Executive summary-Interaction of canopy and air pollution at Ramat Hanadiv

Maor Gabay[1], Chen Dayan, Erick Fredj[2] and Eran Tas[1*]

[1]The Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot, Israel
[2]Department of Computer Science, Jerusalem College of Technology, Jerusalem 91160, Israel

General

Our research in Ramat Hanadiv is aimed at studying the interactions between air pollution and plants. Our main focus is on ozone uptake by the plants and biogenic volatile organic compounds (BVOCs) which are emitted by the plants to the atmosphere. Ozone is the most prevalent and damaging air pollutant to affect natural vegetation, forests and crops (e.g., Global economic loss associated with ozone damage to crops is currently estimated to be $11-26 billion annually; Mills and Harmens, 2011) and it also causes adverse health effects in humans. It is known that ozone deposition rate tends to be relatively high over vegetation, due to its elevated uptake by the vegetation surface and also due to chemical reaction with BVOCs which are emitted from the vegetation.

The role of BVOCs in atmospheric chemistry is complex, because on a local scale they protect the vegetation by destroying ozone, but on a regional scale they can either lead to ozone formation or destruction, depending on the chemical composition of the air. In case that the air masses enriched with nitrogen oxides, the emitted BVOCs will tend to increase the ozone on a regional scale, but in case that the nitrogen oxides are relatively low, and the air is enriched with VOCs, the emitted BVOCs will tend to reduce the ozone concentration on a regional scale. In addition the BVOCs play important role in influencing radiation budget and precipitation, via secondary aerosols formation witch change the radiation scattering and clouds properties.

The currently available knowledge about VOCs emission from plants and the associated impact on key atmospheric processes, as well as ozone uptake by plants is limited, especially for Mediterranean and Semi-arid climatic conditions, where they have been identified as important factors for air pollution-control strategies on a

regional scale (Lelieveld et al., 2002; Richards et al., 2013; Davison et al., 2009; Paoletti, 2009). To a large extent the limitation in the available knowledge on the impact of vexation on these key factors is due to the high complexity and costs that are associated with operating the related scientific measurements.

The shrubbery in Ramat Hanadiv is an excellent site to conclude measurements to study the impact of natural vegetation on ozone removal from the atmosphere, the emission of BVOCs from the vegetation and its impact on regional ozone concentrations, as well as the potential impact of ozone on the vegetation. The structure of the shrubbery also fits well with the requirements of the eddy covariance technique that we apply in our study. We have initiated our measurements in July 2015 and compare the data with short measurement campaigns at different sites in Israel. The research is collaboration between the Hebrew University UC Berkeley, U.S and the Jerusalem College of Technology. It is partially funded by the Israel Science Foundation and the Ring Center for Environmental Interdisciplinary Research.

Scientific background

The uptake of ozone by vegetation and the impact on global warwing

Tropospheric ozone (O_3) is a phytotoxic pollutant that is widely recognized as the cause of considerable damage in natural and cultivated plants (e.g., Kley et al., 1999; Holland et al., 2002; Fiscus et al., 2005; Van Dingenen et al., 2009; Bender et al., 2011; Ashmore et al., 2005). Ozone is a secondary pollutant, formed in reactions involving its precursors, nitrogen oxides (NOx = NO, NO_2) and volatile organic compounds (VOCs), in the presence of UV radiation. Due to its relatively long lifetime (days to weeks in the troposphere; Stevenson et al., 2006) and its relatively long formation time, O_3 concentrations in rural areas are often higher than those in urban areas, (Lorenzini, and Saitanis, 2003), endangering natural and cultivated vegetation. Ozone concentrations tend to increase with solar radiation, temperature and dryness, typically reaching highest concentrations during spring and summer, and at warm and dry areas.

The damaging effect of O_3 is related to its integrated uptake by plant stomata (Reich, 1987; Matyssek et al., 2004), associated with stomatal closure, reduced carbon

dioxide (CO_2) uptake and photosynthesis (Coleman et al., 1995a), and changes in carbon allocation (Coleman et al., 1995b; Karnosky et al., 2003; Ashmore, 2005). Once O_3 is taken up by the plant, it further leads to severe damage in biochemical and physiological processes in the plant (Betzelberger et al., 2010; Fiscus et al., 2005; Kangasjärvi et al., 2005). During the industrial age, anthropogenic emissions of fossil fuel have acted to approximately double the global mean tropospheric ozone concentration (e.g., Gauss et. al, 2006). As a result, surface O_3 levels reach around 40 ppb even in the most remote areas around the globe (Finlayson-Pitts and Pitts, 2000). O_3 levels greater than 40 ppb are commonly considered to significantly (i.e. >10%) reduce the production rate of major food crops (Wang et al., 2004; Van Dingenen et al., 2009). The global economic damage associated with O_3 uptake by crops is currently estimated to be about $11-26 billion annually (Mills and Harmens, 2011), and is expected to significantly increase by 2030 (e.g., $17 - $35 billion annually for the IPCC A2 scenario; Avnery et al., 2011a).

The detrimental effects on plants due to enhanced O_3 stomatal flux, reduce CO_2 sequestration, and therefore are also associated with an increase in atmospheric CO_2 Concentrations. The climate change of the Earth over the 21st century will depend on the uptake rate of anthropogenic CO_2 by oceans and the terrestrial biosphere (Karnosky et al., 2003; Levy et al., 2004). Accordingly, it was recently recognized that elevated surface O_3 concentrations have become a factor in climate change (Ashmore et al., 2005; IPCC, 2007; Sitch et al., 2007) by tending to reduce the carbon sink strength of vegetation (Karnosky et al., 2005; Kubiske et al., 2007, Valkama et al., 2007). This was reinforced by using global modeling which indicated that increased uptake of O_3 by plants can contribute more to global warming than the direct radiative forcing caused by the increase in tropospheric O_3 by itself (Sitch et al., 2007; Kubiske et al., 2007, Valkama et al., 2007).

The role of Biogenic volatile organic compounds in affecting atmospheric chemistry and climate

Biogenic volatile organic compounds (BVOCs) emitted from vegetation account for approximately 90% of total global VOCs emissions with 1150 Tg C/year (Guenther et al., 1995) compared with approximately 180 Tg/C year emitted by anthropogenic sources (EDGAR3.2). Once in the atmosphere, BVOCs play important roles in 1) influencing radiation budget, precipitation, and climate by forming secondary organic aerosols (SOAs; Griffin et al., 1999; Lang-Yona et al., 2010), 2) reducing the oxidation capacity of the atmosphere, which leads to an increase in the greenhouse gas methane, and thereby potentially intensifies global warming (Wuebbles et al., 1989; Chiemchaisri et al., 2001), and 3) influencing tropospheric photochemistry and ozone (O_3) formation (Curci et al., 2009, 2010; Calfapietra et al., 2013). Tropospheric O_3 is widely recognized as negatively affecting human health and natural and agricultural vegetation; it reduces crop yield and acts as a greenhouse gas (Ashmore, 1991; Shindell et al., 2012). The present proposal is primarily focused on the impact of BVOCs on photochemistry and O_3 formation.

Tropospheric O_3 formation is driven by the interaction of VOCs with NO_X ($NO+NO_2$) in the presence of UV radiation. Due to its relatively long lifetime (days to weeks in the troposphere; Stevenson et al., 2006) and its relatively long formation time, O_3 is a regional scale pollutant, negatively affecting the environment tens and hundreds of kilometers downwind of its emission sources (Lorenzini, and Saitanis, 2003). Emitted BVOC (including isoprene, monoterpenes, and sesquiterpenes as well as oxygenated compounds; Kalogridis et al., 2014; Guenther, 2002) from vegetation in rural areas is an important factor in increasing O_3 concentrations on a regional scale (Curci et al., 2009, 2010; Richards et al., 2013; Kalogridis et al., 2014 and references therein).

Emission of BVOCs in the Mediterranean regions has been of special interest in the past few decades (Kalogridis et al., 2014 and references therein), because it has been identified as an important factor for air pollution-control strategies on a regional scale (Davison et al., 2009) and beyond (Lelieveld et al., 2002; Richards et al., 2013). Mediterranean regions (Mediterranean Basin, California, Central Chile, Southwest Australia, and the Western Cape in South Africa) are among the most densely populated areas in the world. They are characterized by high photochemical activity

and O_3 formation, driven by strong anthropogenic emissions combined with relatively warm and dry weather conditions from approximately April to October (McNeill, 2007). BVOCs emissions increase with temperature and light (Guenther et al., 1993), while some abiotic stress factors, such as high temperature, drought, and oxidative stress conditions (e.g., by O_3 uptake), tend to stimulate or change the emission rate and pattern of BVOCs and particularly isoprenoids (Loreto and Schnitzler, 2010 and references therein). Accordingly, emissions of BVOCs in Mediterranean forests are at relatively high rates (Owen et al., 1997; Fares et al., 2009; Richards et al., 2013), induced by high temperatures and sunny conditions. This may be further enhanced by the oxidative stress and drought conditions (Seufert et al., 1997; Davison et al., 2009). Model simulations further predict increases in temperature, drought event frequency, and strong photochemical O_3 formation episodes in the next decades in these regions (Giorgi, 2006; Solomon et al., 2007; Hoerling et al., 2012). These trends are expected to cause changes in both BVOC emission strength and pattern in the Mediterranean regions (Lang-Yona et al., 2010; Kalogridis et al., 2014).

The Mediterranean Basin is an excellent region to study BVOC emission and contribution to photochemical activity under warm and dry conditions. The Mediterranean Basin in particular is characterized by strong photochemical pollution (Lelieveld et al, 2002; Kalogridis et al., 2014), which in part is being imported by long-range transport. Air pollution effects in this region extend far beyond the basin and triggered calls for international efforts to cope with its large pollution levels, which further affect climate (Lelieveld et al, 2002). Furthermore, the Mediterranean Basin has been consistently identified as a highly responsive region to climate change and was named a primary “climate change hot spot” (Giorgi 2006; IPCC, 2007; Lelieveld et al., 2012). Recently, Richards et al. (2013) showed a dominant sensitivity of O_3 concentrations in the Mediterranean Basin to BVOC emissions over anthropogenic VOC emissions.

Regional and global scale models are crucial tools to investigate and cope with the contribution of BVOC emissions to atmospheric chemical processes (Davison et al., 2009). However, recent studies highlight the large uncertainties in modeling the impact of BVOC emissions on O_3 formation (Curci et al., 2009, 2010; Kalogridis et al., 2014); these uncertainties are associated with more than 30% of global O_3 concentrations (von Kuhlmann et al., 2004) and even larger deviations when related to

smaller scales (Curci et al., 2009). Uncertainties that are attributed to the Mediterranean and other regions reflect insufficient knowledge about the BVOCs emission rate and speciation (associated with different plants, ecosystems, and regions) (Davison et al., 2009; Kalogridis et al., 2014), the complex dependency of BVOC emissions on meteorological conditions (mostly temperature and radiation), vegetation type, and leaf area index (Guenther et al., 1995; Curci et al., 2009; Davison et al., 2009). Furthermore, emission models frequently fail to correctly account for within-canopy gas-phase and heterogeneous chemical removal processes, providing inaccurate input data to regional and global models (Seufert et al., 1997; Ciccioli et al., 1999; Kalogridis et al., 2014). Another major source of uncertainty is inaccuracy in photochemical mechanisms currently incorporated in regional models, which do not treat accurately enough the related photochemical pathways (Seufert et al., 1997; Ciccioli et al., 1999; Kalogridis et al., 2014). To a large extent, this is due to highly complex chemical mechanisms being condensed into simplified chemical mechanisms, which are frequently used to reduce computational time in regional to global scale simulations (Curci et al., 2009). Newly developed methodologies incorporated in new instrumentation [e.g., proton transfer reaction–time of flight–mass spectrometer (PTR-TOF-MS)] currently enable the measurement of a much larger number of BVOC species compared with previous studies (Park et al., 2013). Park et al. (2013) demonstrated that using such instrumentation greatly improves current emission, air quality, and climate models that do not account for the extremely large range of compounds identified by using this novel instrumentation.

Research Objectives

1. Studying the impact of vegetation on ozone deposition rate, under Mediterranean conditions.

2. Evaluating the impact of ozone deposition on vegetation functioning, under the studied conditions.

1. Identifying the local BVOC species emitted from the investigated vegetation at the measurement sites, using PTR-TOF-MS instrumentation and quantifying their net canopy-boundary-layer exchange flux.

2. Evaluating the contribution of the emitted BVOCs from the forested vegetation at the measurement site to regional scale photochemical activity and O_3 concentrations

under different anthropogenic scenarios and meteorological conditions (solar radiation, temperature and relative humidity).

4. Identifying the impact of meteorological parameters (light, temperature, relative humidity and soil water content) as well as O_3 concentrations on BVOCs emission rate.

Methods

In order to approach the objectives of the study, ecosystem-atmosphere gas exchange of water vapor (H_2O), carbon di-oxide (CO_2) and ozone (O_3) were measured continuously starting in summer 2015. VOCs flux was measured in two different campaigns, during summer 2016 and 2017. We apply the eddy covariance technique (EC) in order to evaluate the vertical flux of these species. The EC is considered the most reliable micrometeorological flux determination method (e.g., Cieslik et al., 2009). However, the EC technique is highly sensitive to non-homogeneous topography and environmental conditions and requires a fast and precise detector (in conjunction with a sonic anemometer) to measure the species concentration (c) and vertical wind velocity (w) as instantaneous deviations from a mean (Hogg et al., 2007). The derivation of the flux calculation (e.g., Shuttleworth et al., 1984; Baldocchiet al., 1988) equals $\overline{w'c'}$ where the prime (′) indicates a fluctuation from the mean and the overbar indicates an average over the time period.

The eddy covariance technique allows us calculating the flux rate by placing meteorological and chemical (specific for the investigated gases) sensors over the ecosystem. All used sensors need to be highly precise and operate at high frequency (>10Hz). The water vapor and carbon di-oxide measurement enables us to follow the plants activity and functioning. The ozone flux measurement allows us to determine the ozone flux through the plants stomata, based on the water and carbon di-oxide fluxes. The VOCs fluxes will be determined using the Proton-Transfer-Reaction-Time-of-Flight Mass Spectrometry (PTR-ToF-MS). This newly developed methodology currently enable the scientific community measure a much larger number of VOCs species compared with previous studies, allowing the simultaneous quantification of hundreds of species, while many of them were not recognized as

being emitted from vegetation so far (Park et al., 2013). During the research the concentration of other trace gases were monitored continuously including, carbon monoxide, nitrogen oxides and sulfur di-oxide. The quantification of these gases along with complementary meteorological data enables us to analyze air pollution processes and sources.

Results and discussion

Photochemical air pollution characterization in Ramat Hanadiv

The following results summarize the photochemical activity at Ramat Hanadiv site during summer and winter. Surprisingly, relatively high concentrations were measured during both seasons, with 8-hourly average concentrations frequently exceeding 55ppb and 60 ppb, during winter and summer, respectively (see Figs. 1 and 2). Note that the corresponding World Health Organization (WHO) standard is 55ppb. Daytime ozone concentrations frequently exceeded 70 and 80 ppb during winter and summer, respectively. These results are surprising considering that daytime ozone concentrations tend to increase downwind of major emission sources of its precursors, towards eastern Israel and more inland (e.g., Asaf et al., 2011).

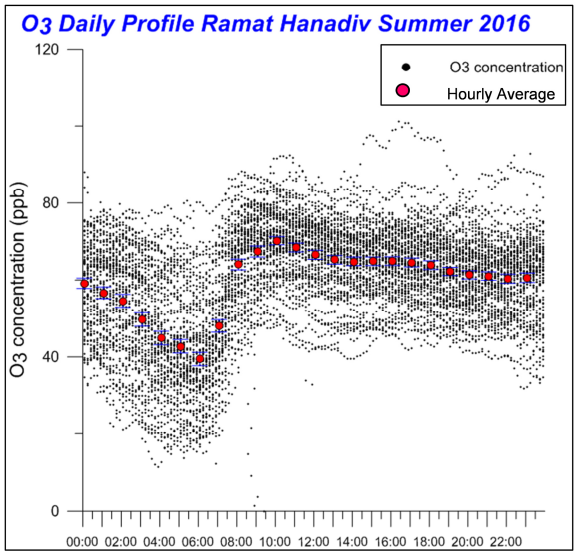

Figure 1. Average diurnal profile of ozone concentrations during summer 2016 at Ramat Hanadiv

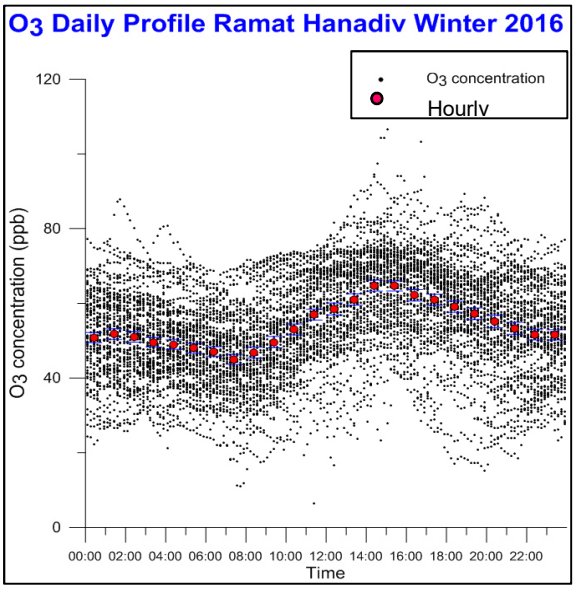

Figure 2. Average diurnal profile of ozone concentrations during winter 2016 at Ramat Hanadiv

Figure 3 presents the average diurnal profile of NO_X, which use as chemical precursors for ozone formation. The figure indicates high NO_X concentrations at the site, especially around morning, at time when the inversion base height is relatively low. Based on the NO_2/NO ratio we know that the major source of the NO_X is not local and cannot be associated with transboundary transport from south-east Europe.

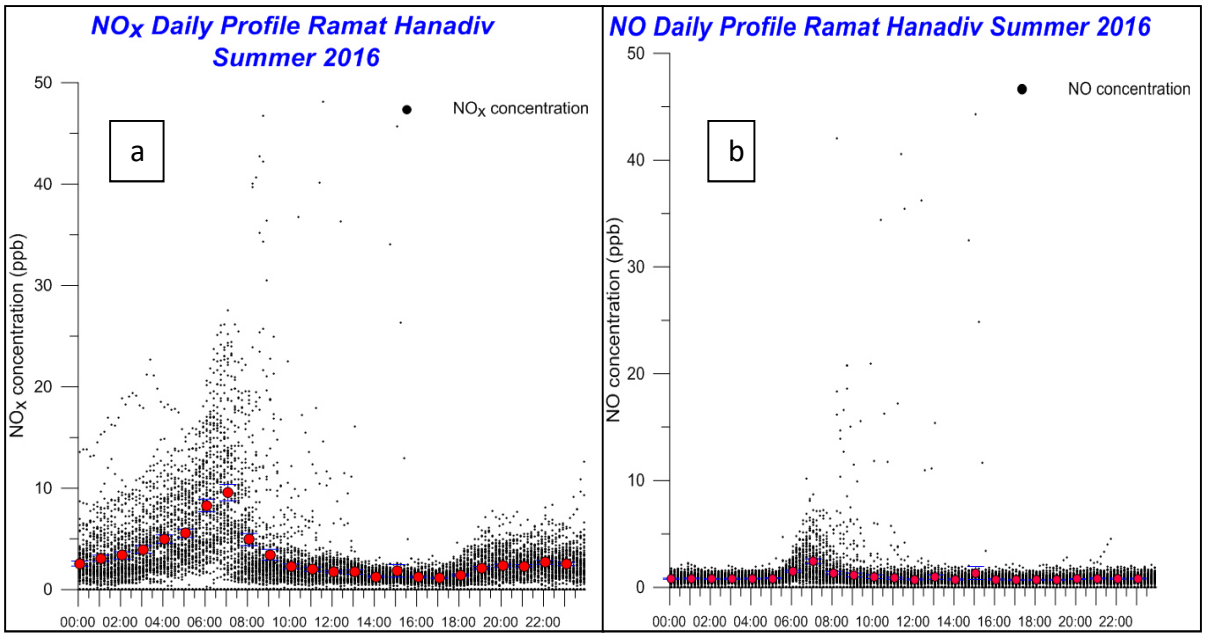

Figure 3. Average diurnal profile of NO and NO_X during summer 2016

Analyzing the dependency of ozone concentrations on the locally measured wind direction reveals that summer high ozone concentrations are contributed mostly by westerly winds during daytime and to some extent also during nighttime (Fig. 4).

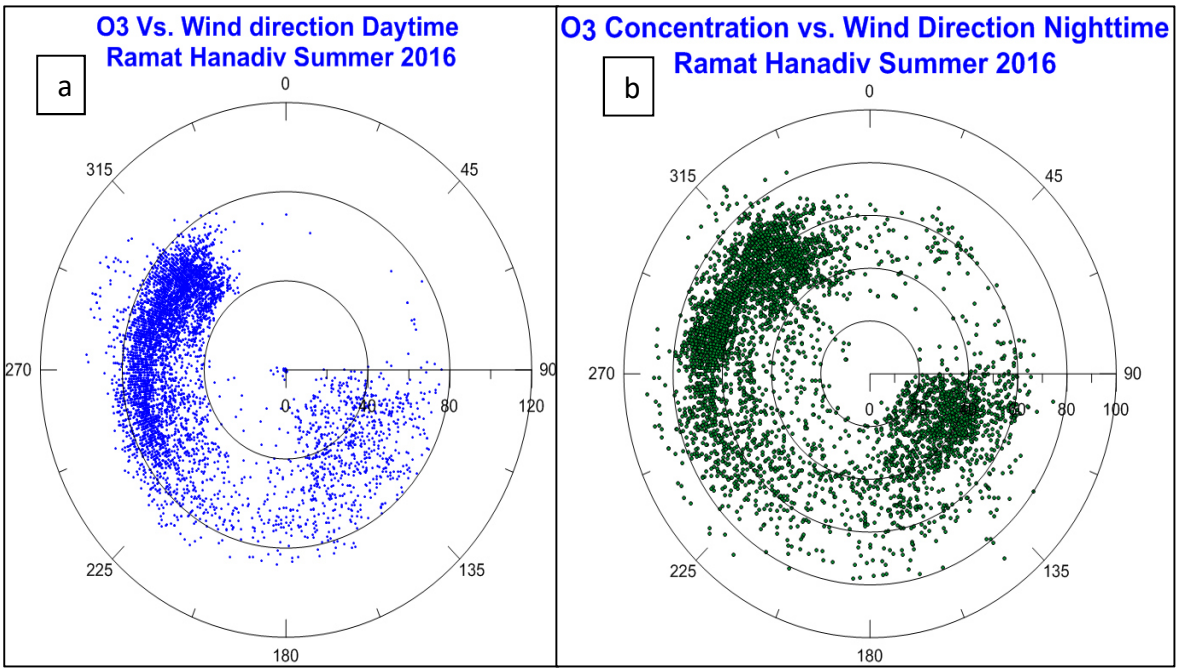

Figure 4. Dependency of ozone concentrations on wind direction during summer 2016 in Ramat Hanadiv

During summer local westerly winds were also associated with high NO_X and SO_2 concentrations. Back trajectories analysis using HYSPLIT (http://ready.arl.noaa.gov/HYSPLIT.php) also points out that in most cases the high NO_X, SO_2 and O_3 concentrations originated in air masses that were transported from the west (e.g., see Fig. 5 below).

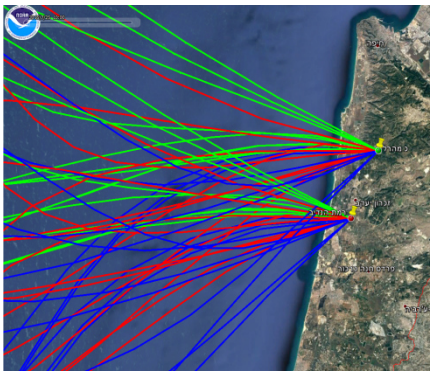

Figure 5. Air masses back trajectories to Ramat Hanadiv and Kerem Maharal during 25.7.2006

Generally the source for the elevated SO_2, NO_X and O_3 concentrations could be either emission from south-east Europe or cargo ships. However the high NO_X and SO_2 concentrations together with the relatively small $[NO_2]/[NO]$ points out to high contribution from relatively close emission sources. Therefore, it is more probable that the major source for the high air-pollution, including the strong photochemical pollution, is cargo ships.

Measured fluxes

In this section we present some examples of the evaluated CO_2, H_2O and O_3 fluxes. The CO_2 and H_2O fluxes reflect the photosynthesis and transpiration rate at the ecosystem level, respectively. We will investigate the potential impact of the ozone fluxes on the magnitude of these two fluxes. Figures 6 and 7 are examples for the evaluated fluxes over Ramat Hanadiv shrubbery during two contrasting seasons, summer 2015 and spring 2016. The figures demonstrate negative ozone flux during daytime, reflecting the fact that ozone is being uptaken by the vegetation and/or ground. The water vapor flux is positive, while the carbon-dioxide flux is negative during daytime and positive at nighttime. The comparison between the two figures reveals significantly higher ozone flux during spring compared with summer. Also the evapotranspiration tends to be higher during spring.

Fig. 6. Ozone (O_3), carbon-dioxide (CO_2) and water vapor (H_2O) flux over Ramat Hanadiv shrubbery during August and September 2015.

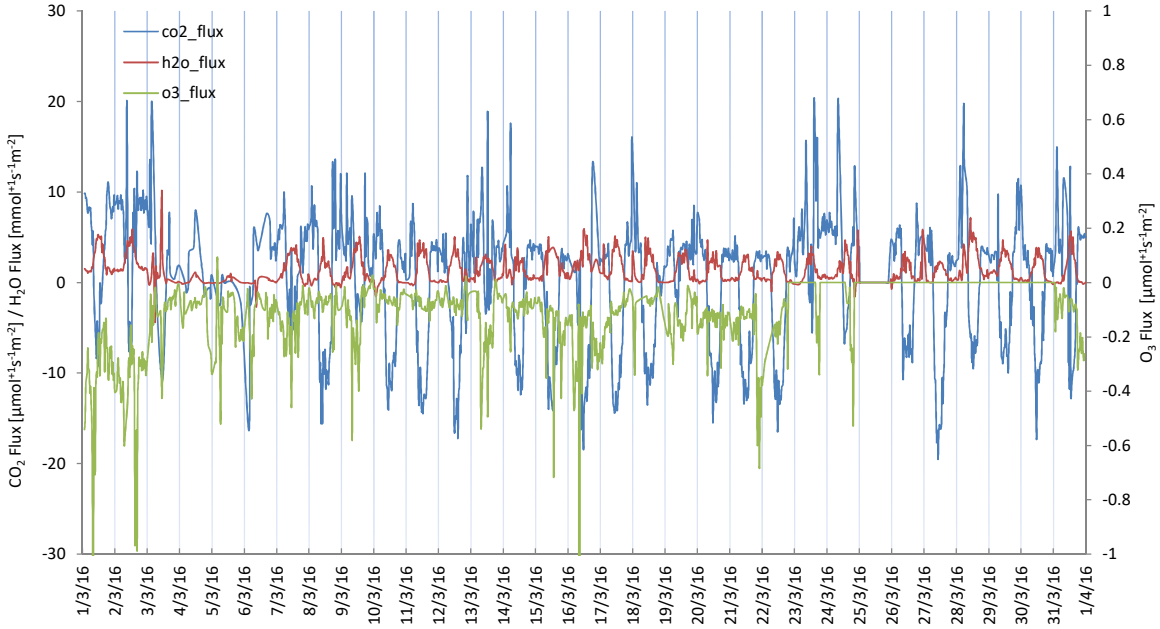

Fig. 7. Ozone (O_3), carbon-dioxide (CO_2) and water vapor (H_2O) flux over Ramat Hanadiv shrubbery during March 2016.

Figures 8 and 9 present the total versus the stomatal O_3 flux (Fst). The stomatal O_3 flux tends to be significantly higher during spring, compared with summer. Also the relative portion of the stomatal flux tends to be higher during spring. Table 1 summarizes the total ozone fluxes, that were obtained for the different seasons (see tables 1,2 and 3).

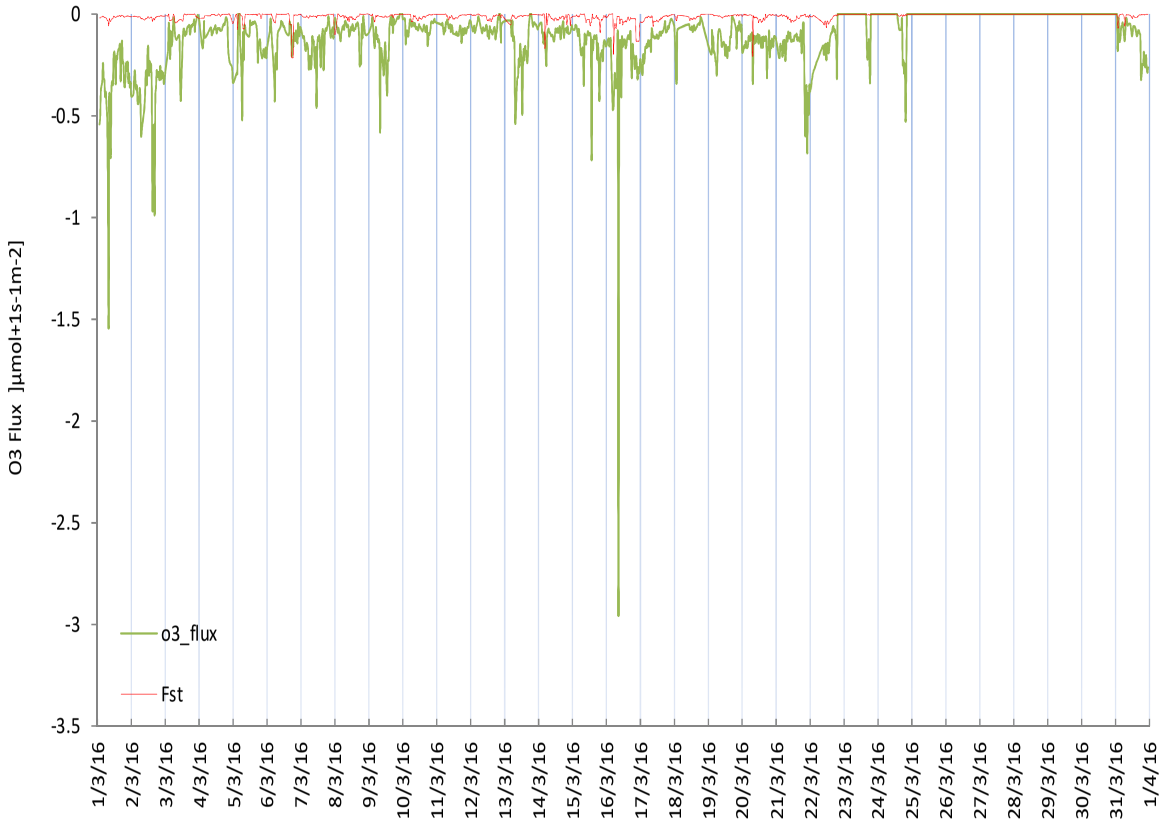

Fig. 8. Total and stomatal ozone flux over Ramat Hanadiv shrubbery during March 2016

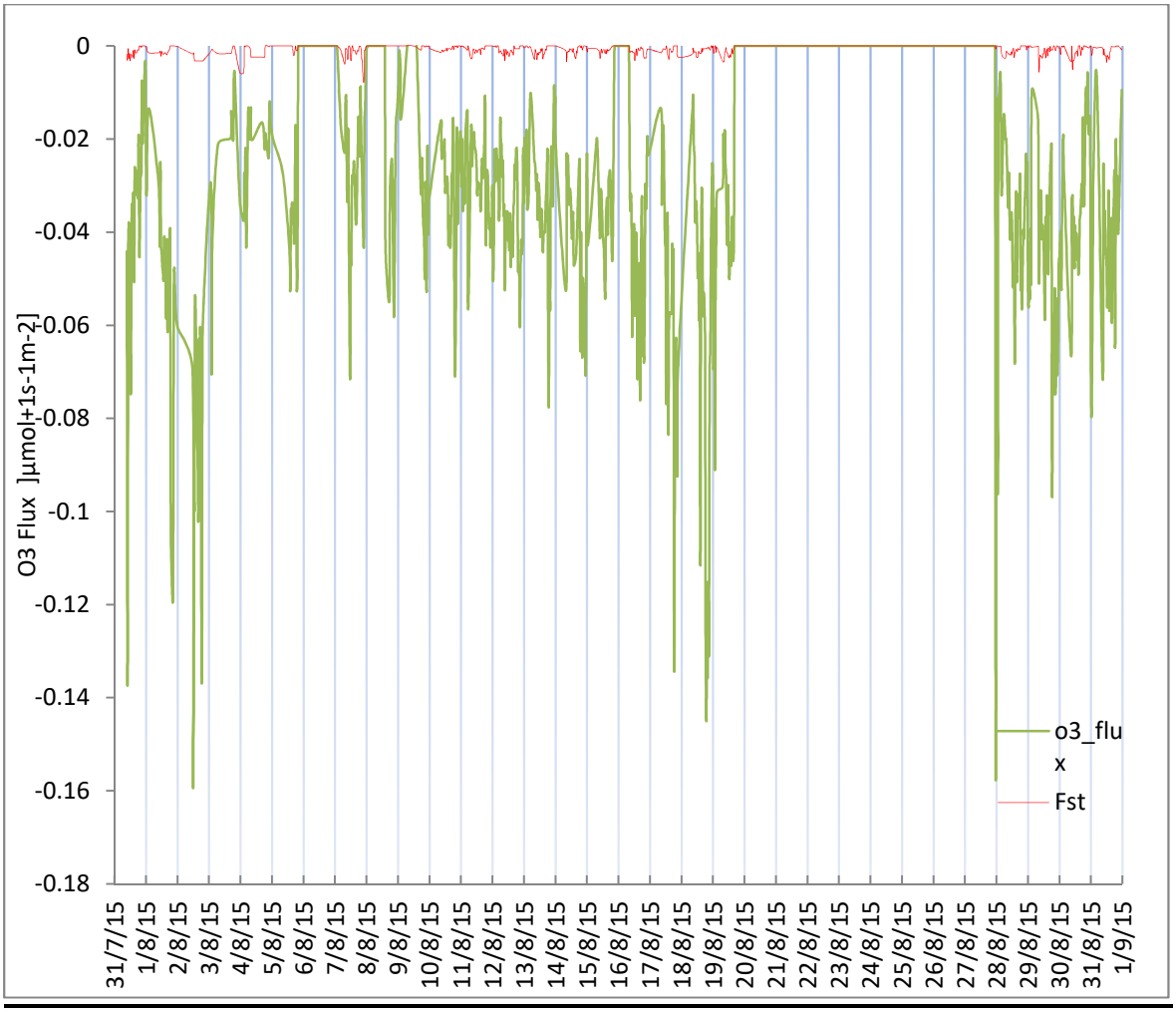

Fig. 9. Total and stomatal ozone flux over Ramat Hanadiv shrubbery during August and September 2015.

Figures 10 and 11 present the average diurnal profile carbon-dioxide, water vapor, total ozone andstomatal ozone flux over Ramat Handiv shrubbery, for two contrasting season, summer 2015 and winter 2016, respectively.

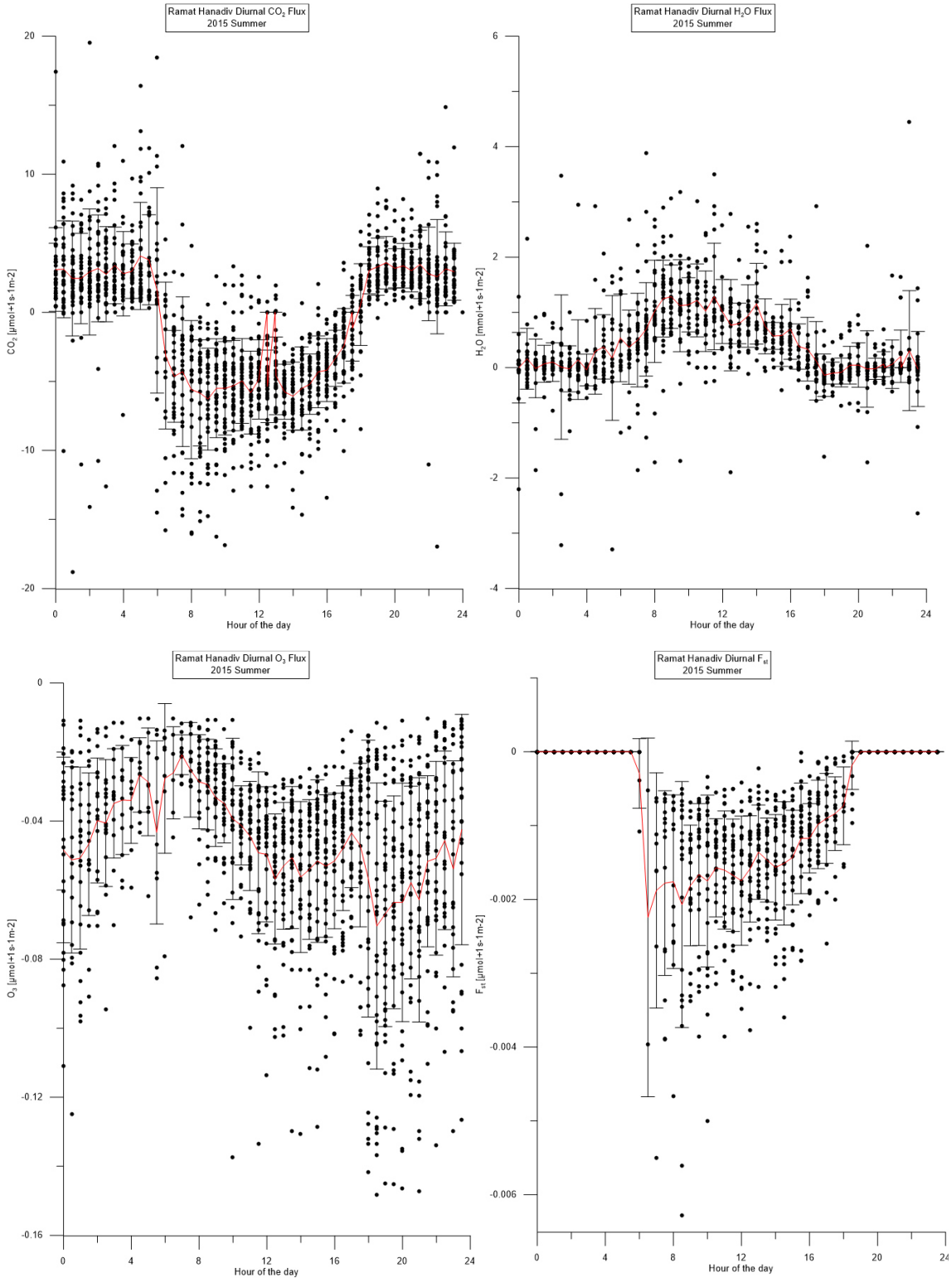

Figure 10. Average diurnal profile for carbon-dioxide (CO_2), water vapor (H_2O), total ozone (O_3) and stomatal ozone flux (F_{st}) over Ramat Hanadiv shrubbery during summer 2015.

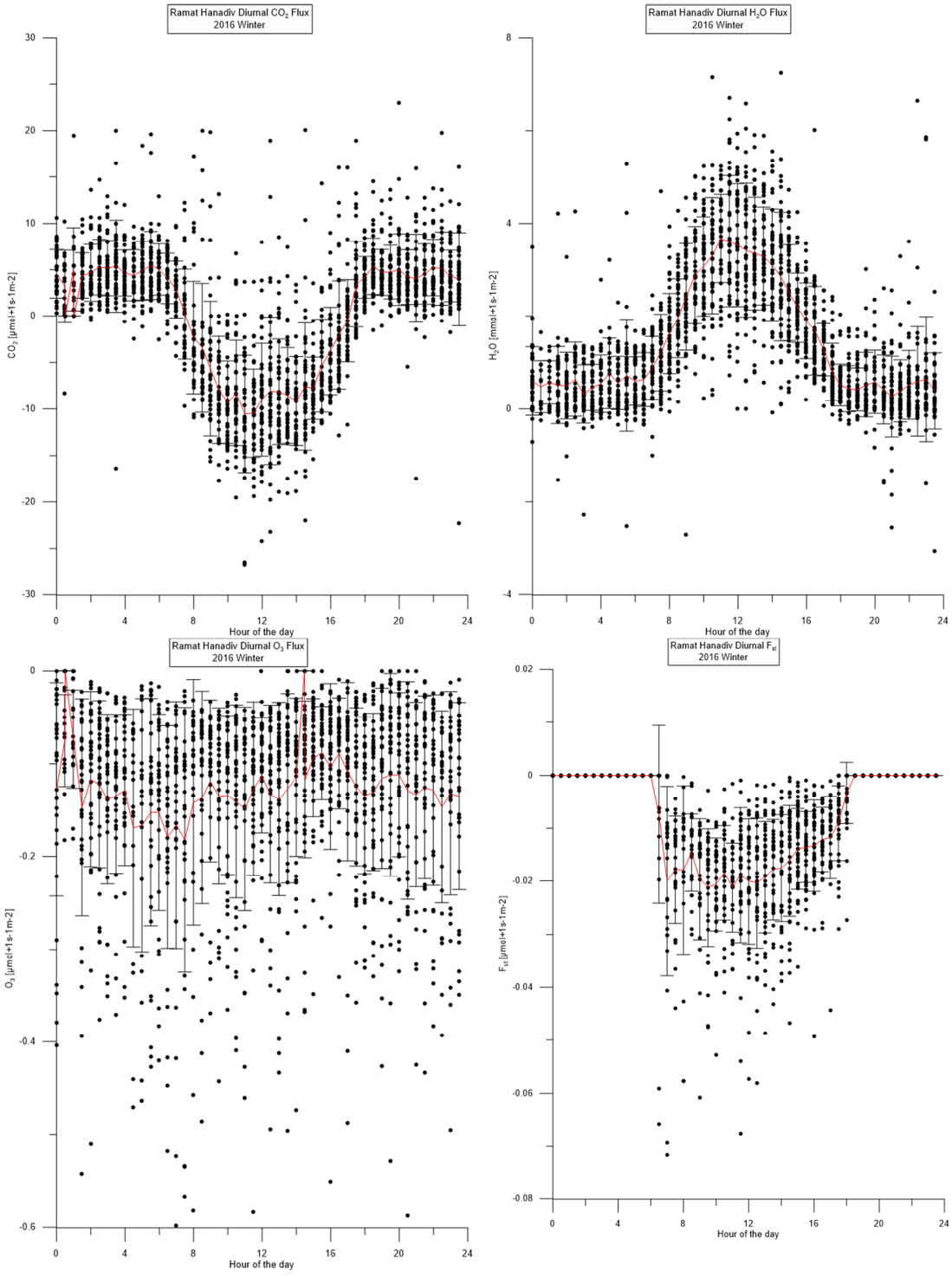

Figure 11. Average diurnal profile for carbon-dioxide (CO_2), water vapor (H_2O), total ozone (O_3) and stomatal ozone flux (F_{st}) over Ramat Hanadiv shrubbery during winter 2016.

Table 1 presents statistical information regarding the total ozone flux over Ramat Hanadiv shrubbery during the different seasons. Tables 2 and 3 present statistical information regarding the stomatal ozone flux and the relative portion of the stomatal flux, over Ramat Hanadiv shrubbery during the different seasons, respectively. Tables 4 and 5 presents statistical information about the CO_2 and H_2O fluxes that were obtained over Ramat Hanadiv shrubbery during the different seasons, respectively.

	F_{tot} mean	F_{tot} std	F_{tot} max	Time of max
Ramat Hanadiv summer 08/2015	-0.0389	0.0256	-0.1374	10:00
Ramat Hanadiv summer 09/2015	-0.0564	0.0387	-0.2080	18:00
Ramat Hanadiv winter 02/2016	-0.1234	0.1201	-0.8664	7:30
Ramat Hanadiv winter 03/2016	-0.1547	0.1358	-0.9885	16:30
Ramat Hanadiv summer 08/2016	-0.0486	0.0282	-0.2233	6:00

Table. 1. Average (mean), standard deviation (std), maximum (max) and the maximum timing of the total ozone flux (in µmol s^{-1} cm^{-2}) over Ramat Hanadiv shrubbery during the different seasons.

	F_{st} mean	F_{st} std	F_{st} max	Time of max
Ramat Hanadiv summer 08/2015	-0.0012	0.0013	-0.0078	8:30
Ramat Hanadiv summer 09/2015	-0.0020	0.0122	-0.0063	8:30
Ramat Hanadiv winter 02/2016	-0.0177	0.0238	-0.1586	8:00
Ramat Hanadiv winter 03/2016	-0.0208	0.0526	-0.2143	17:30
Ramat Hanadiv summer 08/2016	-0.0015	0.0019	-0.0173	7:30

Table. 2. Average (mean), standard deviation (std), maximum (max) and the maximum timing of the stomatal ozone flux (in µmol s^{-1} cm^{-2}) over Ramat Hanadiv shrubbery during the different seasons.

	F_{st}/ F_{tot} mean	F_{st}/ F_{tot} std	F_{st}/ F_{tot} max	Time of max
Ramat Hanadiv summer 08/2015	4.04%	3.16%	17.84%	08:00
Ramat Hanadiv summer 09/2015	2.71%	3.33%	26.48%	08:30
Ramat Hanadiv winter 02/2016	16.71%	20.45%	175.11%	08:00
Ramat Hanadiv winter 03/2016	18.11%	49.04%	131.41%	11:00
Ramat Hanadiv summer 08/2016	2.25%	4.67%	28.24%	07:00

Table. 3. Average (mean), standard deviation (std), maximum (max) and the maximum timing of ratio between the stomatal and total ozone flux (in µmol s^{-1} cm^{-2}) over Ramat Hanadiv shrubbery during the different seasons.

	F_{water} mean	F_{water} std	F_{water} max	Time of max
Ramat Hanadiv summer 08/2015	0.5856	0.7906	4.2933	14:30
Ramat Hanadiv summer 09/2015	0.5244	0.7748	5.2283	15:00
Ramat Hanadiv winter 02/2016	1.6121	1.9036	9.8795	13:00
Ramat Hanadiv winter 03/2016	1.4315	1.5778	5.9336	12:00
Ramat Hanadiv summer 08/2016	0.2122	0.4861	3.1305	08:30

Table. 4. Average (mean), standard deviation (std), maximum (max) and the maximum timing of the water vapor (evapotranspiration) flux (in µmol s^{-1} cm^{-2}) over Ramat Hanadiv shrubbery during the different seasons.

	GPP mean	GPP std	GPP max	Time of max
Ramat Hanadiv summer 08/2015	-3.8007	3.2544	-34.9331	07:30
Ramat Hanadiv summer 09/2015	-3.6112	3.2009	-18.9459	12:30
Ramat Hanadiv winter 02/2016	-2.1654	4.3830	-12.1940	11:00
Ramat Hanadiv winter 03/2016	-1.7757	5.3205	-9.9540	14:30
Ramat Hanadiv summer 08/2016	-1.3579	2.1199	-20.3179	07:00

Table. 5. Average (mean), standard deviation (std), maximum (max) and the maximum timing of the carbon-dioxide gross primary production flux (photosynthesis; GPP; in µmol s^{-1} cm^{-2}) over Ramat Hanadiv shrubbery during the different seasons.

Summary and Outlook

Our research indicates relatively high photochemical activity in the area of Ramat Hanadiv, associated with relatively elevated ozone concentrations, particularly from spring to fall. Accordingly, the total ozone flux in Ramat Hanadiv is significantly higher compared with other sites in Israel in which we also performed similar measurements (including Yatir, Birya, Eshtaol and Solelim forests). The stomatal flux, however tends to be smaller than in the other sites. This suggests that the non-stomatal component of the flux is influenced by BVOCs emission. We will evaluate the BVOCs measured data and investigate this hypothesis in the coming next months. In addition, we will study the impact of stomatal ozone flux on the vegetation functioning and the potential impact of the BVOCs emission from the vegetation on photochemical activity, both locally and regionally.

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