Fluxes of BVOC and tropospheric ozone from a *Citrus* orchard in the California Central Valley*

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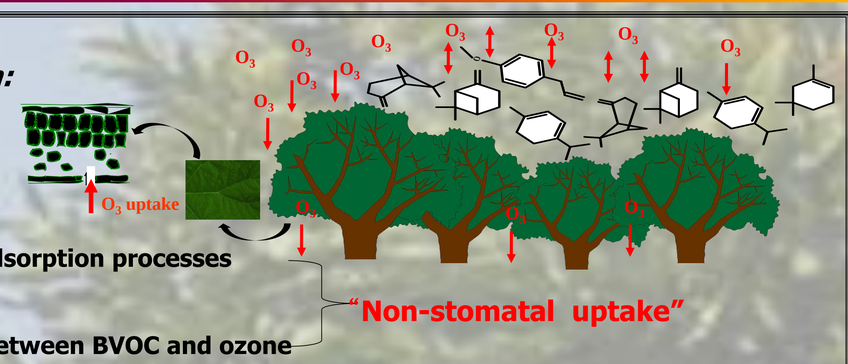
Abstract

Citrus plants, especially oranges, are widely cultivated in the Central Valley of California and in many other countries experiencing Mediterranean climates. In many of these areas, orchards are often exposed to high levels of tropospheric ozone (O_3) due to their location in polluted airsheds. Citrus take up O_3 through their stomata and emit biogenic volatile organic compounds (BVOC), which can contribute to non-stomatal O_3 removal through fast gas-phase reactions with O_3. The research is aimed at: 1. Characterize the ecophysiology of the citrus orchard. 2 Quantifying the uptake of O_3 by citrus and partitioning it into stomatal and non-stomatal processes; 3. Quantifying the BVOC emissions and their dependence on physical and ecophysiological parameters.

Ozone sinks in the orange ecosystem:

1. Stomata. Absorption process
2. Surface deposition on plants and soil. Adsorption processes
3. Chemistry in the gas phase. Reactions between BVOC and ozone



Experimental Method

Between fall 2009 and winter 2010, an experimental station was installed in an orange orchard in Exeter, California, and continuous measurements were made. Meteorological parameters (rain, leaf wetness, PAR, air & leaf temperatures, relative humidity, wind speed & direction) were recorded. Water, CO_2 & ozone were measured with fast-response sensors which allowed calculation of fluxes from their concentrations correlated with the vertical wind velocity using the eddy covariance technique. A PTR-MS (Proton Transfer Reaction – Mass Spectrometer) was used to measure the concentration of volatile organic compounds including methanol, isoprene, monoterpenes and some oxygenated BVOCs at 4 heights of a vertical gradient from the soil to above the canopy.

Fluxes of the 4 dominant BVOCs were measured above the canopy with the eddy covariance technique. Canopy transpiration was measuring using sap-flow systems installed on the stem of 10 citrus trees.

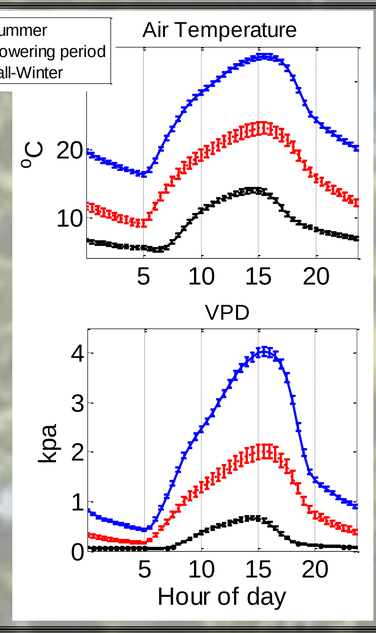
The stomatal ozone flux was calculated by relating fluxes to concentrations through a series of resistances by analogy with an electric circuit obeying Ohm's law:

$$\Phi_{O3} = \Phi_{O3sto} + \Phi_{O3nsto} = \frac{[O_3]_c}{R_{sto}} + \frac{[O_3]_c}{R_{nsto}}$$

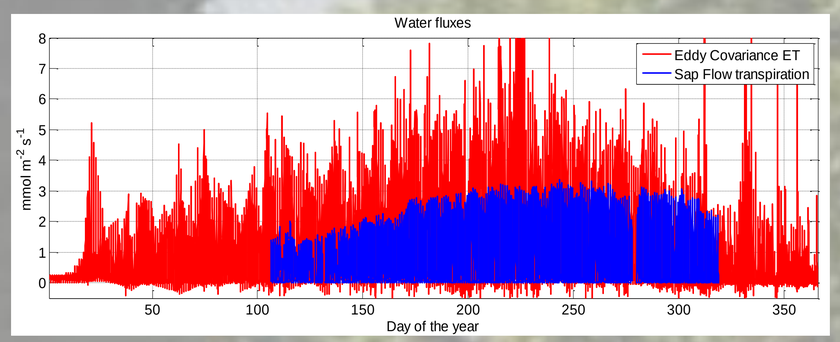
Ozone concentration at canopy level

Stomatal flux, calculated using stomatal conductance from the inversion of the Monteith equation using both Eddy Covariance evapotranspiration and Sap Flow transpiration

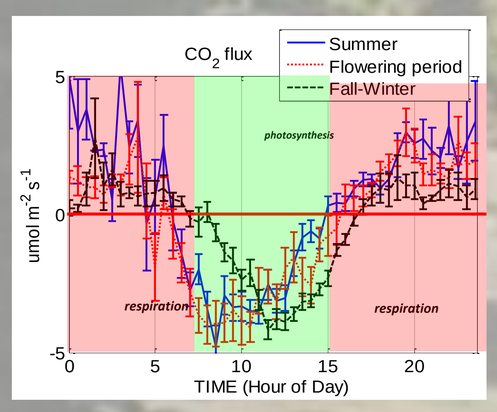
Calculated subtracting Φ_{o3sto} to Φ_{o3}

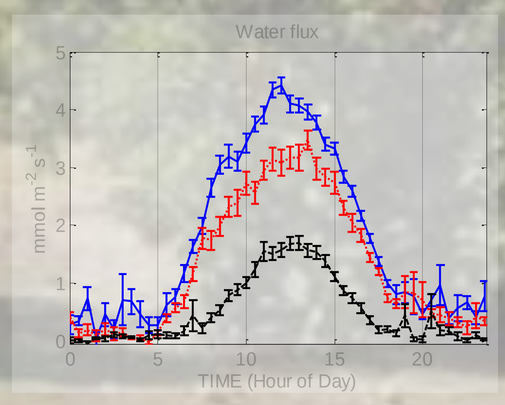


Water, & CO_2 fluxes



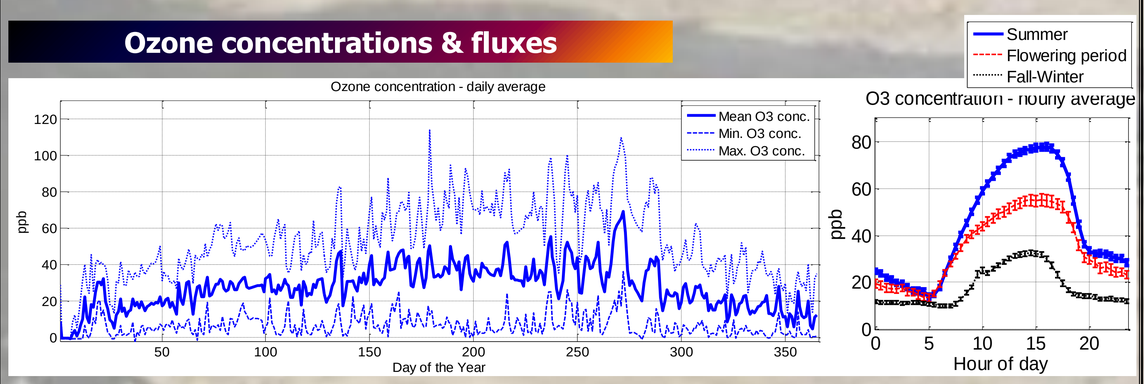
Total evapotranspiration includes up to 40% of soil evaporation in this ecosystem characterized by open canopy (see picture)



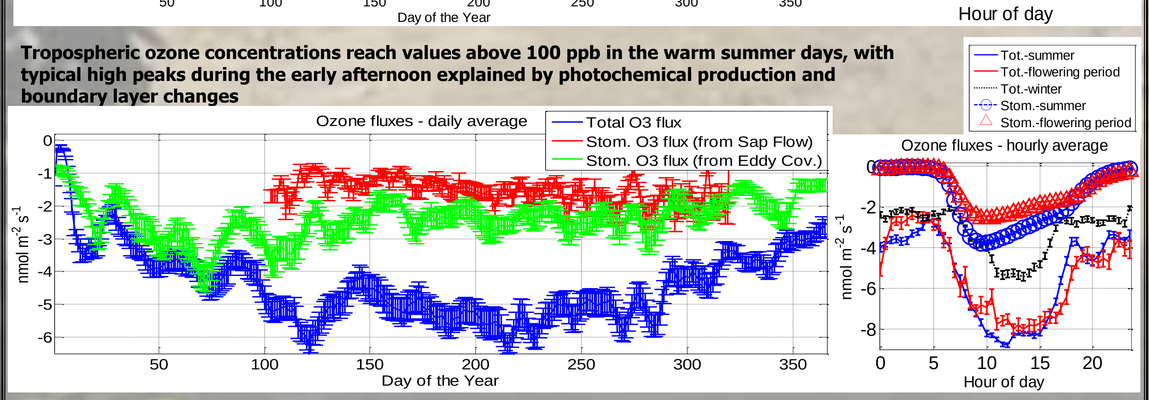


NEE is low in summer, even comparable to winter period, due to the large component of Ecosystem respiration in the warm days

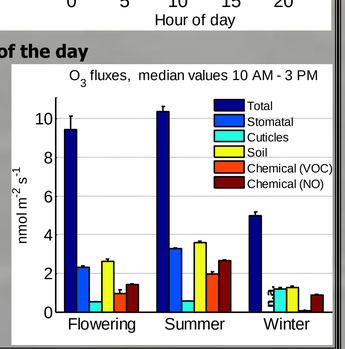
Ozone concentrations & fluxes



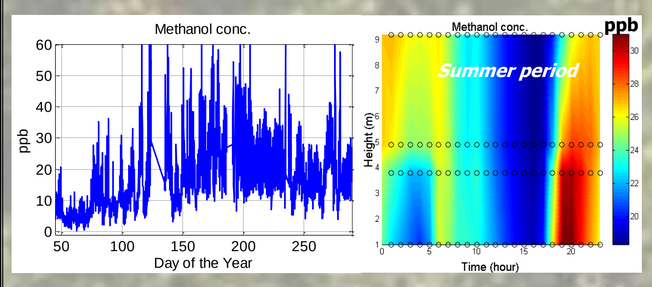
Tropospheric ozone concentrations reach values above 100 ppb in the warm summer days, with typical high peaks during the early afternoon explained by photochemical production and boundary layer changes

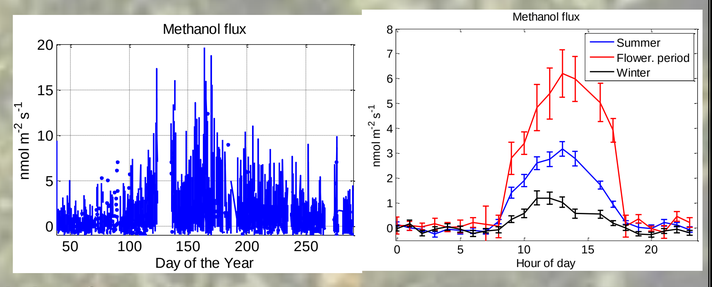


- The orchard is a sink for ozone, with maximum uptake rates during the central hours of the day
- When canopy transpiration is calculated using sap flow detectors, stomatal ozone fluxes are consistently higher (lower in absolute terms) than those calculated using eddy covariance due to soil evaporation term included in the EC approach
- Stomatal ozone fluxes are a minor percentage of total ozone fluxes, coherent with models which suggest a predominant role of non-stomatal deposition on soils and canopies and chemistry in the gas- phase
- The hourly dynamic of total ozone fluxes is typically bell-shaped with peaks in the central hours of the day, while stomatal fluxes are more sensitive to the high levels of stomatal conductance in the morning hours



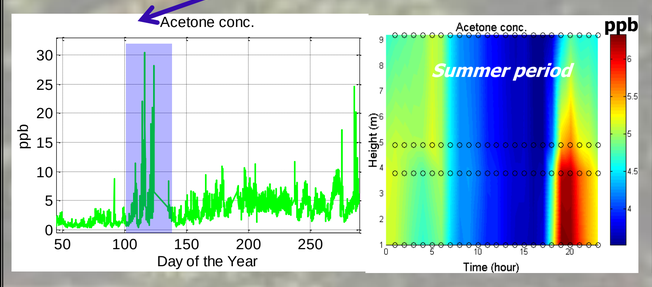
BVOC concentrations & fluxes

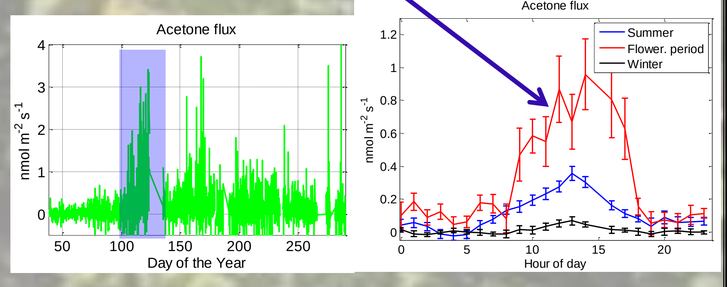




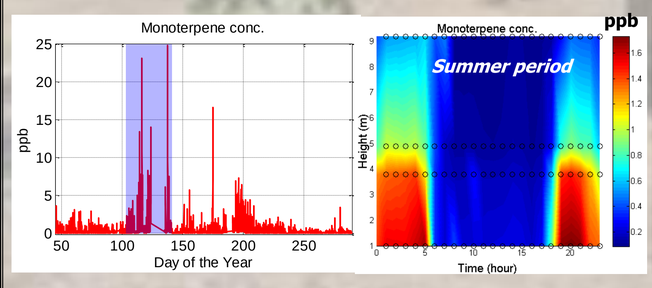
Methanol dominated BVOC emissions, followed by acetone

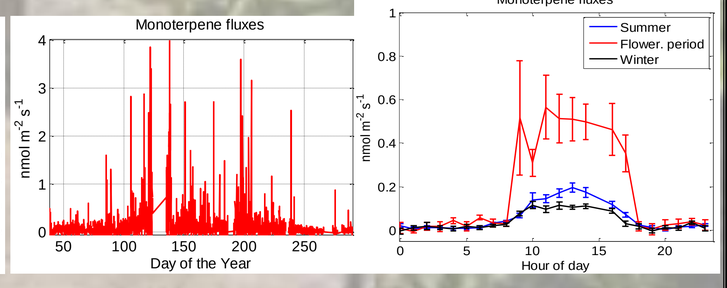
This is the flowering period: concentration and fluxes are higher!





Monoterpene fluxes were also recorded during the all vegetative period, with the highest emissions during flowering periods

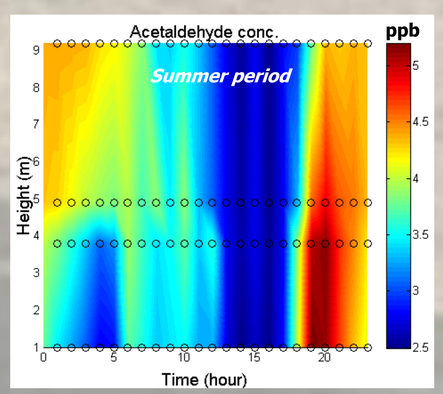




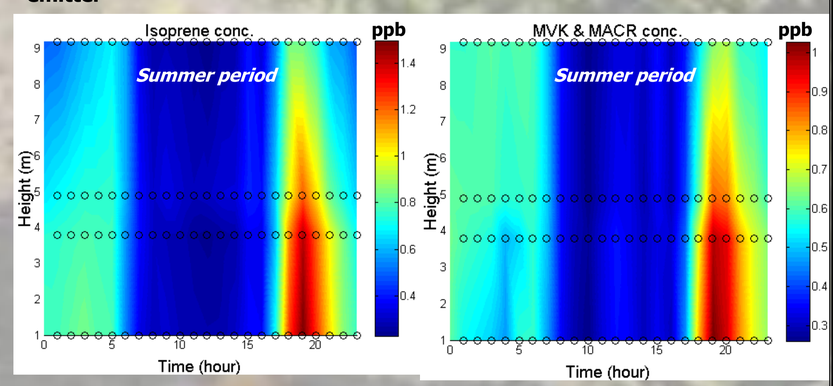
Maximum fluxes between 10pm - 4pm are due to light and temperature dependencies; minimum fluxes during night time

Concentration is high during night time due to low vertical mixing and a shallow boundary layer

Acetaldehyde concentration reached up to 6 ppb in the night time



Isoprene and its oxidation products (methyl-vinyl-ketone and metachrolein) were also measured at concentrations up to 2 ppb, but their fluxes were negligible, suggesting that orange is not a relevant isoprene emitter



BVOC fluxes were highly temperature dependent (correlations not showed). Current research is aimed at quantifying their contribution to non-stomatal ozone uptake and the r possible involvement in reactions in the gas –phase

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