

Interannual variability of biogenic oxygenated volatile organic compound fluxes over a managed mountain grassland

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about

Volatile organic compounds (VOCs) play a complex and diverse role in atmospheric chemistry [1]. Recent technological advances gave new insights into ways how VOCs can directly or indirectly affect the chemical and physical properties of the atmosphere and into pathways and interactions that can lead to emission or deposition of specific compounds.

The development of the proton transfer reaction-mass spectrometer (PTR-MS) [2] made real-time measurements of VOC volume mixing ratios (VMRs) with concentrations as low as pptv possible. In combination with the eddy covariance method (EC) VOC fluxes can be calculated, allowing the quantification of the VOC exchange over long time periods in different ecosystems.

In the past, VOC flux research mainly focused on the highly reactive group of isoprenoids (isoprene, monoterpenes and sesquiterpenes) over forest. Especially over grassland, measurements of biogenic oxygenated volatile organic compounds (BOVOCs, e.g. methanol, acetaldehyde and acetone [3]) are still sparse and usually have been conducted over relatively short time periods of several weeks or months. Recent studies described BOVOCs to be abundant throughout the troposphere [4]. However, global estimates of their sources and sinks are still highly uncertain and little is known about the controls on BOVOC exchange and their influence on carbon budgets.

Here we present BOVOC flux measurements of METHANOL, ACETALDEHYDE and ACETONE during the vegetation period in four years (2008-09 and 2011-12) at a managed mountain grassland near Neustift, Stubai Valley, Austria. The meadow is cut three times per year, liquid / solid manure is brought out once, typically at the end of October. The measurement campaigns started in March of the respective year, with the exception of 2008 when measurements started two months later in May.

Study site near Neustift, Austria



Figure 2

vertical red lines show management dates

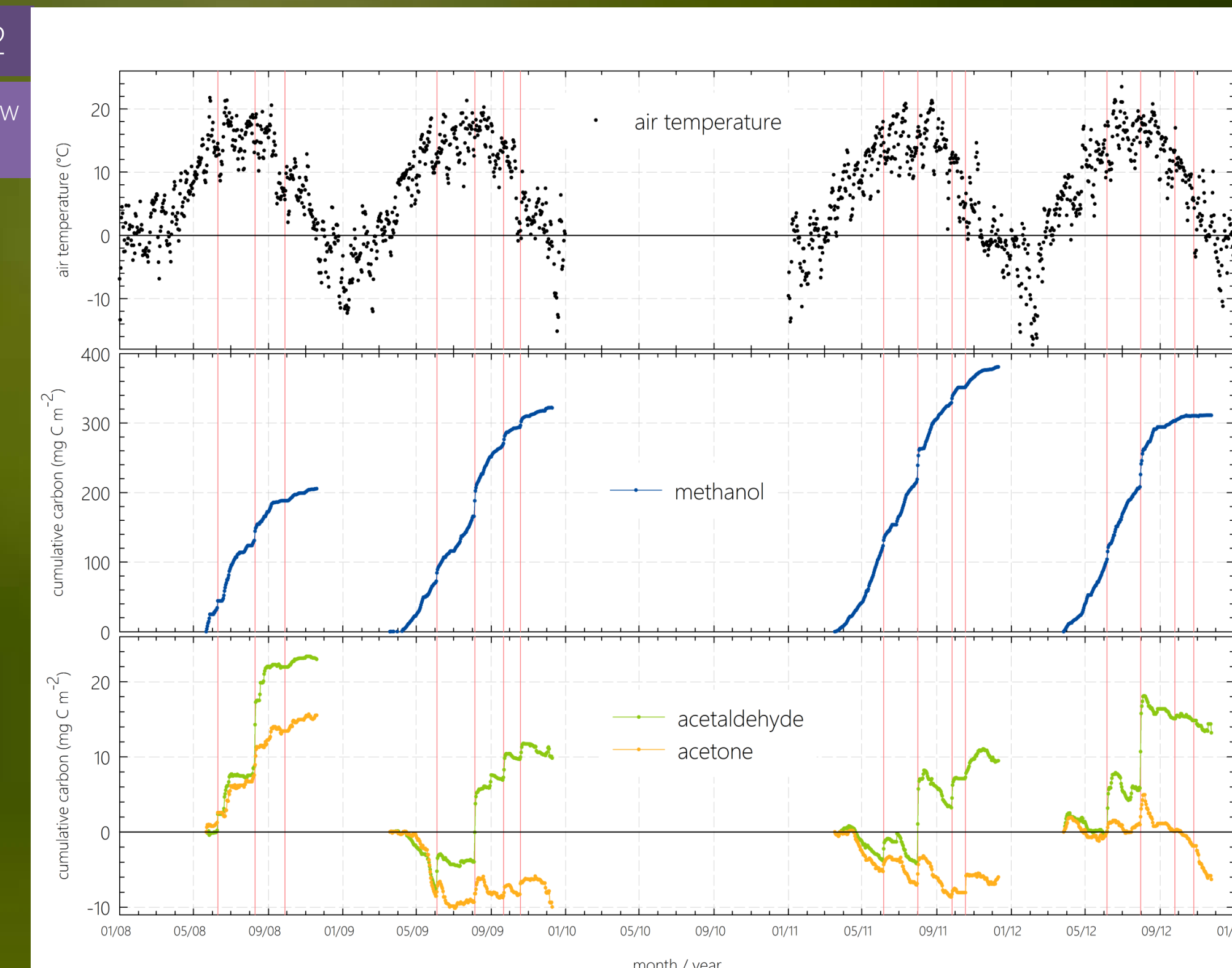
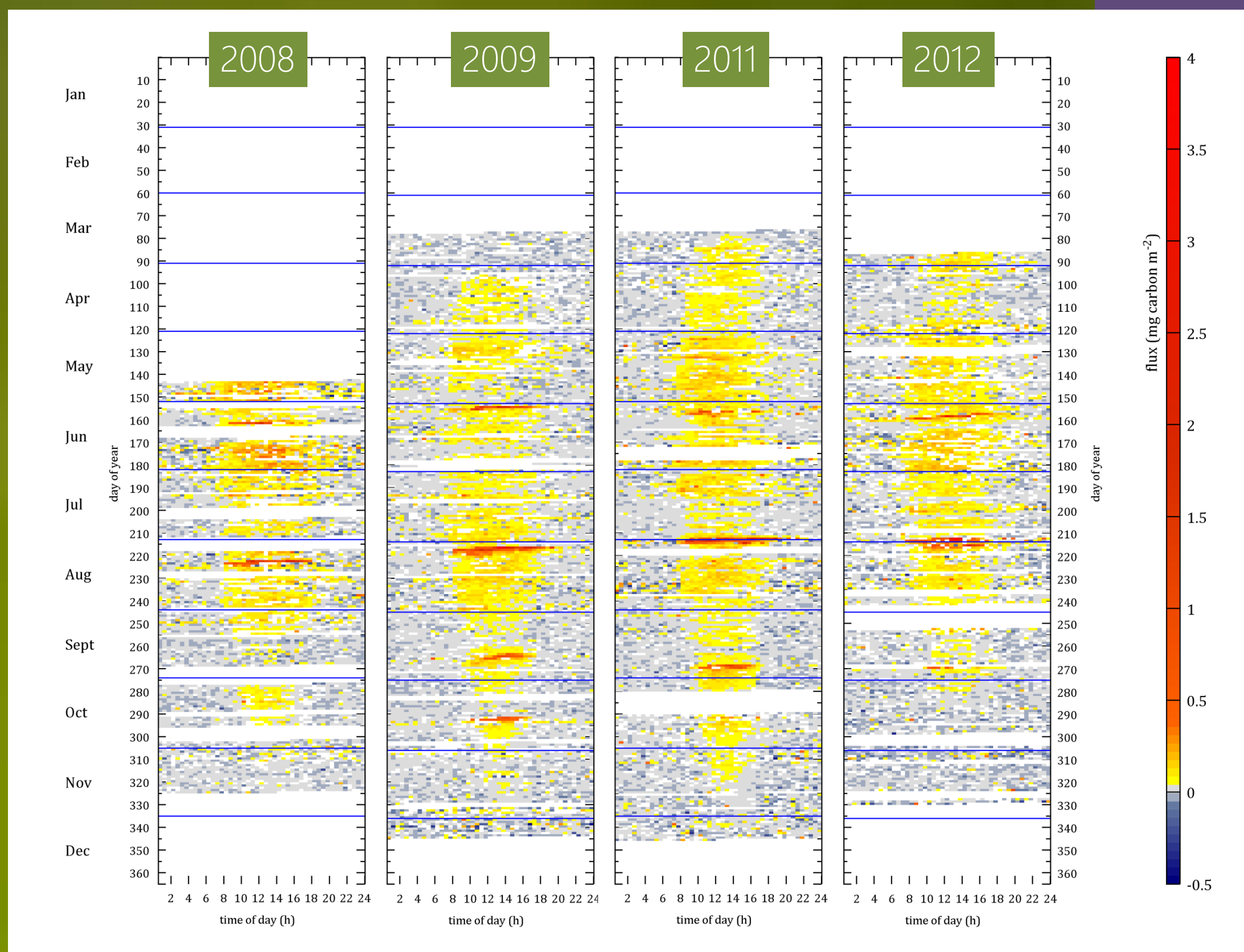


Figure 1



BOVOC fluxes 2008 - 2012 | Figure 1

Figure 1 shows HALF-HOURLY CARBON FLUXES associated with the exchange of the three measured BOVOCs over the course of 4 years and underlines the influence of MANAGEMENT EVENTS on the carbon balance of the meadow.

99% of all recorded half-hourly carbon emissions during conditions not disturbed by management events were below 0.2 mg C m^{-2} .

Highest half-hourly carbon emissions were recorded on the day of the 2nd CUT in 2012 with 4.2 mg C m^{-2} , other days influenced by cutting showed peak emissions between 0.9 mg C m^{-2} one day after the 3rd cut in September 2012 and 3.8 mg C m^{-2} during the 2nd cut in 2009.

The spreading of liquid / solid MANURE resulted in elevated carbon emissions, with the fertilizer probably catalyzing the activity of soil microorganisms and causing carbon emissions of up to 1.0 mg C m^{-2} in October 2009.

cumulative fluxes | Figure 2

Cumulative carbon fluxes associated with the emission of METHANOL were between 205.4 and $380.7 \text{ mg C m}^{-2}$ per vegetation period, showing a net emission in all four years.

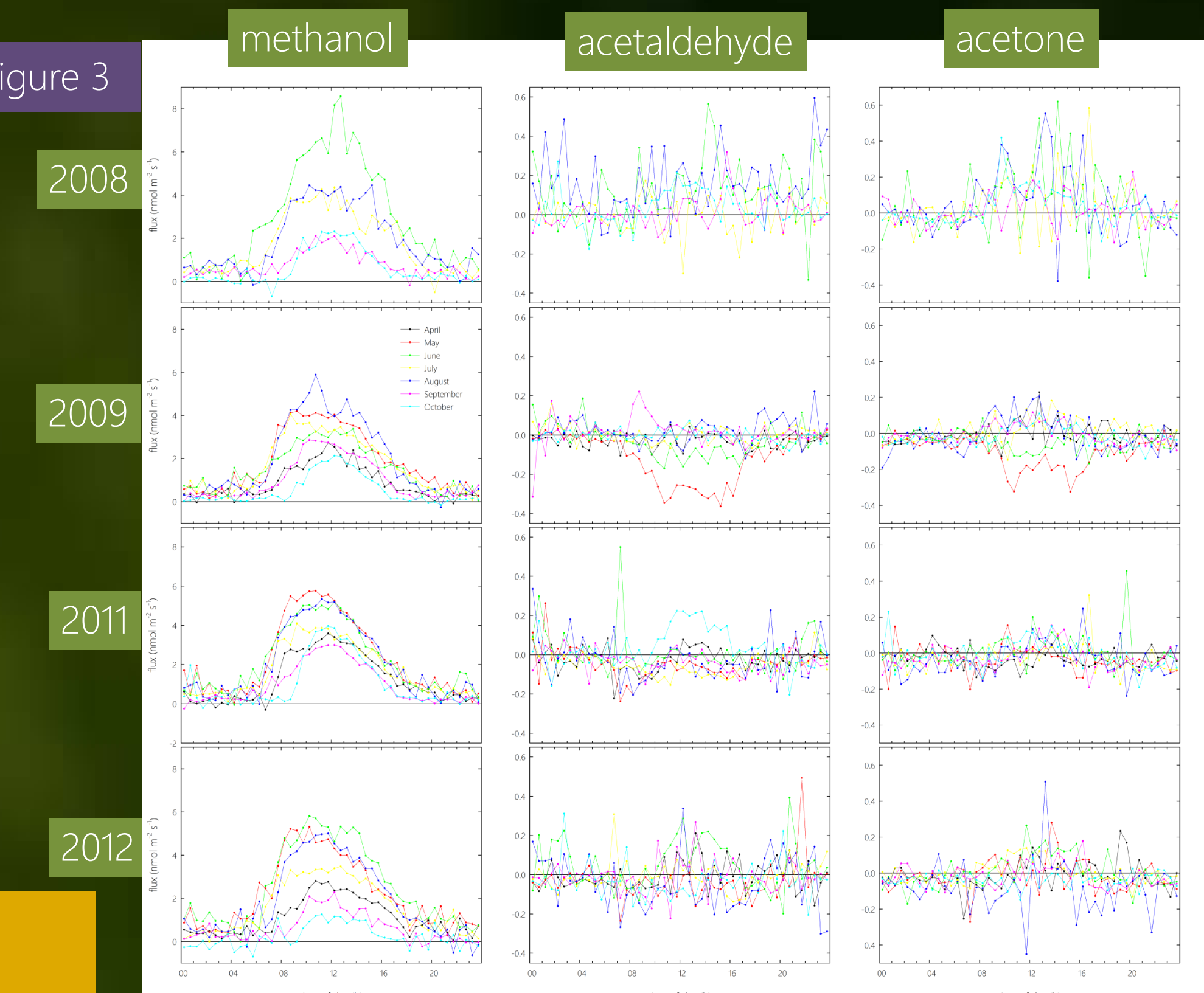
The meadow also acted as a net source of ACETALDEHYDE in each of the four vegetation periods, with emissions between 9.5 and 23.0 mg C m^{-2} .

ACETONE showed a more diverse behavior. In three of the four years the meadow acted as a sink for acetone, with net uptake rates between -10.0 and -6.0 mg C m^{-2} , while the grassland was a source for acetone in 2008 with 15.5 mg C m^{-2} .

The measured total amount of carbon emitted by the meadow over the vegetation period due to BOVOC fluxes was $243.9 \text{ mg C m}^{-2}$ in 2008 (183 days), $321.6 \text{ mg C m}^{-2}$ in 2009 (268 days), $384.2 \text{ mg C m}^{-2}$ in 2011 (270 days) and $317.9 \text{ mg C m}^{-2}$ in 2012 (243 days).

Cumulative carbon fluxes over all four years showed the meadow to be a net source of carbon associated with methanol ($1218.8 \text{ mg C m}^{-2}$) and acetaldehyde (55.5 mg C m^{-2}), and a sink for acetone (-6.8 mg C m^{-2}).

Figure 3



diurnal cycles

Figure 3

METHANOL was the only compound to show distinct diurnal cycles throughout all vegetation periods, its maximum emission was recorded in June 2008 with more than $8 \text{ nmol m}^{-2} \text{ s}^{-1}$ around noon.

ACETALDEHYDE and ACETONE often exhibited close-to-zero or erratic flux patterns, but also showed clear periods of emission or uptake.

In the case of acetaldehyde highest emissions were recorded in October 2008 and 2011 with $0.2 \text{ nmol m}^{-2} \text{ s}^{-1}$, June 2012 showed similar values. May 2009 showed clear uptake ($-0.4 \text{ nmol m}^{-2} \text{ s}^{-1}$).

May and June 2009 showed deposition fluxes of acetone (around $-0.2 \text{ nmol m}^{-2} \text{ s}^{-1}$).

4-YEAR CUMULATIVE BOVOC-FLUXES

METHANOL

+1220

ACETALDEHYDE

+56

ACETONE

-7

BOVOC-total
+1269

numbers are given in mg C m^{-2}

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Generally, cutting events had a dominant effect on resulting BOVOC carbon budgets due to the injured plant tissue and - as a consequence thereof - the release of compounds that were stored inside the plant.

METHANOL is the dominant VOC throughout the vegetation period due to its constant production, release and storage during plant growth.