Acetone and Acetaldehyde Exchange above a Managed Temperate Mountain Grassland

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Background

Volatile organic compounds (VOCs) have received increasing attention in the past two decades due to their role in atmospheric chemistry [1]. Plants emit a wide spectrum of biogenic VOCs to the atmosphere, and although anthropogenic sources can dominate in urban areas, terrestrial vegetation is the main source on a global scale [2]. In the past, most studies focused on hydrocarbon compounds such as isoprenoids, but recently there is a growing interest in a small group of biogenic oxygenated VOCs [3] (BOVOCs) which have been measured in surprising abundance throughout the remote troposphere [4].

BOVOCs include three compounds: methanol, acetaldehyde and acetone. Their combined biogenic source strength amounts to around 268 Tg C y^{-1}, which is about half the source strength of isoprene. Previous studies have shown that land ecosystems can act both as sources and sinks for all three species [5,6,8].

Acetaldehyde

has a lifetime of less than one day and plays an important role as a precursor of ozone, peroxyacetylnitrate [7] and hydrogen radicals [4] and is considered a hazardous air pollutant. The global source is dominated by atmospheric production (< 60 % [8]), but plants represent a non-negligible source (~ 10 % [8]). During periods of high soil water content when the roots are oxygen limited acetaldehyde is produced through oxidation of ethanol which is transported from the roots to the leaves [9]. Production of acetaldehyde has also been reported during light-dark transitions by a pyruvic acid overflow mechanism [10]. Dry deposition to land has been reported before [11], but is considered a minor sink on a global scale.

Acetone

stays considerably longer in the atmosphere than acetaldehyde with a lifetime of 53 days and is a major source of PAN and hydrogen oxide radicals . Land ecosystems can act both as major sources and sinks, whereby pathways from which acetone emissions can arise are currently poorly understood [3]. Acetone is produced as a byproduct from the cell walls from cyanogenic plants and was reported to be light dependent [13].

Methods

Acetaldehyde and acetone fluxes were measured above a managed, temperate mountain grassland in Stubai Valley (Tyrol, Austria) during two growing seasons (2008 and 2009). Half-hourly flux values were calculated by means of the disjunct eddy covariance method using 3-dimensional wind-data of a sonic anemometer and mixing ratios of both species measured with a proton-transfer-reaction-mass-spectrometer (PTR-MS).

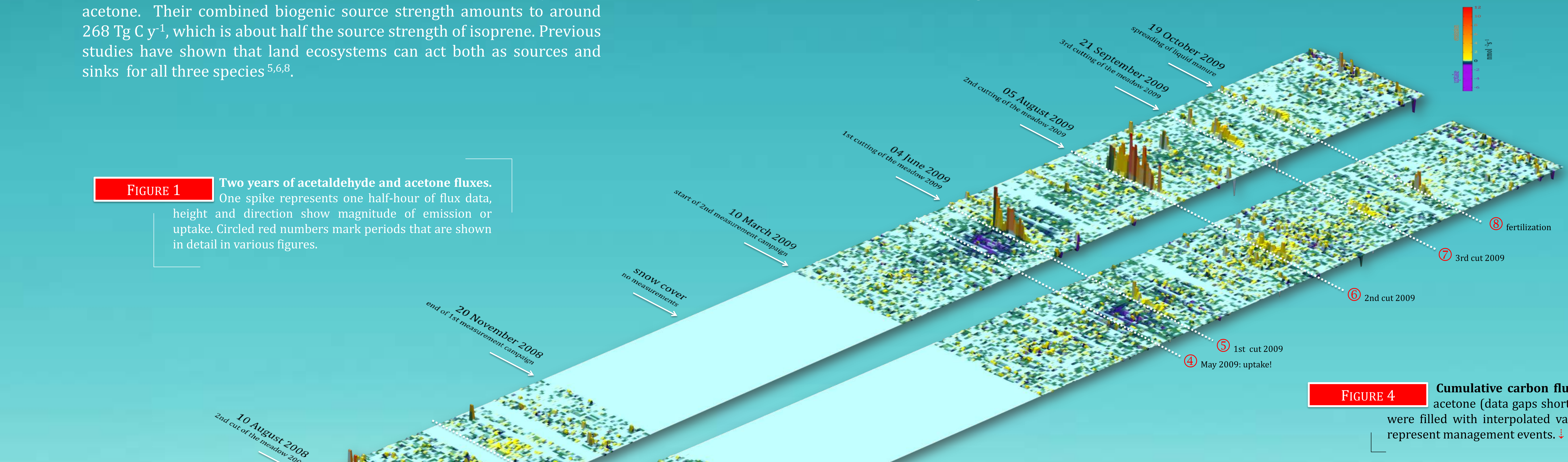

FIGURE 1 **Two years of acetaldehyde and acetone fluxes.** One spike represents one half-hour of flux data, height and direction show magnitude of emission or uptake. Circled red numbers mark periods that are shown in detail in various figures.

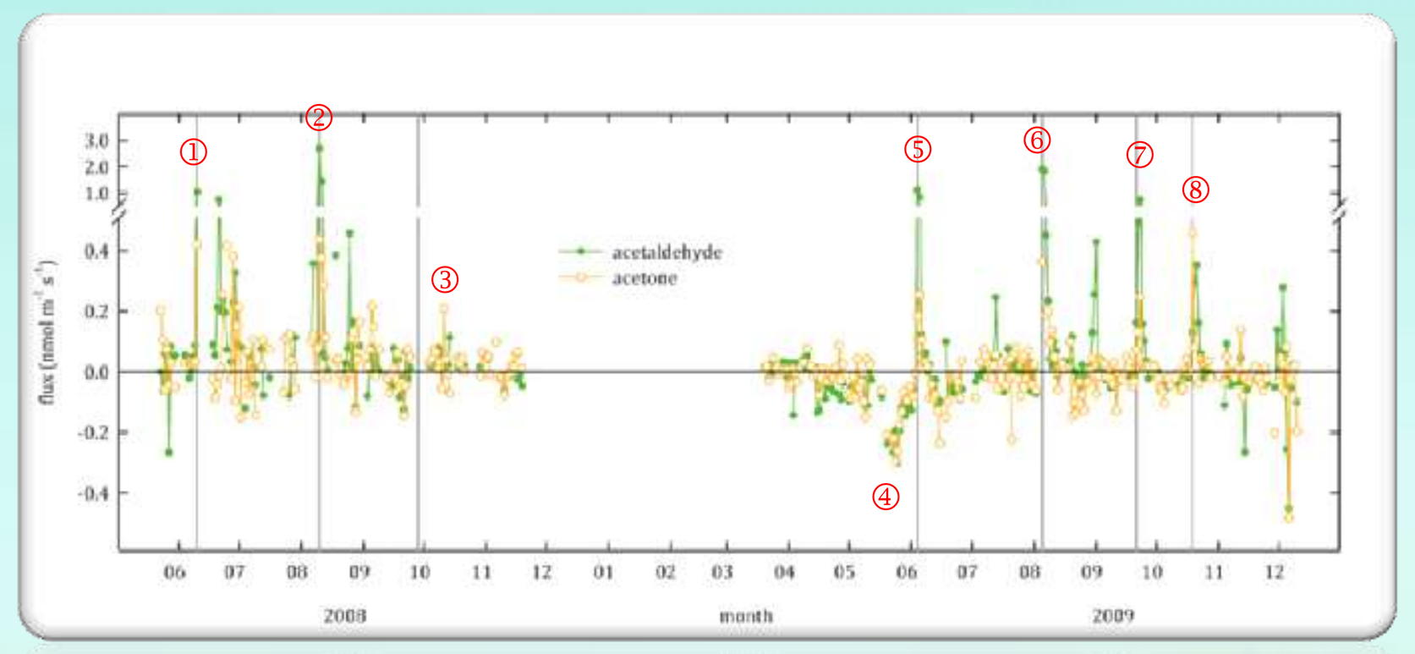

FIGURE 2 **Daily average** acetaldehyde and acetone flux measurements during the vegetation periods 2008 and 2009 at the study site Neustift. Grey vertical lines represent management events. →

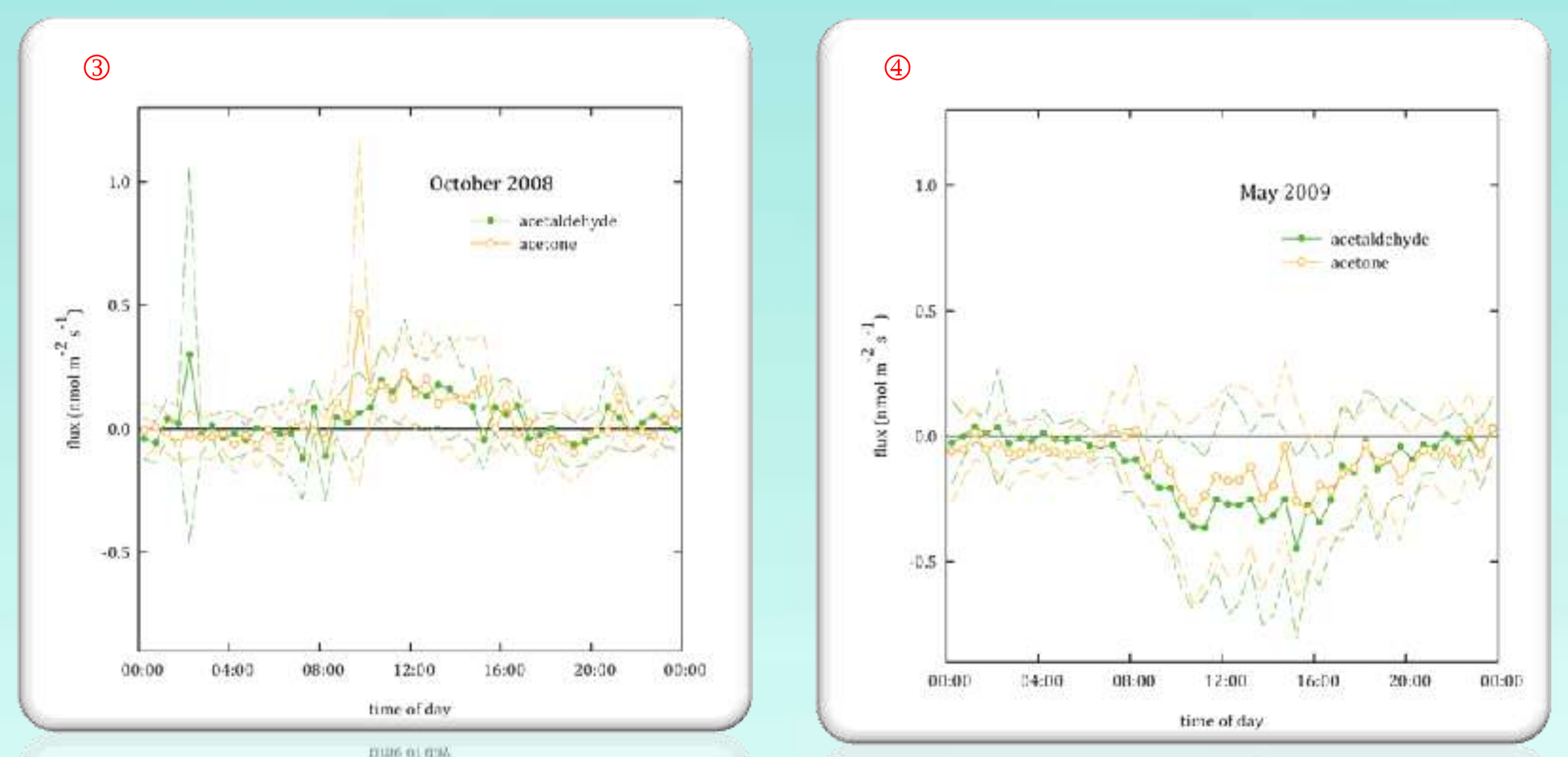

FIGURE 3 **Average diurnal cycles** in October 2008 and May 2009 during undisturbed conditions (not influenced by management events). ↓

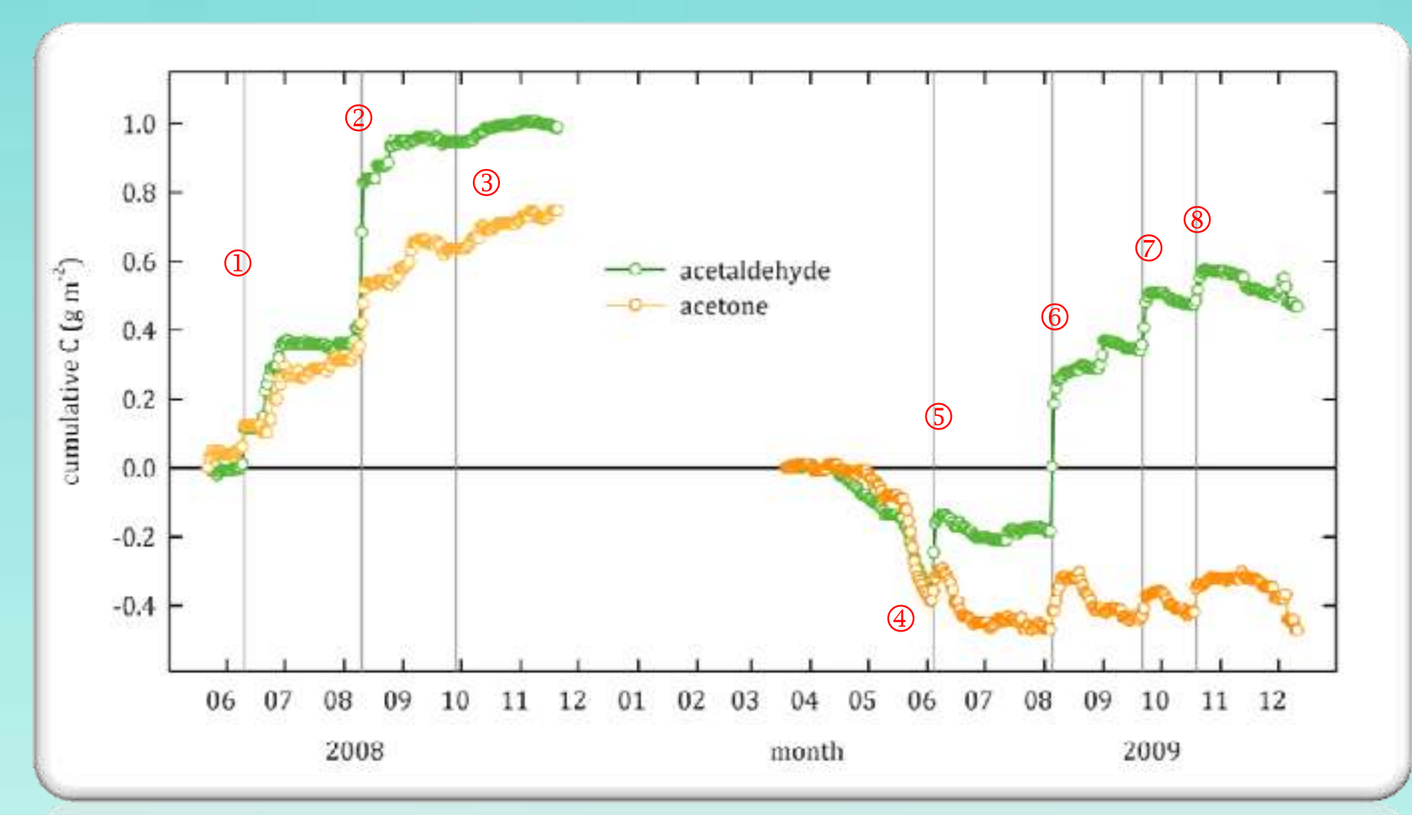

FIGURE 4 **Cumulative carbon fluxes** of acetaldehyde and acetone (data gaps shorter or equal to two hours were filled with interpolated values). Grey vertical lines represent management events. ↓

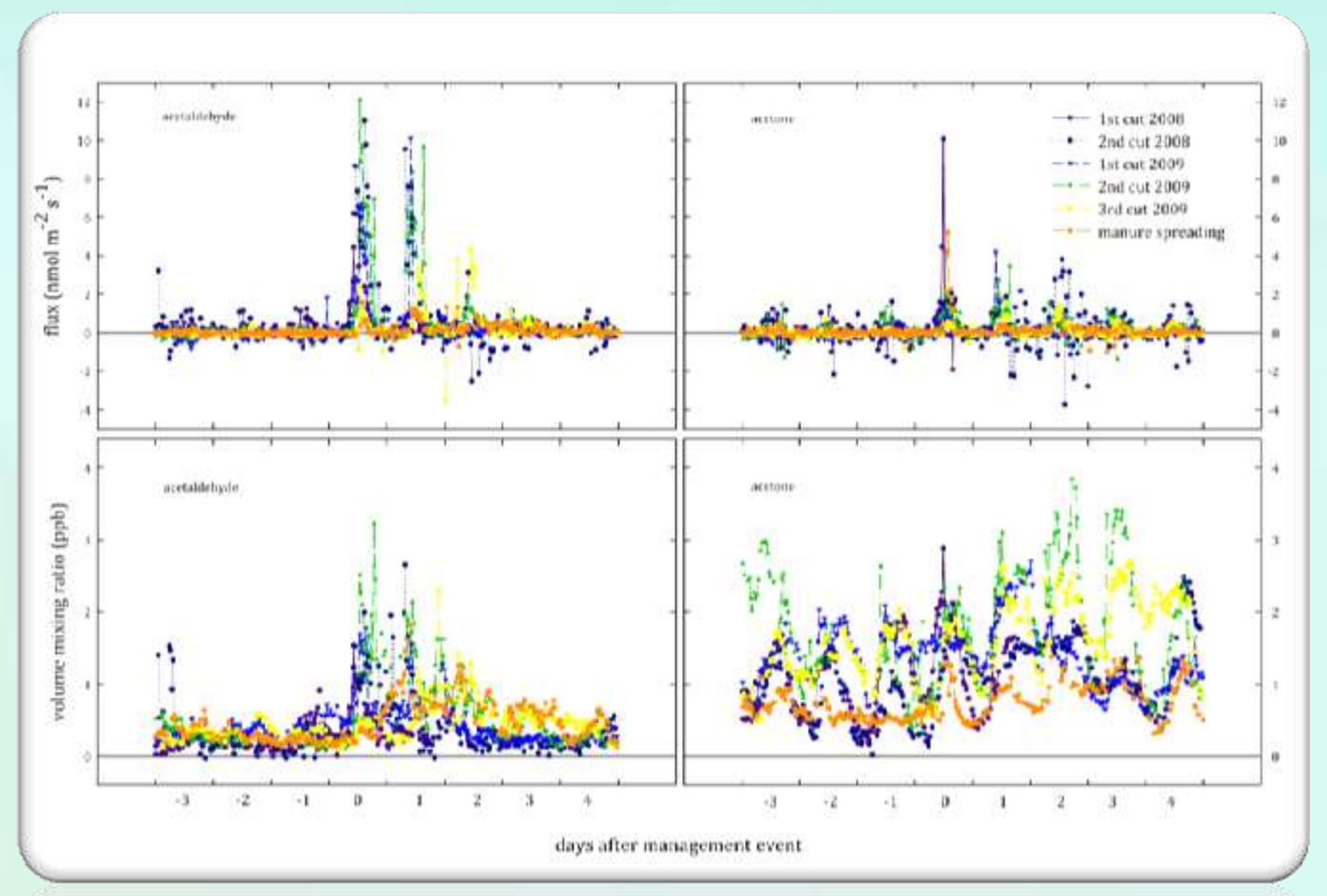

FIGURE 5 The effect of cutting and fertilization on acetaldehyde and acetone exchange. Symbols represent one half-hour of data. →

Results & Discussion

Largest perturbations of the exchange of acetaldehyde and acetone were caused by the **cutting** of the meadow, causing half-hourly peak emissions of 12.1 nmol m^{-2} s^{-1} for acetaldehyde and 10.1 nmol m^{-2} s^{-1} for acetone (Fig. 1,2,5).

During most of the two-year investigation period no clear diurnal cycles could be observed, both species exhibiting close-to-zero or noisy fluxes. However, both species exhibited a clear diurnal cycle during certain time periods: Distinct emissions of acetaldehyde and acetone were observed in **October 2008** (Fig. 3), with emission rates of up to 3.7 nmol nmol m^{-2} s^{-1} for acetaldehyde and and up to 3.2 nmol nmol m^{-2} s^{-1} for acetone. Uptake of both acetaldehyde and acetone could be observed in late **May 2009** (Fig. 3), with rates up to 1.8 and 2.1 nmol nmol m^{-2} s^{-1}, respectively.

The reason for this clear emission/uptake has yet to be explained, a statistical analysis using ancillary data like soil water content yielded no satisfying results. However, in **May 2009** the concentrations of both acetaldehyde and acetone showed highly-significant, negative correlations with their respective fluxes and **compensation points** of 0.3 and 1.2 ppb, respectively.

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