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Gap-filling strategies for annual VOC flux data sets

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Abstract

Up to now the limited knowledge about the exchange of volatile organic compounds (VOCs) between the biosphere and the atmosphere is one of the factors which hinders more accurate climate predictions. Complete long-term flux data sets of several VOCs to quantify the annual exchange and validate recent VOC models are basically not available. In combination with long-term VOC flux measurements the application of gap-filling routines is inevitable in order to replace missing data and make an important step towards a better understanding of the VOC ecosystem-atmosphere exchange on longer time scales.

We performed VOC flux measurements above a mountain meadow in Austria during two complete growing seasons (from snowmelt in spring to snow reestablishment in late autumn) and used this data set to test the performance of four different gap-filling routines, mean diurnal variation (MDV), mean gliding window (MGW), look up tables (LUT) and linear interpolation (LIP), in terms of their ability to replace missing flux data in order to obtain reliable VOC sums. According to our findings the MDV routine was outstanding with regard to the minimization of the gap-filling error for both years and all quantified VOCs. The other gap-filling routines, which performed gap-filling on 24 h average values, introduced considerably larger uncertainties. The error which was introduced by the application of the different filling routines increased linearly with the number of data gaps. Although average VOC fluxes measured during the winter period (complete snow coverage) were close to zero, these were highly variable and the filling of the winter period resulted in considerably higher uncertainties compared to the application of gap-filling during the measurement period.

The annual patterns of the overall cumulative fluxes for the quantified VOCs showed a completely different behavior in 2009, which was an exceptional year due to the occurrence of a severe hailstorm, compared to 2011. Methanol was the compound which contributed with 381.5 mgCm⁻² and 449.9 mgCm⁻² most to the cumulative VOC carbon emissions in 2009 and 2011, respectively. In contrast to methanol emissions, however, considerable amounts of monoterpenes (-327.3 mgCm⁻²) were deposited to the mountain meadow in consequence to the hailstorm in 2009. Other quantified VOCs had considerably lower influences on the annual patterns.

1 Introduction

The net ecosystem carbon balance (NECB) refers to the exchange (fluxes) of all forms of gaseous (FC_g), solid (FC_s) and liquid (FC_l) carbon (C) through the boundaries of an ecosystem, i.e.

$$\text{NECB} = \text{FC}_g + \text{FC}_s + \text{FC}_l = dC/dt \quad (1)$$

and equates to the time-rate-of-change in ecosystem carbon pools (Chapin et al., 2006). Gaseous carbon fluxes include carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO) and the large group of volatile organic compounds (VOCs). The exchange of solid and liquid forms of carbon involves input/export of (in)organic carbon through harvesting, fertilizer application, erosion and dissolved carbon. Typically, the NECB is evaluated at annual to decadal time scales. However, component fluxes that exhibit significant temporal variability at shorter time scales require much more frequent measurements. Gaps in these time series need to be filled before integration to the annual time scale.

There exist a large number of different options for the imputation of these gaps (aka gap-filling) and for CO₂, which is generally thought to represent the largest component flux of the NECB, these have been evaluated extensively (Falge et al., 2001a; Moffat et al., 2007). Other gaseous carbon fluxes and especially fluxes of non-methane VOCs tend to be neglected for the NECB for several reasons. First the exchange fluxes of VOCs as trace gases are, in terms of quantity, minor compared to the carbon dioxide fluxes and are therefore thought to be much less important for the carbon balance although many abundant VOCs contain 5–10 carbon atoms. Global inventories estimate the total emissions of VOCs to the atmosphere at 1300 Tgyr⁻¹ (Goldstein and Galbally, 2007). The majority of these emissions are of biogenic origin (Laothawornkitkul et al., 2009). It is estimated that 98% of the biogenic VOC emissions can be categorized in the following five compound classes: Isoprene (C₅), monoterpenes (C₁₀) and oxygenated VOCs like methanol, acetone, and acetaldehyde (Lathiere et al., 2006). Despite of their low atmospheric concentrations (low ppb range and less), the influence of VOCs on tropospheric ozone levels and the production of secondary organic aerosols (Atkinson, 2000; Hallquist et al., 2009) is, owing to their high reactivity, significant. Aerosols and ozone have a considerable influence on the radiative forcing, but the scientific understanding of the effects is low compared to the effect of the major greenhouse gases (Forster et al., 2007). Second, flux measurements of VOCs are difficult especially as the collectivity of VOCs is estimated to comprise at least 1000 (but probably many more) compounds (Goldstein and Galbally, 2007). Therefore, studies are usually confined to a few weeks and compounds at most and only recently several groups have started to conduct long-term flux measurements (Bamberger et al., 2010, 2011; Bouvier-Brown et al., 2012; Hörtnagl et al., 2011; Laffineur et al., 2011, 2012). Published estimates of biogenic VOC budgets thus heavily rely on modeling of the most important VOCs using simple light and temperature dependent algorithms (Guenther et al., 1995, 1993). As of this writing, neither closed annual time series of measured VOC fluxes exist, nor comprehensive comparisons of gap-filling methods for VOC fluxes have been conducted.

The objective of the present paper is to draw upon the experience with the imputation of annual CO₂ fluxes and to systematically compare different options for filling gaps in long-term VOC flux time series. To this end we used data from a managed temperate mountain grassland in Austria, where fluxes of several VOCs, including the most prominent biogenic VOCs (acetaldehyde, acetone, isoprene, methanol and monoterpenes), have been measured over two vegetation periods by means of a proton transfer reaction – mass spectrometer

(PTR-MS). As a result of the gap-filling we provide annual estimates of the VOC source/sink strength and make an important step towards quantifying the NECB.

2 Materials and methods

2.1 Measurement site and data acquisition

The measurement site is located at 47°07' N, 11°19' E in an intensely managed mountain meadow in the Stubai Valley, Austria. The prevailing grass species in the flux footprint are graminoids and forbs. Management events of the grassland included three cuts and one fertilization (manure spreading) each year. Detailed information about the study site and the footprint is given by Bamberger et al. (2010), vegetation and soil at the study site have been described by Hammerle et al. (2008) and Wohlfahrt et al. (2008).

The VOC exchange between the vegetation and the atmosphere was measured by means of a high sensitivity proton-transfer-reaction mass spectrometer (PTR-MS) using the virtual disjunct eddy covariance method (Karl et al., 2002). Continuous measurements of 6 different m/z values of volatile organic compounds, methanol (m/z 33), acetaldehyde (m/z 45), acetone (m/z 59), isoprene and fragments of pentenols and methylbutanals (each of the volatiles found at m/z 69), the sum of monoterpenes (m/z 137), and the hexenal group belonging to the green leaf volatiles (m/z 99) were performed from 19 March until 11 December during 2009. Four different volatiles (methanol, acetaldehyde, acetone and the sum of monoterpenes) were quantified from 18 March 2011 until 12 December 2011. Operating conditions of the PTR-MS, which was positioned in a container next to the meadow, were set to a drift tube voltage of 600 V at a pressure of approximately 2.3 mbar (Bamberger et al., 2011). Hansel et al. (1995) and Lindinger et al. (1998) give further details about the operating principle of the PTR-MS. Approximately 9 SLPM (standard liter per minute) ambient air were pumped towards the PTR-MS through a 12 m long, heated (35 °C) Teflon® tube of 3.9 mm inner diameter. Mixing ratios of six/four different VOCs were measured by PTRMS continuously at dwell times of 0.2 s for each m/z value. The set of compounds was repeatedly measured every 2.3 s/1.6 s in 2009/2011, respectively. Four step gas calibrations were automatically performed every 50 h diluting a standard gas (Apel Riemer Inc., United States) with VOC free zero air. The zero air was generated by drawing ambient air through a home-built catalytic converter heated to 350 °C. VOC-free air from the catalytic converter was also used to determine the instrumental background at the end of every half-hourly measurement cycle. Methanol, acetaldehyde, acetone, isoprene and the monoterpene alpha-pinene were included in the standard gas, a representative of the hexenal group (measured on m/z 99), however, was not included in the standard. The green leaf volatile hexenal is known to show distinct break-up patterns in the PTR-MS (Fall et al., 1999). The sensitivity for this VOC was estimated by the identification of break-up patterns and sensitivities from a liquid calibration of (E)-2-Hexenal. The ratio of the liquid calibrations of the green leaf alcohol and acetone was used to account for temporal variations in the sensitivities.

The 3-D wind components and the speed of sound were measured at 20 Hz using a sonic anemometer (R3IA, Gill Instruments, Lymington, UK) and processed on a separate PC running the EddyMeas software (O. Kolle, MPI Jena, Germany). The synchronization of the internal clocks of the VOC PC and the PC processing the sonic anemometer data was done by the network time protocol (NTP, Meinberg, Germany). The sonic anemometer was mounted at a height of 2.5 m above ground and the gas inlet for the PTR-MS was located 0.1 m below the center of the sonic anemometer.

2.2 Flux calculation and quality control

Fluxes of VOCs were calculated from turbulent departures of the vertical wind and the simultaneously measured VOC mixing ratios using the virtual disjunct eddy covariance method (Karl et al., 2002). In order to align the axes of the coordinate system to the mean streamlines of the wind a 3-D coordinate rotation was performed according to Kaimal and Finnigan (1994). The lag time for each VOC was estimated by looking for the maximum or minimum correlation coefficient between the vertical wind speed and the corresponding VOC concentration within a time window of ± 50 s and ± 20 s in 2009 and 2011, respectively. Methanol was the only compound for which a constant lag time of 1.5 s could be found throughout the vegetation period in both years. Therefore, if the maximum correlation between a specific compound and the corresponding vertical wind speed was not found within 3 s of the previously determined methanol lag, the time shift was set to the peak of the frequency distribution of the corresponding methanol lag times. The flux calculation procedure is described in more detail by Bamberger et al. (2010). Positive flux values describe the transport from the ecosystem to the atmosphere (emissions), correspondingly negative flux values describe deposition.

Flux data were rejected when (i) the third rotation angle exceeded $\pm 10^\circ$ (McMillen, 1988), (ii) the flux stationarity test or the deviation of the integral similarity characteristics was above 60% (Foken and Wichura, 1996) and (iii) the maximum of the footprint function (Hsieh et al., 2000) was outside the site boundaries (Novick et al., 2004). In addition, half-hourly periods with background problems like unusual high background values or a significant change of consecutive background values were removed prior to the flux calculation (Bamberger et al., 2010). During 2011 half-hourly periods with instrumental spikes originating from problems with a secondary electron multiplier were also rejected.

2.3 Gap-filling procedures

Half-hourly VOC flux values passing the quality control were retained, while not quality approved flux values were termed as missing values. Data gaps with two or less hours of missing values in the time series were filled with interpolated values prior to further treatments. Afterwards, the data set was subjected to different gap-filling routines in order to replace missing data values in the series on a half-hourly or daily scale.

2.3.1 Gap-filling on a half-hourly basis (MDV)—With the MDV (Mean Diurnal Variation) method missing data values were filled by calculating average diurnal cycles within a time window of ± 8 days around the missing value. Afterwards, the missing value was replaced by the corresponding value in the diurnal cycle of the desired time period. The gliding time window of ± 8 days around the missing value was chosen long enough to include a representative amount of data points for the averaging in order to reduce the random flux uncertainty, but short enough to respond to seasonal changes. Data gaps exceeding 75% or more of the MDV time window were observed only for one compound at the end of the measurement period when the meadow was covered by snow (m/z 69). The advantage of this gap-filling method is the retention of the high time resolution of the original data series and the ability to capture the average diurnal flux pattern.

2.3.2 Gap filling of daily averages—For most purposes it is easier, faster, and cost-effective (in terms of computing power) to have long-term data sets with a lower time resolution. For purposes where diurnal patterns are not required, gap-filling routines working on diurnal average values are of interest.

Daily average VOC fluxes were calculated from the half hourly values for each measurement day with a data coverage exceeding 85%. Days with 8 or more missing values

(data coverage below 85%) were rejected and treated as missing values for the following gap-filling routines:

Gap-filling by interpolated values (LIP): Missing values in the daily averages of the measurement data were filled by Linear InterPolation (LIP) between adjacent days with available measurement values. Gaps at the beginning or end of the measurement period, when a linear interpolation was not possible, were filled by nearest neighbour interpolation.

Gap-filling by Look Up Tables (LUT): In order to create look up tables, days were divided into combined categories of average temperature (5 classes selected in order to guarantee equally balanced number of measurement days in every class $3\text{ }^{\circ}\text{C}$, $3\text{--}9\text{ }^{\circ}\text{C}$, $9\text{--}11.5\text{ }^{\circ}\text{C}$, $11.5\text{--}15\text{ }^{\circ}\text{C}$ and $15\text{ }^{\circ}\text{C}$), photosynthetic active radiation (PAR) (low $< 300\text{ Wm}^{-2}$ /high 300 Wm^{-2}), precipitation (yes/no) and green area index (GAI) (low $< 3.5\text{ m}^2\text{ m}^{-2}$ /high $3.5\text{ m}^2\text{ m}^{-2}$). Days with snow-coverage at the beginning or end of the measurement period were grouped separately, independent of other conditions. Average VOC fluxes were calculated for each category and missing values in VOC flux time series were replaced by these averages for the respective category in the Look Up Table (LUT). The size of the combined temperature, PAR, precipitation and GAI ranges was chosen in order to guarantee at least six to eight measurement days within each category. In cases where the number of measurements days in a special group was low and the gap-filling was not successful (category without valid VOC flux averages), categories were extended stepwise (merging of neighboring categories with poor occupation) until a group average was found in order to guarantee a successful imputation.

Gap-filling by Mean values within a Gliding Window (MGW): With this method missing daily values were replaced by the running average of ± 8 days centered on the day of the gap. Data gaps during the first and last eight days of the measurement period were filled averaging a fixed time window covering the first/last 17 days of measurements, respectively. The size of the time window was chosen in order to match the length of the observed data gaps.

2.3.3 Gap-filling winter period—During the winter period, when the meadow was covered by snow, the VOC measurements were stopped and the data set thus included only 20/5 days of measurements out of 116/100 days with snow cover during 2009/2011, respectively. In order to get a complete annual time series imputation of the winter data was essential, but none of the methods described above was well suited for these sparse data. Therefore we treated the winter-period separately and used available VOC-flux data during days with full snow cover in 2009 and 2011 to evaluate possible flux values for the corresponding winter period. We used: (a) average values/average diurnal cycles and (b) median values/diurnal cycles of all available days with snow cover during 2009 and 2011 to fill each day/half hour of the corresponding winter period. A third approach was the padding of snow cover days with zeros, assuming that there is no exchange of volatiles between the meadow and the atmosphere when the vegetation is covered by snow.

2.4 Error analysis

For the error analysis of the different gap-filling procedures the original dataset (with data gaps) was used as the reference. Short term peaks in the fluxes, caused by cutting and subsequent drying of the grass or fertilization (Brilli et al., 2012; Ruuskanen et al., 2011), were additionally removed from the dataset. In order to fill the missing values in the sample time series for the different VOCs we extracted random days using bootstrapping within a time window of ± 20 days around the data gap and used the corresponding flux value to fill the data gap. In case the bootstrapped day was also a day with missing flux data the

procedure was repeated until a day with a valid flux value was found. On a half-hourly scale the bootstrapping was performed in the same way with respect to the time of day. The resulting (gap-free) time series was used as reference time series for the estimation of errors due to the gap-filling. Gaps were simulated by removing data from the reference time series at random places (preserving the size and composition of the original data gaps) and the resulting intermittent data series (with artificial gaps) was patched by the four gap-filling routines mentioned above.

This procedure was repeated 500 times leading to 500 different reference and gap-filled time series. For each of the 500 samples, cumulative fluxes for both the reference and gap-filled time series were calculated. The difference between the cumulative fluxes of reference and the gap-filled time series was calculated for each of the 500 steps and reflects the error introduced by the gap-filling. Three metrics were calculated to quantify this error: (1) the mean error, reflecting any systematic bias; (2) the root mean square error; and (3) the maximum error.

For the winter period the error regarding the gap-filling was estimated separately using an error propagation of the standard deviation/75% percentiles of the available snow data accounting for the gap-filled period. In addition, maximal errors, which are hypothetically introduced by gap-filling of the winter data, were calculated by filling data gaps during snow cover with maximal/minimal values measured on days with snow cover.

3 Results and discussion

3.1 VOC flux data

Fluxes of six different m/z values corresponding to specific VOCs – m/z 33 (methanol), m/z 45 acetaldehyde, m/z 59 (acetone/propanal), m/z 99 (e.g. hexenals), m/z 137 (sum of monoterpenes, MTs), and m/z 69 representing isoprene and especially during management actions fragments of methylbutanals and pentenols (Fall et al., 2001; Karl et al., 2001) – were measured above the mountain grassland during the time period from 18 March 2009 until 11 December 2009 including 20 days with snow cover. During the 267 days of half-hourly flux measurements data gaps accumulated to a total of 11.1%, 11.3%, 11.6%, 11.2%, 11.7% and 16.7% for m/z 33, m/z 45, m/z 59, m/z 99, m/z 137 and m/z 69 respectively. During 2011 only fluxes of methanol, acetaldehyde, acetone and monoterpenes were quantified for the time period between 17 March 2011 and 12 December 2011, including only 5 days of snow cover. The percentage of data gaps on a half-hourly scale was with 11.2% (methanol), 10.9% (acetaldehyde), 10.9% (acetone) and 11.2% (monoterpenes) quite comparable to the year 2009.

Due to the restriction regarding the calculation of diurnal averages (see above), the procedures applied on a daily scale tended to reject on average 6% and 3% more data compared to the gap-filling procedure on a half hourly scale for the years 2009 and 2011, respectively. Consequently, on a daily scale 17.2% (m/z 33), 18.3% (m/z 45), 18.3% (m/z 59), 17.2% (m/z 99), 17.2% (m/z 137) and 22.8% (m/z 69) of the data were treated as missing values in 2009. The number of rejected data for the daily scale flux calculation was reduced in 2011, when the data gaps accounted only for 14.8%, 12.6%, 14.4%, and 14.1% (for methanol, acetaldehyde, acetone, and monoterpenes) as a consequence of fewer, but longer lasting data gaps.

Figure 1 gives an overview of the environmental conditions, plant canopy development and the measured fluxes of volatiles above the grassland site during the years 2009 and 2011. Methanol fluxes exhibited a clear diurnal cycle throughout the whole growing season reaching peak values up to $9.2 \text{ nmol m}^{-2} \text{ s}^{-1}$ during midday and close to zero fluxes during

night-time in the absence of sunlight (Hörtlagl et al., 2011). In contrast to 2011, monoterpene fluxes in 2009 showed a strong tendency towards deposition (negative values) – a consequence of a severe hailstorm in June 2009. The hailstorm induced elevated terpene emissions from damaged pine trees that grow outside of the flux footprint at the valley slopes (Bamberger et al., 2011). Compounds other than methanol or monoterpenes showed considerably lower, frequently close-to-zero fluxes without clear diurnal patterns under regular growing conditions. During cutting and fertilization of the meadow VOC emissions showed considerably higher peak values than during undisturbed conditions (Brilli et al., 2012; Ruuskanen et al., 2011), especially seen with compounds that normally exhibit less prominent emission patterns (compare Fig. 1).

3.2 Gap-filling and error assessment

3.2.1 Variation of VOC budgets received with different gap-filling routines—

Cumulative carbon fluxes of the gap-filled time series were calculated based on the four different methods and the set of different VOCs. A comparison between the cumulative fluxes of different VOCs, received as a result of the application of different gap-filling methods showed that all methods, yielded similar cumulative carbon fluxes for all VOCs in 2009 and 2011 (Fig. 2). The lowest variability between the cumulative carbon fluxes, received by the application different gap-filling methods on the VOC raw data, was observed for methanol. Depending on the gap-filling method which was applied, cumulative methanol fluxes ranged between 376.0 mgCm⁻² and 401.5 mgCm⁻² in 2009, and between 447.5 mgCm⁻² and 453.6 mgCm⁻² in 2011. The variation between these values was only 6.6% and 1.4% of the methanol average (over all methods) cumulative carbon flux for 2009 and 2011, respectively. Cumulative fluxes for sum of monoterpenes, for example, showed with 9.1% (of the total MT fluxes) a higher variability (–329.3 mgCm⁻² to –300.0 mgCm⁻²) for the different gap filling methods in 2009. Fluxes of the other compounds were considerably lower compared to methanol and monoterpenes (only in 2009) and their contribution to the variability of overall VOC cumulative fluxes was less important. Wintertime fluxes, which are shown separately in Fig. 2, are included in this numbers, but they were generally low and had a minor influence on the yearly values (compare Fig. 2).

3.2.2 Errors due to gap-filling—Table 1 shows the errors introduced by the gap-filling using the 4 different filling methods. Regarding the performance of the individual filling methods, the MDV method yielded clearly the most accurate results for both years and all investigated VOCs. The performance of the LUT and the MGW methods was quite similar compared to each other, with a small advantage of the LUT over the MGW in 2009 for methanol, but a disadvantage for all other measured volatiles and an overall performance which was better for the MGW routine. In 2011 the overall performance for both routines was quite balanced. The linear interpolation resulted in highest root mean square errors and maximum errors overall and for each single VOC separately.

As a compound with a clear diurnal cycle the cumulative sum of methanol was captured with a root mean square error of 0.9%/1.4% and a maximum error of 2.3%/5.2% (with respect to the cumulative methanol flux) using the best gap-filling routine for the year 2009/2011, respectively. The other filling routines introduced root mean square errors around 2% for 2009 and between 2.4% and 2.9% for 2011. Monoterpene cumulative carbon fluxes resulted in a similar absolute cumulative flux compared to methanol, but were quantified with considerably higher root mean square errors (best method 5.1% and other methods between 10.5% and 12.7%, and maximum errors between 25.7% and 78.8%). This was due to the fact that the monoterpene deposition fluxes showed a rapidly changing behavior with partially high deposition fluxes (close to the hail-event), which were

independent of any meteorological parameters and did not follow a regular daily pattern throughout the whole season (Bamberger et al., 2011).

Results showed that accounting for diurnal cycles during gap-filling reduced the uncertainties which were introduced by the data padding considerably. This was even true for VOCs, which showed no distinct diurnal course throughout the year. This is most likely due to the variable position and limited size of the time window used for averaging. With these restrictions it was still possible to reconstruct diurnal patterns, which were only present for a certain time frame quite well. The performance of gap-filling on a daily scale was clearly inferior. Integrating look up tables which calculate fluxes according to ambient conditions and growing state of the vegetation did not show a clear advantage for all VOCs over usual gliding window averaging and even a clear disadvantage in case of rapidly changing flux patterns (e.g. for monoterpene deposition in 2009 and with the application of gap-filling routines across data gaps). While during 2009 we saw slightly lower errors with the application of the LUT routine (compared to other daily methods) for methanol, which is known to correlate with photosynthetically active radiation and temperature at this measurement site (Hörtnagl et al., 2011), this was not visible for the overall VOC balance or for methanol cumulative fluxes in 2011.

Unlike the errors for individual VOCs, both, the absolute and relative error for the sum of the VOCs, which was introduced by the gap-filling, was lower in 2011 (root mean square errors between 2.8% and 6.0%) compared to 2009 (24.2%–60.7%). In addition to the continuous emission of methanol, monoterpenes showed considerable deposition fluxes only in 2009 (Bamberger et al., 2011) resulting in a lower VOC carbon sum in 2009 and a lower second main error source regarding the absolute error in 2011. Although the percentage of missing data was equal or, on a daily scale, even lower than during 2009, the composition of gaps was different with a tendency towards data gaps which span several days in 2011. The lower errors for the individual VOCs in 2009 show that the filling of several shorter gaps (with a larger number of measurements in between) introduces considerably lower errors than the filling of the same percentage of longer-lasting gaps.

3.2.3 Effect of gap-filling during management events—The time series of measurements exhibited no extended (> 2 h) data gaps during management actions of the grassland (cutting and fertilization) and this effect was also excluded from the gap-filling simulation for Table 1. The effect of gap-filling during such management events, which have a large influence on the magnitude and multitude of emitted VOCs (Brilli et al., 2012; Ruuskanen et al., 2011), was simulated exemplarily for the year 2009 and is presented in Table 3. In this case, the root mean square errors increased approximately by a factor of three for methanol, acetaldehyde, and m/z 69, volatiles which are highly influenced by cutting, and even by a factor of five for the hexenal group $C_6H_{10}O$ (measured on m/z 99), which is one characteristic compound class for cutting. Root mean square errors for monoterpenes and m/z 59 (tentatively assigned to acetone), both compounds, which are less sensitive to cutting events, remained almost unchanged or showed only a small increase. Generally, root mean square errors from the look-up-table routine increased considerably more (compared to the example without data gaps during management actions) than for other gap-filling routines, especially for monoterpenes and acetone. The results of Table 3 suggest that gap-filling for cutting days should be performed with special care. The filling of those gaps would probably introduce lower uncertainties if the missing data replacement would rely on information from previous cuts at the same measurement site.

3.2.4 Gap filling for the winter period—The previous paragraphs as well as Tables 1 and 3 describe the errors, which were introduced by gap-filling of values during the growing period of the vegetation. Winter fluxes over the grassland were considered to be negligible a

priori because the vegetation is usually covered by snow. Therefore measurements were conducted mainly during the snow-free time of the year covering only some days of complete snow cover (20 days in the year 2009 and only five days during 2011). There is a considerably higher amount of winter days without measurement data and none of the previously applied gap-filling routines seemed to be suitable as a gap-filling routine for the winter data. Therefore we applied filling routines based on the available days with snow cover on the winter period. Due to the low amount of days with snow cover in 2011 the filling during this year was performed using the complete data series available from snow measurements for 2009 and 2011. Compared to the year 2011, in 2009 two additional VOCs were quantified and the amount of measurements during snow cover was higher. Therefore we used only the 2009 data for the padding of the winter period 2009. Table 2 shows the results for the wintertime cumulative fluxes and corresponding errors based on two different approaches for the half hourly and daily values: first the filling of daily values by average daily fluxes and the filling of half hourly fluxes by average diurnal patterns measured within the snow period and second the filling of daily fluxes by median daily fluxes and half hourly fluxes by median diurnal cycles measured within the snow period. Derived wintertime cumulative fluxes are generally low compared to seasonal fluxes, but the errors which are possibly introduced by a filling of the whole winter period are much higher compared to the errors introduced by a filling of data gaps during the growing season.

Up to now little is known about VOC fluxes during wintertime and most VOC flux measurements are conducted during short-term campaigns for several weeks up to some months during the vegetation period (Brunner et al., 2007; Karl et al., 2003, 2004). Longer campaigns are rare and usually measurements over multiple years are interrupted during the winter period as well (Bamberger et al., 2011; Bouvier-Brown et al., 2012; Hörtnagl et al., 2011; Laffineur et al., 2012). Although our winter data estimates suggested VOC fluxes to be very low compared to the growing period, these revealed as well that there is a considerable variability in the data which makes an exact quantification of the wintertime fluxes difficult. Therefore the trend should go towards VOC measurements covering the complete annual cycle in order to constrain uncertainties during wintertime.

3.3 Effects of gap percentage

The error which is possibly introduced by a gap-filling of a given amount of data gaps in a data series was extensively discussed in Sect. 3.2. This section deals with the effect of an increase/a decrease of data gaps on the error regarding the annual cumulative carbon sum for the different VOCs. Figure 3 shows the change of the root mean square error with varying data gap percentages (with respect to the total number of measurement days) for the four different gap-filling methods (upper panels). For each gap-filling method the root mean square error increased approximately linearly with the percentage of data gaps exhibiting different slopes for different VOCs and different filling methods. The growth of the mean error (blue line), standard deviation of error (grey bar restricted by red lines), and maximal errors (grey lines) with increasing number of data gaps for the single VOCs is shown compressed in the lower panels of Fig. 3. Independent of the percentage of data gaps, the mean diurnal variation method (MDV) introduces the lowest errors for all VOCs.

It has become common to measure vegetation fluxes of CO₂ and H₂O continuously across an extended network of measurement stations all over the world (FLUXNET). Consequently the utilization of gap-filling routines to replace missing values is quite common and several tools have been tested with regard to their performance above different ecosystems (Falge et al., 2001a, b; Moffat et al., 2007; Reichstein et al., 2005). Recently, the performance of gap-filling routines was tested also for other greenhouse gas flux data like nitrous oxide (N₂O) (Mishurov and Kiely, 2011) or methane (CH₄) (Dengel et al., 2013). Due to the diversity of driving factors for the fluxes of different VOCs (Brilli et al., 2012; Ruuskanen et al., 2011),

it was difficult to devise a method which was valid for all VOCs, which limited the choice of methods. A similar problem was observed by Mishurov and Kiely (2011) for N_2O fluxes. Mishurov and Kiely (2011) considered a look-up-table approach on a yearly scale to be the most successful method. Although we used parameters (PAR, temperature) which were observed to have a large influence on methanol for our look up tables, we observed the mean diurnal variation method to be more successful in filling the data gaps and limit uncertainties even for VOCs which did not show a clear diurnal cycle. According to Fig. 3 this was not only due to the reduced number of data gaps in the half-hourly data set (due to the rejection of days with an insufficient data cover for the daily average methods). Even at a slightly higher percentage of data gaps compared to the daily methods, the mean diurnal cycle method showed clearly lowest errors for all VOCs. Generally this method makes use of the full range of information saved in the diurnal patterns for missing data replacement in VOC time series, which is most probably the reason for its outstanding performance.

3.4 Annual VOC budget

Given the superior performance of the MDV method in the error analysis and the fact that the best three methods produced relatively similar results for the actual data set (Fig. 2), the MDV method was chosen for gap-filling the actual 2009 and 2011 data sets.

Cumulative VOC carbon fluxes for the complete year 2009 and 2011 and the monthly contribution of every VOC to the complete cumulative budget are shown in Fig. 4. The two main components contributing to the total VOC carbon flux of 81.0 mgCm^{-2} in 2009 were methanol (381.5 mgCm^{-2}) and the sum of monoterpenes (-327.3 mgCm^{-2}). Fluxes of acetaldehyde (5.5 mgCm^{-2}), acetone (-12.4 mgCm^{-2}), the green leaf volatile hexenal measured at m/z 99 (21.9 mgCm^{-2}) and m/z 69 fragment of methylbutanals, pentenols (and isoprene) (11.8 mgCm^{-2}) were less prominent and their joined contribution to the budget was less than 10% of the methanol cumulative flux. Until July the course of the total carbon flux was dominated by the emissions of methanol, which showed continuous emissions from April to November 2009 with highest values in August (99.0 mgCm^{-2}), May (59.2 mgCm^{-2}) and June (58.8 mgCm^{-2}). With the date of the hailstorm on 16 July 2009 a strong deposition of monoterpenes started to outweigh the methanol emissions for several weeks. The uptake of monoterpenes was strongest in July (-175.4 mgCm^{-2}) and August (-94.6 mgCm^{-2}). Significant emissions of acetaldehyde, $\text{C}_6\text{H}_{10}\text{O}$ (m/z 99) and C_5H_8 (m/z 69) were predominantly detected during the months of cutting (June, August and September 2009). While acetone emissions were quite small (even for the cutting months), we observed acetone deposition fluxes of -9.8 mgCm^{-2} in May 2009 and to a lesser degree also in June and November. Acetaldehyde deposition fluxes were with -7.4 mgCm^{-2} highest in May 2009, but were also observed in April and November 2009. Acetaldehyde fluxes were highly variable, however, and showed periods of emission as well as periods of uptake (Hörtnagl et al., 2013).

During the year 2011 cumulative fluxes behaved differently, especially with regard to the contribution of single compounds to the overall VOC balance which yielded to emissions of 464 mgCm^{-2} to the atmosphere (Fig. 3). The monoterpenes, which were one of the major drivers in 2009 flux patterns, had only a small influence (2.7 mgCm^{-2}) on the overall balance in 2011. Methanol was with emissions of 449.9 mgCm^{-2} the major driving compound for VOC carbon fluxes 2011, showing highest emissions from May to August (76.2 mgCm^{-2} , 76.0 mgCm^{-2} , 53.6 mgCm^{-2} , 102.1 mgCm^{-2}). During 2011 contributions of acetaldehyde to the emissions were mainly visible during June, August, September (cutting months) and October (compare to Fig. 4). Monoterpene emissions were only observed in the summer period (June, July, August). Apart from cutting emissions the monoterpenes,

acetaldehyde and acetone tended to show small deposition values rather than emissions. Fluxes during the winter period (December till March) were generally low.

Cumulative methanol fluxes were significantly higher in 2011 compared to 2009. A possible reason for that are the generally warmer (7.1 °C opposed to 6.8 °C average air temperature), slightly drier (543 opposed to 576 mm rainfall), and sunnier (1754 compared to 1546 sun hours) weather conditions and especially the dry spring in 2011 compared to 2009. The contribution of the hexenal group $C_6H_{10}O$ (21.9 $mgCm^{-2}$ in 2009) and C_5H_8 (11.8 $mgCm^{-2}$ in 2009) to the overall balance of the VOCs is missing for 2011, suggesting that overall VOC fluxes are between 30 and 40 $mgCm^{-2}$ higher in 2011 in addition to the quantified compounds. In general, the estimate of the VOC cumulative carbon flux contains only a restricted set of compounds that includes the most prominent volatiles above grassland. The contribution of other compounds to the VOC carbon balance is thought to be relatively small compared to the overall cumulative flux.

Our quantification of the overall VOC balance from the meadow is with 81.0 $mgCm^{-2}$ and 464.6 $mgCm^{-2}$ in 2009 and 2011, respectively, a lot lower than the complete annual exchange of carbon (between 6.2–12.5 gCm^{-2}) estimated above a ponderosa pine plantation (Bouvier-Brown et al., 2012). Irrespective of substantial deposition fluxes during 2009, the dominance of methanol (a C_1 compound) for the grassland emissions during an average year, in contrast to continuous emissions of C_5 and C_{10} compounds at the ponderosa pine plantation leads to substantially lower carbon emissions for the grassland site.

4 Summary and conclusions

Four different gap-filling procedures were examined with respect to their performance for filling gaps in long-term VOC flux data series. The mean diurnal variation method showed superior performance in filling data gaps, introducing the lowest errors to the data for all VOCs. Applying gap-filling methods on daily average fluxes resulted, regardless of the chosen approach, in considerably larger errors. Accounting for meteorological information by creating daily look up tables to fill data gaps did not entail a clear advantage over gap-filling using mean values within a gliding window. Gap-filling using simple linear interpolation resulted in highest errors. The simulation of the error introduced as a consequence of the gap-filling after an artificial increase in the percentage of data gaps revealed a nearly linear increase of the error with the percentage of missing data. In order to control errors, gap-filling during management actions require separate filling procedures. Highest uncertainties regarding the annual VOC balance, however, were introduced by the filling of the winter period which is a consequence of an insufficient number of measurements during periods of snow cover and the gap of scientific understanding during these conditions. To assure a better quantification of cumulative VOC fluxes, the trend should move away from short periods of measurements in campaign style towards a year-round quantification of VOC fluxes including winter periods.

As a result of the gap-filling we presented a complete annual time series for two years of measured VOC fluxes including management events and winter data above a mountain meadow in Austria. We saw a striking difference in the overall annual course of cumulative VOC fluxes. This difference was a consequence of a severe hailstorm in 2009 leading to exceptionally high ambient concentrations of monoterpenes and considerable monoterpene deposition ($-327.3 mgCm^{-2}$) to the meadow, which would not have been reproduced by the current generation of VOC emission models. Annual cumulative VOC fluxes were quantified to be only 81.0 $mgCm^{-2}$ in the year 2009 as opposed to 464.6 $mgCm^{-2}$ during 2011. Methanol (2009: 381.5 $mgCm^{-2}$ and 2011: 449.9 $mgCm^{-2}$) was during both years the most important compound driving VOC carbon emissions, monoterpene in 2009 the major

compound driving VOC uptake. VOC fluxes of green leaf volatile hexenal found at m/z 99 and fragments of methylbutanals, pentenols (and isoprene) found at m/z 69 accumulated to net emissions during cutting and close-to-zero fluxes otherwise, were not quantified in 2011 and can be expected to lead to an additional increase of the 2011 emissions. Our results underline that the current approach of a quantification of only the VOCs which are thought to contribute most to the emissions for short time periods will probably limit the progress in understanding the complete VOC balance and thus the NECB.

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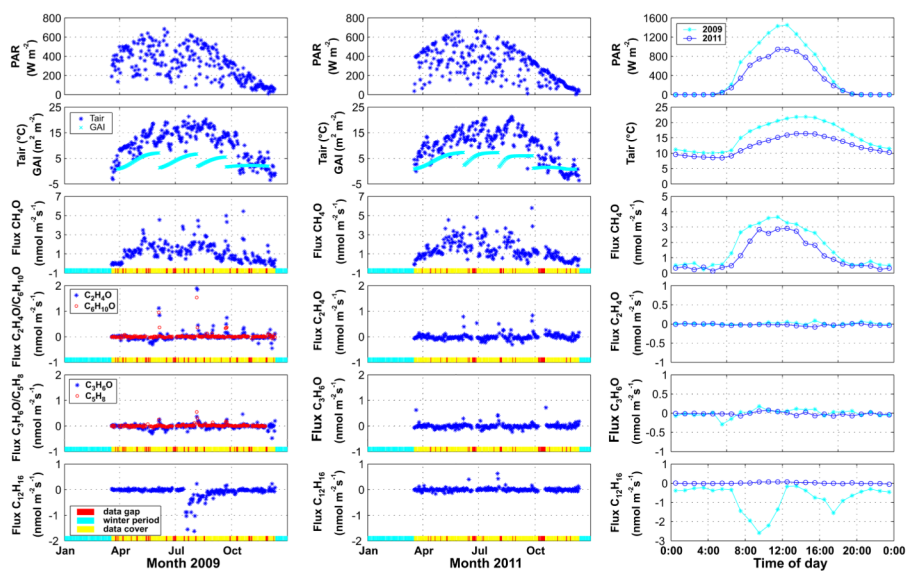


Fig. 1. Time series of measured photosynthetically active radiation (PAR), Temperature (Tair), and VOC fluxes for the year 2009 (left column) and 2011 (center column) and average diurnal cycles for the same compounds and a selected time period in summer 2009 and 2011 (right column).

The winter period (cyan), data gaps (red) and data cover (yellow) for the different VOCs are earmarked as horizontal bar at the lower part of each time series.

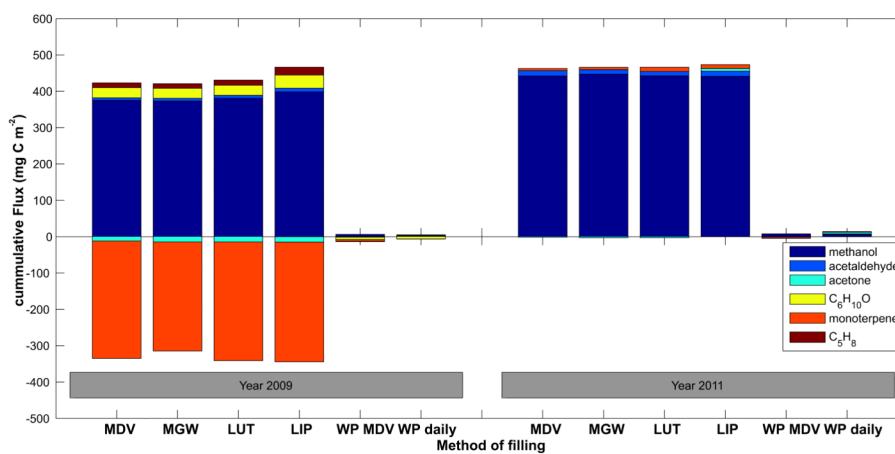


Fig. 2. Bargraph of the cumulative carbon fluxes of the different VOCs (methanol (dark blue), acetaldehyde (blue), acetone (cyan), C₆H₁₀O (yellow), monoterpenes (red) and C₅H₈ (brown)) received by application of the four different gap-filling methods (MDV, MGW, LUT, LIP) for the years 2009 and 2011.

The cumulative fluxes estimated for the winter period on a half hourly base (WP MDV) and on a diurnal base (WP diurnal) are shown as additional information.

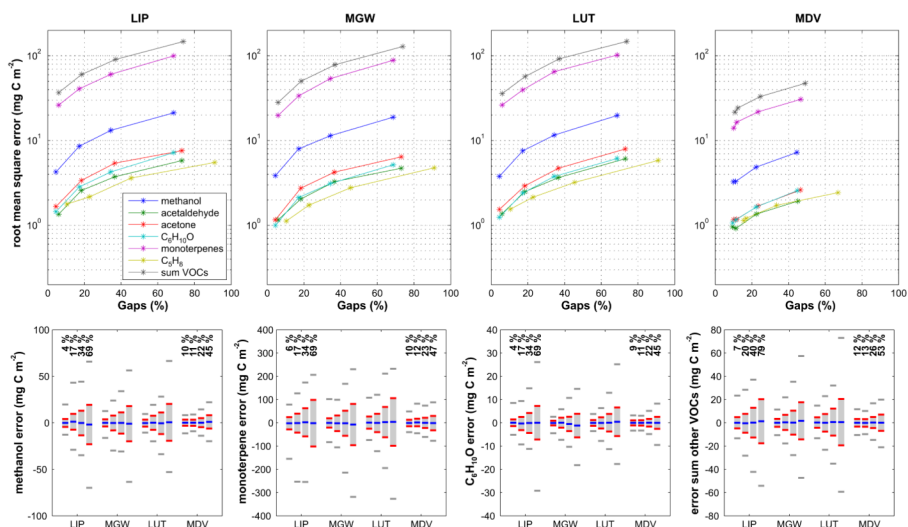


Fig. 3. Increase of root mean square errors introduced by a gap-filling using the four different methods with an increasing number of gaps in the data series of quantified VOC fluxes (upper panels).

Complete error statistics including mean error (blue horizontal line), ranges of root mean square errors (grey bars limited by red horizontal lines) and maximal (grey horizontal lines) errors for methanol (m/z 33), monoterpenes (m/z 137), $C_6H_{10}O$ (m/z 99) and the sum of other quantified VOCs (lower panels). All figures are exemplarily shown for the year 2009 only.

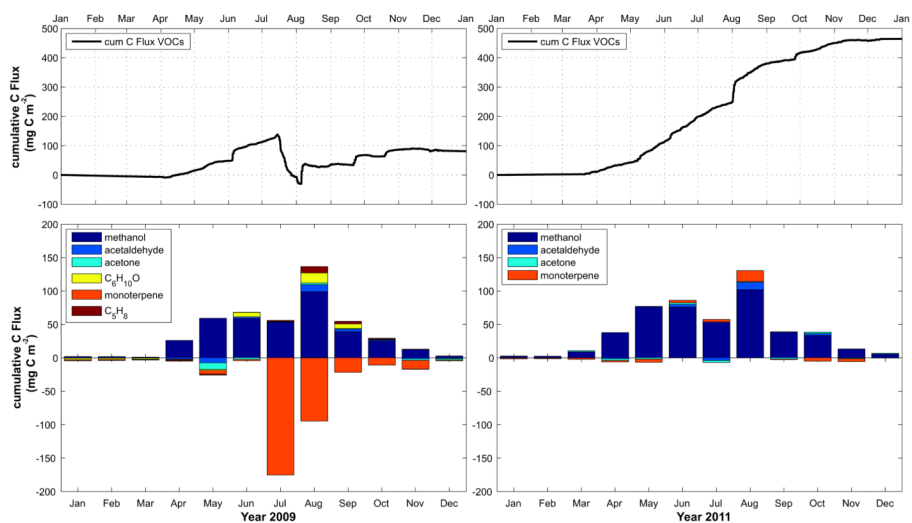


Fig. 4. Time series of the total VOC cumulative carbon flux (upper panels) and the monthly cumulative carbon (C) fluxes (lower panels) for methanol (dark blue) acetaldehyde (blue), acetone (cyan), hexenal C₆H₁₀O (yellow), monoterpenes (red), and C₅H₈ (bordeaux) for the years 2009 (left panels) and 2011 (right panels).

Table 1
Overall cumulative flux (averaged over all methods), mean error (systematic deviation into positive or negative direction), root mean square error and maximal error (maximal deviation from reference) calculated for the four different gap-filling routines (Mean Diurnal Variation, Look Up Tables, Mean Gliding Window, Linear Interpolation) which were applied to the measured VOC data series (including methanol (m/z 33), acetaldehyde (m/z 45), acetone (m/z 59), $C_6H_{10}O$ (m/z 99), the sum of monoterpenes (m/z 137), C_5H_8 (m/z 69) and the sum of quantified VOCs) for the years 2009 and 2011 (cutting times were previously excluded for the error simulation).

Error gap-filling		m/z 33	m/z 45	m/z 59	m/z 99	m/z 137	m/z 69	VOC		
2009	cumulative flux ($mgCm^{-2}$)	385.7	8.2	-12.7	24.2	-320.7	14.3	98.9		
	mean error ($mgCm^{-2}$)	MDV	0.1	0.0	0.1	0.0	1.8	-0.1	-1.9	
		LUT	0.2	0.0	0.0	0.0	-0.3	-0.1	-0.2	
		MGW	-0.1	0.2	0.3	0.1	-1.8	-0.1	-1.4	
		LIP	1.2	0.0	0.0	-0.2	-1.0	-0.3	-0.3	
	root mean square error ($mgCm^{-2}$)	MDV	3.3	0.9	1.2	0.9	16.5	1.2	24.0	
		LUT	7.6	2.5	2.9	1.8	39.6	2.1	56.5	
		MGW	8.0	2.0	2.7	1.6	33.7	1.7	49.7	
		LIP	8.6	2.6	3.4	2.2	40.8	2.2	59.8	
	maximum error ($mgCm^{-2}$)	MDV	9.0	2.6	3.2	2.3	82.5	3.3	102.9	
		LUT	19.8	7.0	9.3	5.9	121.6	7.2	170.8	
		MGW	29.7	6.4	8.2	5.5	105.3	7.4	162.5	
		LIP	43.2	11.3	11.7	7.1	252.8	8.1	334.2	
	2011	cumulative flux ($mgCm^{-2}$)	450.0	14.2	3.4	-	9.3	-	476.8	
		mean error ($mgCm^{-2}$)	MDV	0.3	0.0	0.1	-	0.0	-	0.4
			LUT	0.0	-0.1	0.0	-	0.1	-	0.0
MGW			0.4	0.0	0.0	-	0.4	-	0.8	
LIP			0.3	0.0	0.0	-	-0.2	-	0.1	
root mean square error ($mgCm^{-2}$)		MDV	6.3	2.1	1.6	-	3.3	-	13.3	
		LUT	11.3	2.1	2.6	-	5.1	-	21.1	
		MGW	11.0	2.3	2.6	-	5.2	-	21.1	
		LIP	13.1	3.3	4.3	-	7.8	-	28.5	
maximum error ($mgCm^{-2}$)		MDV	23.3	6.8	4.6	-	12.4	-	47.1	
		LUT	39.0	5.8	9.4	-	14.0	-	68.2	
		MGW	40.6	8.2	14.5	-	18.7	-	82.0	
		LIP	56.7	12.7	23.9	-	28.9	-	122.2	

Table 2
Cumulative fluxes of methanol (*m/z* 33), acetaldehyde (*m/z* 45), acetone (*m/z* 59), C₆H₁₀O (*m/z* 99), the sum of monoterpenes (*m/z* 137), C₅H₈ (*m/z* 69) and the sum of quantified VOCs for the winter phase estimated by mean/mean diurnal cycles and median/median diurnal cycles (during snow lying days) on a diurnal/half-hourly base for the years 2009 and 2011.

In addition the estimated error values (std cum. flux and 75th percentile cum. flux) for the mean and median cumulative winter flux and the possible maximum and minimum cumulative fluxes for the winter period are stated.

Winter data including error estimates			<i>m/z</i> 33	<i>m/z</i> 45	<i>m/z</i> 59	<i>m/z</i> 99	<i>m/z</i> 137	<i>m/z</i> 69	VOC	
2009	mean cum. flux (mgCm ⁻²)	30 min	5.7	-3.9	-8.6	-1.0	5.3	-2.8	-5.7	
		daily	6.4	-3.4	-6.6	-0.1	13.4	-2.0	7.7	
	std cum. flux (mgCm ⁻²)	30 min	108.6	104.5	112.5	113.4	248.7	37.2	760.6	
		daily	16.4	23.9	31.9	16.1	55.5	9.3	158.1	
	median cum. flux (mgCm ⁻²)	30 min	6.3	-1.1	-0.4	-6.4	-4.6	-1.4	-9.6	
		daily	2.8	0.7	1.6	-5.7	0.3	-1.0	-3.1	
	75th percentile cum. flux (mgCm ⁻²)	30 min	33.9	26.5	34.7	46.9	96.3	19.2	272.4	
		daily	12.0	3.4	4.8	7.8	15.4	7.0	52.9	
	maximum cum. flux (mgCm ⁻²)	30 min	244.5	214.9	206.4	288.5	540.9	49.0	1635.2	
		daily	52.7	56.0	58.2	46.4	231.0	10.5	469.5	
	minimum cum. flux (mgCm ⁻²)	30 min	-255.8	-287.7	-293.8	-208.8	-501.4	-57.7	-1671.3	
		daily	-34.6	-90.8	-145.0	-42.0	-73.6	-21.6	-420.9	
	2011	mean cum. flux (mgCm ⁻²)	30 min	9.6	-1.9	-3.8	-	6.8	-	10.7
			daily	10.8	-0.6	-1.2	-	14.5	-	23.5
error mean cum. flux (mgCm ⁻²)		30 min	88.8	79.5	85.1	-	193.1	-	446.4	
		daily	23.2	27.0	37.2	-	68.8	-	156.2	
median cum. flux (mgCm ⁻²)		30 min	7.7	-1.1	0.4	-	-3.6	-	3.4	
		daily	6.2	1.8	4.4	-	1.9	-	14.3	
75th percentile cum. flux (mgCm ⁻²)		30 min	28.0	21.5	25.5	-	73.5	-	148.6	
		daily	24.8	3.3	8.1	-	18.2	-	54.5	
maximum cum. flux (mgCm ⁻²)		30 min	339.8	302.9	273.3	-	777.4	-	1693.3	
		daily	51.6	54.9	57.0	-	226.3	-	389.8	
minimum cum. flux (mgCm ⁻²)		30 min	-354.0	-373.5	-367.8	-	-653.4	-	-1748.7	
		daily	-33.9	-89.0	-142.0	-	-72.1	-	-337.0	

Table 3
Mean error, root mean square error and maximal error introduced to the VOC time series of methanol (m/z 33), acetaldehyde (m/z 45), acetone (m/z 59), $C_6H_{10}O$ (m/z 99), the sum of monoterpenes (m/z 137), C_5H_8 (m/z 69) and the sum of quantified VOCs by missing data replacement using the four different filling routines if the management events of the meadow were not excluded for error simulation (exemplarily shown for the year 2009).

Error if gaps during cutting are filled			m/z 33	m/z 45	m/z 59	m/z 99	m/z 137	m/z 69	VOC
2009	mean error ($mgCm^{-2}$)	MDV	4.3	-0.1	-0.3	0.0	-6.6	0.2	-2.5
		LUT	2.5	-1.1	1.6	-0.4	10.0	-0.6	12.0
		MGW	-0.7	0.1	0.1	0.1	-0.3	0.3	-0.5
		LIP	-0.1	0.2	-0.1	0.4	-0.8	-0.1	-0.5
	root mean square error ($mgCm^{-2}$)	MDV	11.7	2.6	1.6	4.6	17.1	3.0	40.6
		LUT	34.0	9.6	5.4	14.5	56.9	6.5	126.9
		MGW	24.0	6.1	3.2	9.4	33.1	4.8	80.6
		LIP	26.2	6.3	3.6	11.7	42.8	5.3	95.9
	maximum error ($mgCm^{-2}$)	MDV	39.7	11.3	6.3	20.3	71.3	15.1	164.0
		LUT	175.4	55.0	22.7	86.8	294.5	48.6	683.0
		MGW	88.0	23.0	9.7	26.2	116.4	20.4	283.7
		LIP	123.4	27.3	11.7	78.3	260.7	23.5	524.9