 sources and sinks in the Reuss Valley (Table 1).

2.6. Daytime source and sink identification

For the identification of the source and sink mix during daytime (and using all data, daytime and nighttime), we used Monte Carlo Simulation [MCS; e.g. 43] of an extended mass balance equation by solving the fractions of three distinct flux categories (biogenic sources b , non-biogenic sources n , and atmospheric and soil sinks s) and an explicit treatment of the background air (bg) contributing to the observed isotopic signature δ_{obs} (this is an extension of the approach suggested by Phillips and Gregg [44]):

$$\delta_{\text{obs}} = f_b \delta_b + f_n \delta_n - f_s \delta_s + f_{bg} \delta_{bg} , \quad (3)$$

$$1 = f_b + f_n - f_s + f_{bg} , \quad (4)$$

where δ_b , δ_n , δ_s and δ_{bg} denote the isotopic signatures of biogenic and non-biogenic sources, the sinks, and the global atmospheric background, respectively. Since Eqs (3) and (4) constitute a mathematically underdetermined system of two equations in four unknowns [44] it does not allow for a unique solution for f_b , f_n , f_s , and f_{bg} . Hence, we expanded the

approach to a linear system with four equations and four unknowns,

$$\delta_{\text{obs},1} = f_b \delta_{b,1} + f_n \delta_{n,1} - f_s \delta_{s,1} + f_{bg} \delta_{bg,1} , \quad (5)$$

$$\delta_{\text{obs},2} = f_b \delta_{b,2} + f_n \delta_{n,2} - f_s \delta_{s,2} + f_{bg} \delta_{bg,2} , \quad (6)$$

$$\delta_{\text{obs},3} = f_b \delta_{b,3} + f_n \delta_{n,3} - f_s \delta_{s,3} + f_{bg} \delta_{bg,3} , \quad (7)$$

$$1 = f_b + f_n - f_s + f_{bg} , \quad (8)$$

using three instead of only one field measurements for each MCS run.

In detail, using a MCS approach means that a large number of randomly selected triplets of observations ($\delta_{\text{obs},1}$, $\delta_{\text{obs},2}$ and $\delta_{\text{obs},3}$) were sampled out of the dataset from each of the two
 240 field campaigns, or from the combined dataset from both campaigns. At the same time, the prescribed source, sink and background signatures $\delta_{b,1}$, $\delta_{b,2}$, $\delta_{b,3}$, $\delta_{n,1}$, $\delta_{n,2}$, $\delta_{n,3}$, $\delta_{s,1}$, $\delta_{s,2}$, $\delta_{s,3}$, $\delta_{bg,1}$, $\delta_{bg,2}$, $\delta_{bg,3}$, were generated from the prescribed mean signatures ($\overline{\delta_x}$, with $x \in \{b, n, s, bg\}$) and a random perturbation defined by the respective standard error of the signatures ($\Delta \delta_x$) with the constraints $f_b > 0$, $f_n > 0$, $f_s > 0$, $f_{bg} > 0$, $f_b > f_n$, and
 245 $f_s < \min(f_b, f_n)$.

These Monte Carlo simulations were carried out twice, first with daytime data only (between 10:00 and 16:00 CET), and then with both daytime and nighttime data (“all data”). The difference between outcomes based on daytime data only (for which this approach is most meaningful), and based on all data is an indication of how robust the estimated relative
 250 contributions are. Note that we did not use this approach for nighttime conditions alone, but used the much simpler and more widely used “Keeling plot” approach (see Section 2.5) that however is restricted to cases with large changes in CH₄ mole fractions as it is observed during the night.

For the background air we used the global average of -47.4‰ [24] and used a value of 0.2‰
 255 for $\Delta \delta_{bg}$ instead of the local background values reported above for nighttime conditions. An isotopic value of $\overline{\delta_b} \pm \Delta \delta_b = -61.3 \pm 4.6\text{‰}$ was used for biogenic sources as the weighted average of the proportions from enteric fermentation and manure management emissions to total agricultural CH₄ emissions in Switzerland, here 80% and 20%, respectively [45]. For non-biogenic sources the weighted average of $\delta^{13}\text{C-CH}_4$ values for vehicle emissions (95%

European, 3.5% US cars), biomass burning (0.1% C₃ and C₄ plants each) and natural gas (1.3% from North Sea; see Table 1) was used with $\bar{\delta}_n \pm \Delta\delta_n = -27.6 \pm 9.4\text{‰}$. For sink processes a signature of $\bar{\delta}_s \pm \Delta\delta_s = -5.4 \pm 0.9\text{‰}$ was used following Cantrell [46] (see Table 1). As expected from the law of large numbers, tests showed that the outcome of our MCS is very robust against assumptions made for $\Delta\delta_x$ as long as its estimate is kept within a realistic range ($\approx 2\text{--}20\text{‰}$).

The approach used here assumes that the measurements obtained during daytime conditions in a single field campaign can be considered stationary in the way that f_b , f_n , f_s , and f_{bg} are system parameters (i.e., constant during the period), and variations in δ_{obs} simply reflect the short-term variations in source and sink signatures as described by $\Delta\delta_x$.

MCS calculations were repeated 99,999 times (or 9,999 times for the sensitivity analysis in Section 3.4). In a final step the MCS results were scaled by factor ξ so that the sum of the average of the fractional emissions of the two sources (F_b and F_n ; see Eqs (10) and (11)) was 100%,

$$\xi = \frac{100\%}{f_b + f_n}, \quad (9)$$

and the sink fraction F_s was expressed as a negative number to distinguish it from the sources,

$$F_b = \xi \cdot f_b, \quad (10)$$

$$F_n = \xi \cdot f_n, \quad (11)$$

$$F_s = -\xi \cdot f_s. \quad (12)$$

All calculations were done with R version 3.2.4 [47], using the `solve()` function to determine f_b , f_n , f_s , and f_{bg} from Eqs (5)–(8).

3. Results and discussion

3.1. Mean diel cycles of CH_4 and $\delta^{13}\text{C-CH}_4$

280 3.1.1. Stationary set-up

In both campaigns we observed clear diel cycles of CH_4 mole fractions at Chamau (Fig. 3). The nighttime build-up in CH_4 mole fraction at 0–10 m a.g.l. to 2920 ppb in 2011 and to 3830 ppb in 2012 was not strongly correlated with a depletion in ^{13}C relative to the local background values. During the day, the mole fractions and $\delta^{13}\text{C-CH}_4$ values were close to
285 the respective background values. The diel cycle was less pronounced at higher levels above ground, i.e. between 25–50 m and between 100–200 m a.g.l. In 2011, the nighttime CH_4 build-up was reduced to 2840 ppb at 25–50 m a.g.l., and to 2340 ppb above 100 m a.g.l. While the nighttime CH_4 build-up was reduced with increasing height in 2011, no considerable differences in the diel course of CH_4 were found for the different heights in
290 2012, probably due to active vertical mixing processes. In general, highest CH_4 mole fraction peaks within the diel cycle were observed in both campaigns around 05:00 at all measured heights. Unlike CH_4 mole fractions, the $\delta^{13}\text{C-CH}_4$ values were highly variable at all measurement heights, and no single peak could be assigned to a specific hour of day. With the replacement of the NBL by the CBL, the CH_4 mole fraction decreased rapidly at all
295 measured heights. However, isotopic signatures showed a large variability during the day. Particularly in 2011, daytime $\delta^{13}\text{C-CH}_4$ values were highly variable including also very high values above -40‰ compared to daytime values in 2012, which remained close to the background value at all times.

3.1.2. Mobile measurements

300 The diel courses from the mobile measurement set-up sites were comparable to the observations from the stationary set-up, with a clear diel cycle of similar magnitude at the measurement locations on the valley bottom (Fig. 4, A and C). At location C in the south of the valley, the CH_4 mole fraction reached 3310 ppb before sunrise and $\delta^{13}\text{C-CH}_4$ was reduced by -8‰ (-51.4‰ vs. -43.4‰ around 08:00). Highest CH_4 mole fractions at the
305 northern measurement location A were found after 07:00 with 3000 ppb with an associated

decrease in $\delta^{13}\text{C-CH}_4$ by -6.1‰ (-49.6‰ vs. -43.5‰ around 12:00). Since sunrise was shortly before our first measurement at location A, we might however have missed the absolute early-morning peak. No diel trend was found during the observations at the eastern hilltop (B) located next to a lake. At the western hilltop (D), where the measurements were
 310 located at a managed cropland close to a farmstead, only small diel fluctuations were observed. There, a small CH_4 peak occurred delayed at 10:00 and the subsequent decrease in CH_4 mole fractions was accompanied by an increase in the isotopic signature. Due to the less pronounced diel cycle of the observed isotopic signatures with increasing height, no correlation was found between median $\delta^{13}\text{C-CH}_4$ and height a.g.l. (regression
 315 slope: -0.005‰ m^{-1} , $p = 0.06$). No significant correlation was found between $\delta^{13}\text{C-CH}_4$ and wind direction or wind speed. Not all wind directions, however, had been covered with our measurements (Figs S1, S2).

3.2. *Spatio-temporal variability of CH_4 and $\delta^{13}\text{C-CH}_4$*

320 Even under conditions with temporally invariant CH_4 emissions a diel course in CH_4 mole fractions is expected near the surface, since the mixing volume into which these emissions are incorporated varies strongly between daytime (extended planetary boundary layer with a vertical depth of 1000 m and more in which convective mixing is active) and nighttime conditions (stable stratification with a shallow boundary layer in which vertical mixing is
 325 rather limited). This expected diel course is well seen in both campaigns (Fig. 3). Diel cycles with a substantial increase in CH_4 mole fractions during the night were also observed in other studies [48,49]. These studies, focusing on areas with a single CH_4 source, e.g. ruminants, natural gas or landfills, also found a clear diel cycle in $\delta^{13}\text{C-CH}_4$ with a strong nighttime depletion followed by enrichment in ^{13}C in the early morning hours, and a
 330 daytime signal close to background [32,33], which was not as pronounced in our measurements (Fig. 3). A lack of diel variations in $\delta^{13}\text{C-CH}_4$ is only theoretically possible if the local source/sink mix has exactly the same isotopic composition as CH_4 in background air. Under such simplified theoretical conditions, the diel cycle of CH_4 mole fractions is solely due to the diel cycle in atmospheric stability and boundary layer depth. The existence
 335 of a diel cycle of $\delta^{13}\text{C-CH}_4$ thus implies that the local to regional source/sink mixture differs

from the global average and may be subject to diel variation (e.g. one source is dominating during the night and another source is dominating during the day). Our measurements, in contrast to Harvey *et al.* [32] and Lowry *et al.* [33], showed a less pronounced diel cycle in $\delta^{13}\text{C-CH}_4$ compared to CH_4 mole fractions, suggesting that the ratio between enteric fermentation and manure management from agriculture – which have been identified as the main contributors to atmospheric CH_4 in the Reuss Valley – and other sources remains fairly constant over the day.

3.2.1. Valley bottom conditions

With respect to the nighttime data, the nocturnal decrease in $\delta^{13}\text{C-CH}_4$ values at the valley bottom relative to the background value, however, was rather small, whereas the diurnal range of CH_4 mole fractions was substantial (ca. 1600 ppb, from 1900 ppb during the day to a nocturnal maximum around 3500 ppb; see Fig. 3). In particular, the nighttime measurements of 2012 clearly showed that CH_4 -enriched emission plumes resulted in equally high excess CH_4 as the emissions from biogenic sources, probably due to stronger nighttime advective transport of enriched upwind air masses and following mixing processes with the locally depleted NBL. Excess CH_4 of clearly non-biogenic origin, i.e., $\delta^{13}\text{C-CH}_{4\text{source}} > -25\text{‰}$, was only observed during limited time periods before sunrise in both campaigns (Table S1), probably resulting from nighttime fanning of local non-biogenic emissions emitted into the calm and stable nocturnal boundary layer. As these high $\delta^{13}\text{C-CH}_4$ values were observed even at very low measurement heights (0.2, 2 and 10 m a.g.l.), our findings suggest that nearby non-biogenic sources do exist, but that their contributions in the Reuss Valley must be rather low compared to agricultural sources. Possible origins are vehicular CH_4 emissions from less efficient combustion of farm machinery or vintage cars, and emissions from biomass burning (e.g., use of charcoal-fired barbecues). It is however unlikely, that such sources are very strong, since farming vehicles only occasionally are active at night (e.g. to finish harvest before the arrival of forecasted adverse weather), and grilling activities are typically constrained to the hours around sunset, not in the second half of the night and before sunrise. With respect to daytime data, the $\delta^{13}\text{C-CH}_4$ values showed an enrichment in $\delta^{13}\text{C-CH}_4$ at all measured heights, demonstrating that biogenic sources were not alone responsible for the observed diel cycle. Isotopic

enrichment was found after sunrise (Figs 3 and 4), when under fair weather conditions prevailing NNW-winds penetrate into the valley from northern agglomerations, where leakages in gas pipelines are expected to be a major CH₄ source [10,11]. Although no correlation was found between $\delta^{13}\text{C-CH}_4$ and wind direction, we argue that the valley wind system, carrying CH₄ from upwind lying sources into the Reuss Valley, was responsible for the elevated daytime $\delta^{13}\text{C-CH}_4$ values.

3.2.2. Hilltop conditions

Contrastingly, at the hilltop sites the mobile measurements neither showed a diel course in CH₄ mole fractions nor in $\delta^{13}\text{C-CH}_4$ values, as they were located above the NBL and hence remained unaffected by CH₄ emissions from nearby farmsteads. However, we also observed daytime enrichment in ^{13}C at these hilltop locations, as can be seen in a transport-induced peak in $\delta^{13}\text{C-CH}_4$ at the mobile measurement site D around 10:00 (Fig. 4). This observation is in agreement with other studies from the Reuss Valley, where the upward transported air masses dominated the local diel cycle of CH₄ with the onset of the valley wind system [50]. In summary, results showed that the diel patterns in $\delta^{13}\text{C-CH}_4$ were strongly influenced by the local topography and by advective transport processes, which play a major role in atmospheric CH₄ budgets [1,48,49]. Even hilltop locations above the NBL, which do not exhibit a diel course, are affected by the local wind regime during the day.

3.3. Source and sink identification

3.3.1. Nighttime: Keeling-plot approach

Nighttime $\delta^{13}\text{C-CH}_4$ measurements imply that biogenic CH₄ sources were of major importance in the Reuss Valley (Fig. 5): On a Keeling plot, the majority of the data fell into the biogenic source sector and originated from a combination of enteric fermentation, manure and waste management. Only four out of a total of 65 measurements were clearly influenced by non-biogenic sources (in the blue-colored top part of Fig. 5), biomass burning, or a combination thereof. This is also clearly seen in the $\delta^{13}\text{C-CH}_{4\text{source}}$ values obtained from the Keeling plot intercepts (Tables S1 and S2). In 2011, biogenic source mixtures emitted CH₄ with a mean isotopic signature of -56.3‰ (removing all observations from

non-biogenic sources, i.e. $\delta^{13}\text{C-CH}_{4\text{obs}} \geq \delta^{13}\text{C-CH}_{4\text{ref}}$. The 2012 values (-54.8‰) were not
 395 significantly different from the 2011 signatures ($p > 0.05$). However, in 2012 about 40% of
 all nighttime increase in CH_4 was caused by other than biogenic sources (compared to 5.8%
 in 2011). Despite the increased CH_4 mole fractions in 2012 compared to 2011 (Fig. 5), the
 observed $\delta^{13}\text{C-CH}_4$ values were close to the background value and are pointing to a
 combination of biogenic and non-biogenic CH_4 sources. High $\delta^{13}\text{C-CH}_{4\text{source}}$ values
 400 ($> -25\text{‰}$) were only observed before sunrise.

3.3.2. Daytime: MCS simulations

During the day, the mean $\delta^{13}\text{C-CH}_4$ values showed no significant difference between the
 two measurement campaigns ($-44.8 \pm 0.4\text{‰}$ and $-45.2 \pm 0.2\text{‰}$ mean $\pm$ SE in 2011 and
 2012, respectively; $p = 0.39$; $n = 48$ and 43 ; overall daytime mean was $-45.0 \pm 0.2\text{‰}$). Hence
 405 the median contributions to total emissions obtained from MCS were comparable with
 57.8% and 54.1% biogenic, and 42.2% and 46.0% non-biogenic emissions in 2011 and
 2012, respectively (Fig. 6). Of these emissions, 4.6% and 2.5% were offset by sink processes
 (i.e., a combination of both atmospheric OH reaction and soil uptake) in 2011 and 2012,
 respectively. The narrower range of observed δ_{obs} signatures during daytime in 2012
 410 translated to slightly lower uncertainties in the estimates of relative contributions of sources
 and sinks: The inter-quartile ranges (IRQ) of the biogenic and non-biogenic sources in 2011
 (2012) were 53.6–63.7% (51.8–57.4%) and 36.3–46.4% (42.7–48.2%), respectively.
 Conversely, the IRQ of sink estimates was 2.0 to 8.5% in 2011 vs. 1.1 to 4.7% in 2012 (Fig.
 6).

3.3.3. Comparison between methods

The source and sink contributions determined via MCS for daytime conditions were
 generally quite comparable during the 2011 and 2012 campaigns (Fig. 6, Table 2). In both
 cases the observed $\delta^{13}\text{C}$ in CH_4 suggest a dominant contribution of biogenic sources with
 56.9% of the total emissions (daytime average of the 2011 and 2012 campaigns) and 43.1%
 420 non-biogenic emissions, respectively. Contrastingly, the alternative approach using nocturnal
 data with the Keeling plot intercepts suggested more variability in the relative contribution
 of non-biogenic sources (5.8% in 2011 vs. 40% in 2012) which on average was clearly lower

(22.9%) than the daytime MCS estimates (43.1%). This difference between the two approaches most likely simply reflects the different footprints of such measurements during daytime and nighttime: (a) During the day up-valley winds mix the atmosphere rather well, leading to a large footprint area influencing local measurements, whereas (b) during the night (with stable atmospheric stratification) the winds tend to be weak, and thus the footprint area influencing local measurements becomes smaller. This means that advection of non-biogenic CH₄ becomes less important for the source mixture observed at night at our field site, as compared to daytime conditions when emissions from densely populated upwind areas most likely are an important component in the local CH₄ budget.

3.3.4. *Comparison with national emission estimate*

The national estimate of CH₄ emissions based on the Kyoto reporting procedure [51] suggests that in Switzerland 18.6% of total emissions stem from non-biogenic sources on average: 946 of a total of 5,099 kt CO_{2,eq} (estimates reported for 2015 [51]). Our August 2011 estimate of the share of non-biogenic sources obtained from nocturnal data is clearly lower (5.8%) as was expected for the rural location of the CH-CHA site, but the July 2012 estimate obtained in the same way indicated a much higher relevance of non-biogenic sources (40%). Also estimates obtained from MCS simulations (Table 2) indicate a much higher relevance of non-biogenic sources than what the national estimate reports.

3.4. *Sensitivity analysis*

3.4.1. *Robustness of model*

To assess the robustness of the MCS results we performed a set of 79 sensitivity runs with 9,999 MCS repetitions each to explore the gradients around all four input signatures in our simulations (Fig. 7). For this exercise we pooled the 2011 and 2012 data and report the daytime (10–16 hours CET) results. Since background air signature is an explicit parameter in our model (Eqs (3), (5)–(7)), we were interested to determine the relative contributions of biogenic and non-biogenic sources in combination with a sink term in relation to the global background signature of -47.35‰ [24]. The relative shares of biogenic, non-biogenic sources and sink with respect to global background were 55.5% (IRQ 52.5%–59.8%), 44.5%

(IRQ 40.2%–47.5%), and 3.3% (IRQ 1.5%–6.2%)% (Fig. 7a). Assuming a less negative background mole fraction increases the contribution of biogenic and reduces the relevance of non-biogenic sources (Fig. 7a). At the same time the sink becomes more important.

Assuming a background signature of -45.5‰ as we determined for 2012 (vertical line in Fig. 7a) yields relative contributions of 53.9% (IRQ 35.3%–80.4%), 35.6% (IRQ 20.4%–56.4%), and 5.0% (IRQ 2.2%–9.4%).

3.4.2. Sensitivity to model assumptions

The sensitivity of our model to assumptions made for the sink signature is comparatively small (Fig. 7b). The more negative the assumed sink signature, the tighter the IQR and the 95% confidence interval (CI). At -21‰ (soil sink signature, Table 1) the median share of the sink is still 2.6% (IRQ 1.1%–4.8%) as compared to 3.4% (IRQ 1.5%–6.2%). In general, realistic estimates for the sink term remain well below 10% of biogenic and non-biogenic emissions.

Although our model appears to be quite robust, small changes in CH_4 sinks may still be of relevance for the atmospheric CH_4 budget. A sensitivity analysis carried out by Lassey *et al.* [52] for the global CH_4 budget estimated that a 1% increase in absolute global sink strength would lead to an additional 0.11% removal of the global methane burden per year [52].

The assumptions made for the non-biogenic sink signature are of least concern in our modeling (Fig. 7c). The key sensitivity of our model is associated with the biogenic sources (Fig. 7d), for which we assumed $-61.3 \pm 4.6\text{‰}$. If a less negative signature is assumed in the model, the biogenic fraction quickly increases at the expense of the non-biogenic fraction and a slight increase in the sink term (Fig. 7d). As an example: with a biogenic signature of -51.3‰ the biogenic fraction increases from 55.5% to 63.3% (IQR 42.4 to 87.8%). At the same time the non-biogenic source is reduced from 44.5% to 31.2% (IRQ 20.9%–43.7%). An aspect that could however not be solved to full satisfaction is how published isotope ratios of $\delta^{13}\text{C}\text{-CH}_4$ are biased due to potential Kr interference depending on IRMS configuration [40,53].

3.5. Simplification potential for MCS model

Our four-endmember daytime mixing model (Eqs (5)–(8)) is heavily underdetermined with
480 four equations and only one tracer ($\delta^{13}\text{C-CH}_4$). Thus, we tested whether a simplified
three-endmember mixing model similar to the one proposed by Phillips and Gregg [44] that
ignores the isotopic difference between the global $\delta^{13}\text{C-CH}_4$ background and the locally
observed background would have yielded similar results. Table 2 shows that such a
simplified model of reduced complexity (“local” in Table 2) closely represents the more
485 detailed four-endmember model (Fig. 6; “global” in Table 2).

Differences between mean estimates of proportional contributions of biogenic and
non-biogenic sources to total emissions were small (Table 2). Also sink estimates were very
similar. Given the considerable uncertainty of the estimates obtained with both models, our
results did not indicate a clear preference for either model. The 95% confidence intervals
490 from the four-endmember model tended to be slightly narrower, despite the requirement for
one more assumption in the model (i.e., global isotopic background signature).

3.5.1. Mixing of background air into local atmosphere

The relative share of global background air that is mixed into the volume of local air at
CH-CHA is of course a large percentage, which, however, does not contain any signal of
495 local to regional emission sources and sinks, since the lifetime of CH_4 in the atmosphere is
ca. 10 years [54]. In Figure 8 the overall share of background air that our primary mixing
model (Eqs (5)–(8)) determined is shown. This indicates that using a global background
signature of -47.4‰ translates to 60.6% of air at CH-CHA being background air without a
local (to regional) signal. Using the locally determined maximum background signature of
500 -44.4‰ suggests that 76.4% of the air at CH-CHA is well mixed with the global
background, and thus the local to regional source and sink signals are actually extracted
from 23.6% of the CH-CHA air when using the simplified model (vs. from 39.4% of air in
our primary model). Using Eqs (9)–(12) for scaling eliminates most of the effect of
background air in the overall air mixture at our site.

505 Using a locally determined background $\delta^{13}\text{C-CH}_4$ value leads to a mean relationship
between biogenic and non-biogenic sources that suggest that biogenic sources are $\approx 36\%$
more important than non-biogenic sources at the CH-CHA site (the ratio of daytime

fractions in Table 2 is $57.6\%/42.4\% = 1.36$). Similarly, using our primary model with a global $\delta^{13}\text{C-CH}_4$ this estimate suggests a $\approx 32\%$ greater importance of biogenic vs.

510 non-biogenic sources. In summary, both approaches indicate that the ratio between biogenic and non-biogenic sources is on the order of 4:3.

3.6. *Relevance of sinks*

Sinks remove ca. 4.4% of CH_4 emissions on average (daytime average of 2011 and 2012, Table 2). This sink estimate obtained from the MCS mixing model is rather large but
515 realistic. We used an isotopic sink signature ($\delta^{13}\text{C-CH}_4$ of $-5.4 \pm 0.9\text{‰}$, Table 1) strongly dominated by tropospheric OH oxidation and much less by soil CH_4 uptake. Although our sensitivity analysis (Section 3.4) only showed a weak dependence of the sink fraction estimate on the assumptions made for its isotopic signature (Fig. 7b), a better separation between these two main sinks would be desirable to increase our understanding of trends in
520 CH_4 mole fractions. Long-term trends in the tropospheric OH sink [27], and uncertainties in isotopic source signatures in general [55] are potential explanations for mismatches between global and regional models and field observations.

The main CH_4 sink, i.e., atmospheric OH, reacts on a longer timescale and on larger spatial scales [2,13,20,25], and the sink strengths of different soils, which largely depend on the
525 land-use type, are yet to be resolved on shorter timescales [18]. While CH_4 uptake of the nearby grasslands with $-0.21 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ do not contribute significantly to the CH_4 budget [56], forest soil uptake rates were estimated at up to $-1.5 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ [10,11]. This is only 1% of the nocturnal boundary-layer budget flux of $138 \pm 27 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ computed by Stieger *et al.* [57]. If this estimate is correct, then the atmospheric OH sink
530 removes an additional 3.4% of CH_4 emissions, in addition to the 1% removed by forest soils to yield the 4.4% relative sink strength obtained from our MCS mixing model.

3.7. *Implications for CH_4 emission budgets*

It has been shown that during anticyclonic fair weather conditions, trends in background levels of CH_4 mole fraction give information about the regional emission strength of major
535 sources [33]. The impact of agricultural CH_4 emissions from the Reuss Valley on the local

background atmospheric CH₄ burden, however, appears to be small, given the very weak trend in mole fractions observed during the day (Fig. 6). While background CH₄ mole fractions showed almost no diel cycle, the $\delta^{13}\text{C-CH}_4$ background value showed a marginal daytime dip of -0.3‰ .

540 This suggests that nighttime CH₄ emissions are compensated by convective dilution during the day, thereby only leaving a clear signal in the isotopic composition of CH₄ but not in the CH₄ mole fraction per se. This $\delta^{13}\text{C-CH}_4$ signal however shows a less pronounced diel cycle than what would be expected from purely biogenic (agricultural) emissions, and it allowed us to estimate the potential contribution of non-biogenic sources contributing to the CH₄ 545 emission budget of the Reuss Valley.

4. Conclusions

This study showed that measurements of CH₄ mole fractions and $\delta^{13}\text{C-CH}_4$ that resolve the diel cycle improve our understanding of the temporal and spatial variability of emissions from different CH₄ sources within a specific region. We used the stable ¹³C signature in CH₄ 550 to quantify the relative contributions of two source categories (biogenic and non-biogenic) and one sink term (a combination of CH₄ removal via atmospheric OH, and uptake by soils and vegetation surfaces) in the local CH₄ boundary-layer budget. With nocturnal data we used a conventional “Keeling-plot” approach, whereas daytime conditions (and with all data combined) we used Monte Carlo simulation approach.

555 In contrast to what could have been expected from an agriculturally dominated area, our isotope measurements lead us to the conclusion that biogenic emissions alone cannot explain the variability in our $\delta^{13}\text{C-CH}_4$ observations. Non-biogenic emissions, most likely from urban and more densely populated areas upwind of our site, are responsible for more than 40% of the CH₄ emissions, and only ca. 60% are of biogenic (predominantly agricultural) 560 origin. Using Monte Carlo simulations a sink strength on the order of 4% of total emissions was estimated. This may be an overestimation of real conditions, and thus we recommend to add $\delta^2\text{H}$ measurements in future studies to better constrain the two source and one sink terms in the isotopic mixing model calculations. Such isotopic tracer measurements are highly needed in order to improve the agreement between modeled and measured emissions

565 and give relevant information about the interpretation of CH₄ budgets.

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Figure 1. Sketch of the technical configuration of the PRECON pre-concentrator prepended to the isotope-ratio mass spectrometer (IRMS) used in this study. Using a post-combustion gas chromatography column (PORAPLOT-Q) is considered the best technical solution to eliminate potential Kr interferences according to Schmitt *et al.* [40].

Figure 2. Topographic map of the stationary (Chamau) and mobile (A–D) set-up sites in the Reuss Valley, Switzerland (map source: © swisstopo, reprint permission JD100042).

Figure 3. Diel course of $\delta^{13}\text{C-CH}_4$ and CH_4 mole fractions at the stationary set-up site Chamau Research Station given in means and standard deviations (SD) for the respective height levels. The background values are determined as the mean of all profile measurements during well-mixed daytime conditions (see text for details). Vertical broken lines indicate sunrise and sunset.

Figure 4. Diel courses of $\delta^{13}\text{C-CH}_4$ and CH_4 mole fractions of the mobile set-up sites during July 2012. The background values (horizontal solid line for $\delta^{13}\text{C-CH}_4$ and broken horizontal line for CH_4 mole fractions) are determined as the mean of all profile measurements during well-mixed daytime conditions from stationary set-up site. Each point represents a single measurement obtained at one of the locations A–D shown in Figure 2 where mobile measurements were carried out in 2012 (see Section 2.3).

Figure 5. Display of nighttime carbon isotopic data of observed CH_4 mole fractions (symbols) and different CH_4 source types taken from the scientific literature (lines). ^a Average of the background values of 2011 and 2012, calculated as the mean of all profile measurements during well-mixed daytime conditions from the stationary set-up site (see text for details). ^b Miller [2]. ^c Weighted average according to Switzerland's gas import statistics of the year 2011 [58]. ^{d,e} Calculated according to the proportions of C_4 - and C_3 -vegetation in the forage mixture used at the Chamau research station, i.e., 30% and 70%, respectively (pers. comm. H.-R. Wettstein). ^f Unweighted average of $\delta^{13}\text{C}-\text{CH}_4$ values from landfill, domestic sewage, and animal waste. This graphical display uses the same concept as Keeling plots. The lines are not fits to our data, but derived from the scientific literature. Colored background depicts the typical ranges of biogenic vs. non-biogenic sources (but note that biomass burning – which is not considered an important source in the study area – cannot be distinguished from vehicle emissions).

Figure 6. Flux proportions of biogenic and non-biogenic sources and a sink term (atmospheric oxidation and soil uptake) in the local CH_4 budget at the CH-CHA field site using a four-endmember model with global background $\delta^{13}\text{C}-\text{CH}_4$. Each group of five boxplots shows daytime data (10–16 hours CET; August 2011, July 2012, and both campaigns combined) and all data (00–24 hours CET) from August 2011 and July 2012. The 100% reference for flux proportions is the total emissions, and the sink strength is expressed as a percentage of total emissions, but with negative sign (removal of CH_4 from the atmosphere). All boxplots show the distribution of the outcomes of 99,999 Monte Carlo Simulation runs (see text for details).

Figure 7. Sensitivity analysis of assumptions made for (a) background, (b) sink, (c) non-biogenic, and (d) biogenic $\delta^{13}\text{C}-\text{CH}_4$ values. Thick lines show the median, the color bands indicate the IQR (25th to 75th percentile), and the dashed lines show the 95% confidence interval. Calculations were performed in 78 model runs at regular intervals along each interval with 9,999 Monte Carlo Simulation for each run. The vertical lines (“global” in (a), “this study” in (b), (c), and (d)) show the values used in Figure 6. The lines for 2011 and 2012 in panel (a) show the local background signature determined from nocturnal data, and the hashed area indicates the range of uncertainty related to the uncertainty of the global background $\delta^{13}\text{C}-\text{CH}_4$ estimate. In (b) the hashed area for the “soil sink” signature (see Table 1) shows the typical literature range of the sink signatures.

Figure 8. Sensitivity analysis of overall share f_{bg} of background air in Eq. (8) contributing to local $\delta^{13}\text{C-CH}_4$ measurements at the Chamau site during daytime (10–16 hours CET). Thick lines show the median, the color bands indicate the IQR (25th to 75th percentile), and the dashed lines show the 95% confidence interval. The maximum median contribution of background air is 76.4% (IQR 62.9% to 85.6%) at a background signature of -44.4‰ . Assuming a global background value of -47.4‰ yields a median contribution of background air of 60.6% (IQR 46.9% to 73.7%).

Table 1. Source and sink types of CH₄ in the Reuss Valley and their $\delta^{13}\text{C-CH}_4$ characteristics. Weighted averages were used for the source identification of nighttime measurements (see text for details).

Source / Sink	Isotopic signature $\delta^{13}\text{C-CH}_4$ [‰]	Weighted average $\delta^{13}\text{C-CH}_4$ [‰]	Reference
Sources			
<i>Vehicle emissions</i>			
American	-16 ± 6		[33]
European	-28 ± 3		[33]
Toronto, gasoline (summer)	-28.1 ± 0.3		[59]
Toronto, diesel (summer)	-29.3 ± 0.2		[59]
<i>Natural Gas</i>		-39.7 ± 3.0^a	
North Sea	-34 ± 3		[4,33]
Siberia	-50 ± 3		[4,33]
UK, closed	-36.3 ± 0.3		[60]
UK, active	-35.7 ± 1.2		[60]
Boston Area	-36.8 ± 0.7		[61]
<i>Biomass Burning</i>			
C ₄ vegetation	-18 ± 3		[4,33]
C ₃ vegetation	-26 ± 3		[4,33]
<i>Enteric fermentation</i>		-64.5 ± 1.0^b	
C ₄ diet (maize), Switzerland	-57.5 ± 0.6		[62]
C ₄ diet, typical range	-53 to -45		[31]
C ₃ diet (hay+barley), Switzerland	-67.5 ± 0.6		[62]
C ₃ diet, typical range	-76 to -61		[31]
<i>Manure Management</i>		-48.2 ± 1.0^b	
C ₄ diet	-49.1 ± 0.5		[62]
C ₃ diet	-46.0 ± 0.5		[62]
<i>Waste Management</i>		-56.4 ± 3.0^c	
Landfills	-53 ± 2		[4,33]
UK Landfills	-58.0 ± 3.0		[60]
Domestic Sewage	-57 ± 3		[4,33]
Animal Waste	-58 ± 3		[4,33]
Boston Area	-57.8 ± 1.6		[61]
Sinks			
		-5.4 ± 0.9^d	[46]
Tropospheric OH	$-5.4/-3.9$		[46,63] in [2] ^e
Soils	-21		[64] in [2]
Stratosphere	-12		[65] in [2]

^a Weighted average according to Switzerland's gas import statistics of the year 2011 [58].

^b Calculated according to the proportions of C₄- and C₃-vegetation in the forage mixture used at the Chamau research station, i.e., 30% and 70%, respectively (pers. comm. H.-R. Wettstein).

^c Weighted average of $\delta^{13}\text{C-CH}_4$ values from landfill (29.0% weight), domestic sewage (12.2%) and animal waste (58.8%) based on Switzerland's greenhouse gas inventory of the year 2012.

^d the value given here is the one used in our modeling

^e Miller [2] tabulates two estimates, one of -5.4‰ from Cantrell et al. [46], and -3.9‰ reported by Saueressig et al. [63], and reports that these two estimates differ at the 95% confidence level.

Table 2. Proportion of biogenic and non-biogenic sources in percents of total emissions, and the percentage of total emissions removed by sinks (mean $\pm$ SD and 95% confidence intervals, CI). The comparison of model runs using global background $\delta^{13}\text{C-CH}_4$ (Figure 6) are compared with a simplified model according to Phillips and Gregg [44] using a campaign-specific local background $\delta^{13}\text{C-CH}_4$ derived from measured daytime maximum values as a model background. Daytime measurements were obtained between 10 and 16 hours CET, and all data between 00 and 24 hours CET.

Campaign	Subset	Biogenic		Non-biogenic		Sinks	
		global	local	global	local	global	local
August 2011	daytime	59.6 $\pm$ 7.8	58.0 $\pm$ 6.1	40.4 $\pm$ 7.8	42.0 $\pm$ 6.1	6.1 $\pm$ 5.6	5.2 $\pm$ 4.2
	(95% CI)	(50.3, 79.2)	(50.3, 72.5)	(20.8, 49.7)	(27.5, 49.7)	(0.2, 20.8)	(0.2, 15.6)
July 2012	daytime	55.1 $\pm$ 4.1	57.1 $\pm$ 5.4	44.9 $\pm$ 4.1	42.9 $\pm$ 5.4	3.2 $\pm$ 2.8	4.7 $\pm$ 4.0
	(95% CI)	(50.2, 65.1)	(50.3, 70.1)	(34.9, 49.8)	(30.0, 49.7)	(0.1, 10.5)	(0.2, 14.6)
2011/2012	daytime	56.9 $\pm$ 5.8	57.6 $\pm$ 5.8	43.1 $\pm$ 5.8	42.4 $\pm$ 5.8	4.4 $\pm$ 4.0	5.0 $\pm$ 4.1
	(95% CI)	(50.2, 71.2)	(50.3, 71.1)	(28.8, 49.8)	(28.9, 49.7)	(0.1, 14.5)	(0.2, 15.2)
August 2011	all data	56.7 $\pm$ 5.6	57.2 $\pm$ 5.6	43.4 $\pm$ 5.6	42.8 $\pm$ 5.6	4.2 $\pm$ 3.9	4.8 $\pm$ 4.1
	(95% CI)	(50.2, 70.5)	(50.3, 70.8)	(29.5, 49.8)	(29.2, 49.8)	(0.1, 14.0)	(0.2, 15.0)
July 2012	all data	55.2 $\pm$ 4.3	56.8 $\pm$ 5.3	44.9 $\pm$ 4.3	43.2 $\pm$ 5.3	3.3 $\pm$ 2.9	4.7 $\pm$ 3.9
	(95% CI)	(50.2, 65.6)	(50.3, 69.6)	(34.4, 49.8)	(30.4, 49.8)	(0.1, 10.9)	(0.2, 14.4)
2011/2012	all data	56.0 $\pm$ 5.1	57.0 $\pm$ 5.5	44.0 $\pm$ 5.1	43.0 $\pm$ 5.5	3.9 $\pm$ 3.6	4.8 $\pm$ 4.0
	(95% CI)	(50.2, 68.4)	(50.3, 70.0)	(31.6, 49.8)	(30.0, 49.8)	(0.1, 12.8)	(0.2, 14.8)