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Seasonal variation of volatile organic compounds exchange above a periurban Holm oak forest on the Mediterranean coast

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Bi-directional exchanges of Volatile Organic Compounds (VOCs) were investigated on a Mediterranean Holm oak forest in Castelporziano presidential estate, a peri-urban forest near the coast of Tyrrhenian sea, 20 Km from Rome downtown, Italy. Two field campaigns were carried out in January and August 2014 to explore VOCs fluxes in two seasons with different climate conditions and physiological activity of plants.
Concentration of 23 compounds was measured using a proton transfer reaction - mass spectrometer (PTR-MS). These included biogenic products (BVOC – isoprene, monoterpenes), oxygenated BVOC (OVOC – methanol, acetaldehyde acetone) and VOC of anthropogenic origin (AVOC – acetonitrile, benzene, hexenal, toluene, xylenes). Each half-hour, we switched between measurement at high frequency above the canopy and sampling through a 5-levels gradient from soil to above the canopy. We used the eddy covariance technique to calculate fluxes above the canopy, while gradient measurements were used to estimate in-canopy source and sink distribution by applying an Inverse Lagrangian Transport Model (Karl et al., 2004, J.Geophys.Res). Ozone and NO_x concentrations were also measured to better correlate VOCs exchanges with this important secondary pollutant.
Low temperatures lead to almost negligible BVOC fluxes during Winter. Summer fluxes were largely represented by BVOC (mainly monoterpenes). The highest fluxes (up to 2.4 nmol m-2 s-1) were recorded in the central hour of the day in response to high light and temperature. Oxygenated compounds (methanol and acetone) showed different behaviour during the two seasons: in Winter a net release of these compounds was observed, while in Summer the canopy acted as a sink for OVOC except for the hottest hours when we observed significant emissions. OVOC source-sink distribution analysis helped identifying the canopy layers which mostly contributed to VOCs exchanges, thus underlining the importance of forest canopies in VOCs exchanges in the soil-plant-atmosphere continuum.
AVOC (xylene, toluene and benzene) concentration in Winter was double than in Summer, despite the intense vehicular traffic towards the beach nearby the forest stand in August. Both in Winter and Summer, emission of AVOC from the forest were measured, although we excluded a biogenic source but rather a resuspension of compounds previously accumulated at night under shallow atmospheric boundary layer.
Photochemically produced ozone was high during the central hours of the day (up to 40 and 70 ppb in Winter and Summer, respectively), while nocturnal concentration went down to less than 20 ppb. Stomata explained almost the totality of ozone fluxes during day (Fares et al., 2014, Agr.Forest.Meteorol), while other non-stomatal sinks including chemical reactions with VOcs were responsible for nocturnal ozone removal.
We discuss here the importance of forest canopies in the interaction between VOC and secondary pollutants, such as ozone and NO_x in a peculiar Mediterranean site where the sea-land breeze circulation allows a strong mixing between contaminated air from the city and cleaner air from the sea under high UV radiations and air temperatures.