Eddy covarince fluxes in support of canopy exchange modelling

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INTEGRATED CARBON OBSERVATIO SYSTEM

Relevance of plants for CO2 and atmospheric pollutant removal

1. Stomatal sink. Stomatal opening regulate carbon uptake and largely contribute to pollutant removal in the atmosphere

CO2 uptake, photosynthesis. Detoxification of pollutants





2. Surface deposition on cuticles and soil. Adsorption processes

NO_x SO₂ O₃

3. Chemistry in the gas phase. Reactions between BVOC and ozone

"Nonstomatal uptake"

Ozone in low troposphere: an increasing threat for plants

Ozone in the stratosphere is GOOD!

protects life on Earth from the sun's harmful ultraviolet (UV) rays

Ozone in the troposphere is **BAD**!

Damages humans and plants, greenhouse gas



ground-level ozone, a primary component of smog.

EPA (2010)



Ozone formation in the troposphere



Plants interact with the ecosystem using BVOC





 Key component in the biosphere-atmosphere interactions.
Sunlight

VOC + NOx → Ozone

- Affect other plants and organism
- Favour the ecosystem perturbation

 Play an additional or alternative role in plant defences

Types of Biogenic VOC

• Hemiterpenoids $\rightarrow C_5$, only a few produced naturally

Isoprene



 $(C_5H_8, alkene)$

• Monoterpenoids $\rightarrow C_{10}$, thousands of different structures

- Limonene
- myrcene (alkene)



 α- pinene (alkene)

(C₅H₁₀O, alcohol)

Methylbutenol

 linalool (alcohols) ОН

• Sesquiterpenoids $\rightarrow C_{15}$, most varied class of terpenoids

ß-caryophyllene

farnesene

Amount Known

- Isoprene (C₅H₈)
- Monoterpenes (C₁₀H₁₆)
- Oxygenated VOC
- Sesquiterpenes (C₁₅H₂₄)

Biogenic emission of VOC is about 10 times higher than anthropogenic emissions globally!



BVOC Isoprene C_5H_8 Monoterpene $C_{10}H_{16}$ Sesquiterpenes $C_{15}H_{24}$

AVOC Industrial processes Biomass burning Animal husbandry Vehicular traffic Mining, energy production



A canopy-scale approach: Eddy Covariance flux measurements



CO2 flux: Subtracting modelled ecosistem respiration to the Net Ecosystem Exchange (NEE), Gross Primary Productivity (GPP) is calculated

Water flux: Stomatal conductance is calculated from measured transpiration by inversion of Monteith equation, therefore an estimate of stomatal ozone fluxes is possible

Ozone fluxes: sum of stomatal and non stomatal components

Case studies: the Holm oak urban forest in Castelporziano, Rome

Above the canopies of Mediterranean oaks and pines a complex photochemistry takes place with concurrent phenomena of ozone formation and ozone deposition



Mediterraneo

Tunisia

Marocco

https://www.icos-cp.eu/icoscapes/castelporziano

Wet years in Castelporziano = higher GPP



Circa 600 g CO2 m-2 per anno rimossi dal bosco in anni con scarsa precipitazione, quasi il doppio nel 2014!

- Tot. GPP in 2013: 1793 g (C) m-2 (665 mm precip.)
 - Tot. GPP in 2014: 2242 g (C) m-2 (900 mm precip.)
 - Tot. GPP in 2019: 1870 g (C) m-2 (694 mm precip.) •

Ecophysiological Responses to Rainfall Variability in Grassland and Forests Along a Latitudinal Gradient in Italy

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in Forests and Global Change



field measurements in Exeter(Central valley, CA)







Long term field measurements in Blodgett Forest

Through a multiyear analysis (2001-2006), we observed different sinks of ozone uptake, elucidating their dependence on plant physiology and environmental conditions

> Blodgett Forest, Ameriflux site (38°53'42.9"N, 120°37'57.9"W) 1315 m a. s. l., Sierra Nevada Mountains of California



The Hom Oak is a relevant O3 sink

Ozone fluxes are higher during late spring, when stomatal conductance is high. Up to **8 g O3 m-2** are sequestrated every year!



O₃

Atmospheric O3 concentration gradient from the soil to above the canopy





Fares et al. Atm. Env. 2013; Fares et al. Agr. For. Met. 2014; Savi et al. 2014; Fares et al. Env. Sci. Poll. Res. 2017

Ozone flux partitioned between stomatal and non-stomatal sinks

A **RESISTANCE** is the inverse of a **CONDUCTANCE**. A **FLUX** is driven by concentration differences between the canopies and the atmosphere

A series of resistances (e.g. **aerodynamic**, **boundary layer, stomata, cuticles, trace gases**) reduce flux magnitude from the atmosphere to the ground, obeying Ohm's law.

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

$$F_{O3sto} = G_{sto} * [O_3]$$



O₃ sink partitoning: stomata are the main sink

• Evaporative/resi O_3 sto = $[O_3]$ canopy $\cdot 0.61 \cdot G_{sto,H2O}$ sitve method for the stomatal component: $\lambda E = \frac{\rho c_p [e_s(T_0) - e(z_m)]}{\gamma (R_a + R_b + R_{sto})}$



• Soil sink:

(Zhang et al., 2002)

$$R_{ac} = \frac{14 \times LAI \times z_c}{u^*}$$
$$R_g = R_{g1} + R_{g2} \cdot \frac{SWC10}{SWC_{fc}}$$

Validated with EC measurements below canopy (Fares et al. Agr For Met 2014)

Cuticoles:

(Zhang et al., 2002)

$$R_{\text{cut}(\text{dry})} = \frac{R_{\text{cut}(\text{dry})_0}}{e^{0.03RH} \times \text{LAI}^{1/4} \times u^*}$$
$$R_{\text{cut}(\text{wet})} = \frac{R_{cut}(wet)_0}{\text{LAI}^{1/2} \times u^*}$$

Up to 60% of total O3 sink is stomatal.



Dramatic levels of tropospheric ozone concentrations in the central



Daily ozone concentration & fluxes at Blodgett

The daily ozone concentrations showed maximum diurnal peaks above 90 ppb!



Stomata represented a significant sink of ozone for this ecosystem, but not the major sink, similarly to Citrus site!



Fares et al. Agr. For. Met. 2010

Evidence of non-stomatal ozone removal at Blodgett:



Non-stomatal ozone fluxes

VOC emission: Fluxes at Castelporziano peak during the day because primary emitted BVOC depend on light and temperature





Deployment of PTRMS to the field site

Back in 2007 in a dune ecosystem: Clear diurnal fluxes of isoprene, monoterpenes and of Methyil Vinyl Chetone (MVK), one of the main oxidation products of isoprene



Davison et al. Biogeos. 2009; Fares et al. Biogeos. 2009

Evidences of Ozone – scavenging by VOC

Norm. concentrations and meteor. variables



BVOC concentration in the Orchard:

Fares et al. ACP 2012



BVOC fluxes



Large fluxes during the flowering period...

Fares et al. ACP 2012

Stomatal and non-stomatal fluxes: final balance

We believe that the model underestimates Fvoc during flowering, because not fully accounting for the burst of BVOCs coming from flowers.







Eddy covariance fluxes to test and validate canopy models

AIRTREE- Aggregated Interpretation of the Energy balance and water dynamics for Ecosystem services assessment



Model sensitivity: major effects of soil properties and drought on photosynthetic parameters

Optimization routines by PEST (Doherty, 2016). PEST is a nonlinear parameter estimation and optimization package based on the Gauss-Marquardt-Levenberg algorithm



Photosynthetic perfomances change in time and along the vertical canopy profile

Vc_{max} extinction



Measured vs simulated ozone fluxes



AIRTREE performances: The Castel di Guido periurban forest, Rome

1 ton carbon/ha 8.1 kg ozone and PM /ha



Environmenta	Science	& Tec	hno	logy
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Article



Figure 1. Map of the vegetation surveyed at the park of Castel di Guido, Rome. Map data 2020 Google.

Fares et al. ES&T 2020

Environmental Science & Technology

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Table 1. NPP, Tropospheric Ozone (O_3) , and Particle $(PM_{10} \text{ and } PM_{2.5})$ Dry Deposition Simulated by the AIRTREE Model for the Year 2018 at Castel di Guido Natural Reserve^{*a*}

species	dbh (cm)	NPP (g m^{-2})	NPP class	$O_3 (g m^{-2})$	O3 class	$PM_{10} (g m^{-2})$	PM ₁₀ class	$PM_{2.5} (g m^{-2})$	PM _{2.5} clas
A. campestre	35	354.23 ± 38.76	IV	2.97 ± 0.02	V	1.01 ± 0.0482	п	0.09 ± 0.0041	I
Acer negundo	15	46.6	I	2.75	V	0.77	I	0.06	I
A. cordata	35	438.59 ± 39.9	v	3.27 ± 0.05	VI	1 ± 0.0405	п	0.08 ± 0.0034	I
C. atlantica	35	938.24 ± 128.36	х	5.67 ± 0.33	х	7.39 ± 1.272	VIII	1.01 ± 0.1739	х
C. australis	35	392.79	IV	2.8	V	0.93	I	0.08	I
C. sempervirens	55	1084.6	х	7.4	х	16.23	x	2.27	х
Eucalyptus spp.	55	490.78	V	3.34	VI	1.44	п	0.12	п
Fraxinus angustifolia	15	253.71 ± 79.24	III	2.19 ± 0.09	IV	0.83 ± 0.1507	I	0.07 ± 0.0125	I
F. ornus	35	562.24 ± 95.6	VI	2.88 ± 0.26	v	1.42 ± 0.1802	п	0.12 ± 0.0155	п
Juglans nigra	15	140.48 ± 126.39	п	2.17 ± 0.09	IV	0.82 ± 0.1714	I	0.07 ± 0.0145	I
Juglans regia	35	370.26	IV	2.51	V	1.05	п	0.09	I
Malus sylvestris	35	225.31	ш	2.02	IV	0.66	I	0.06	I
Ostrya carpinifolia	35	528.65 ± 91.68	VI	2.85 ± 0.25	V	1.32 ± 0.1603	п	0.11 ± 0.0138	п
Pinus eldarica	35	704.89 ± 97.32	VIII	6.19 ± 0.61	х	9.58 ± 2.4196	X	1.31 ± 0.333	х
Pinus halepensis	55	894.86	IX	6.67	х	13.73	х	1.88	х
Pinus pinaster	55	847.47	IX	6.46	х	12.01	х	1.65	х
Pinus pinea	55	794.22 ± 30.14	VIII	6.39 ± 0.12	х	10.86 ± 0.7685	х	1.49 ± 0.1055	х
Populus nigra	15	83.25	I	2.01	IV	0.69	I	0.06	I
Prunus avium	35	375.44	IV	2.76	V	1.12	п	0.1	I
Pyrus amygdaliformis	15	27.91	I	2.15	IV	0.66	I	0.06	I
Pyrus pyraster	35	319.2	IV	2.57	V	1.08	п	0.09	I
Q. cerris	35	412.27 ± 51.97	V	2.89 ± 0.21	V	1.21 ± 0.1192	п	0.1 ± 0.0103	I
Quercus frainetto	35	332.5 ± 16.7	IV	2.54 ± 0.09	V	1.12 ± 0.0405	п	0.1 ± 0.0035	I
Q. ilex	35	656 ± 162.43	VII	3.43 ± 0.48	VI	2.79 ± 0.7179	III	0.31 ± 0.0803	IV
Q. pubescens	35	486.99 ± 61.35	v	2.98 ± 0.22	V	1.21 ± 0.1192	п	0.1 ± 0.0103	I
Q. robur	15	250.37 ± 77.66	III	2.45 ± 0.12	IV	0.7 ± 0.1171	I	0.06 ± 0.01	I
Quercus suber	35	854.12 ± 87.2	IX	3.52 ± 0.2	VII	2.09 ± 0.1795	III	0.23 ± 0.0201	III
Quercus trojana	15	159.36 ± 80.58	п	2.24 ± 0.08	IV	0.56 ± 0.1356	I	0.05 ± 0.0115	I
R. pseudoacacia	35	474.66	V	2.65	V	1.16	п	0.1	I
Sorbus domestica	15	189.59	п	2.07	IV	1.01	п	0.09	I

⁴⁷Model simulations were carried out for each species at different dbh. We grouped results according the highest dbh group. The groups were: 15 (dbh ranging from 5 to 15 cm), 35 (dbh ranging from 20 to 35 cm), and 55 (dbh ranging from 40 to 55 cm). SD is shown in cases where more dbh classes were present within each group. Evergreen species are marked in bold.

Can we appreciate moderate drought effects on Monoterpene emissions from canopies?



EC VOC fluxes to determine canopy emission factors



- New Basal Emission factors calculated for key Mediterranean ecosystems in Castelporziano were used to run MEGAN for estimating BVOC emissions in central Italy form the main plant functional types coupled with a Comunity Land Model developed at the NCAR
- The global model run with realistic BEF from prevailing MT emitting species predicted lower concentrations of tropospheric ozone compared with an isoprene emitting scenario used in the previous MEGAN version.



Fares et al. Env. Sc. Tech. 2013

Integration of vegetation maps & national forest inventories: **Emission Factor attribution for** a realistic estimate

Do we have enough information on BEF? Is it still worth measuring BEF at leaf/ecosystem scale?





Can we estimate ozone damage to vegetation using continuous EC field measurements?

Case studies on Pinus ponderosa forest, an orange orchard, and a mixed Mediterranean forest









Stomatal ozone fluxes (green line) correlate with GPP better than total ozone fluxes (blue line)



Emerges Saf Prade Res (2010; 2532:0-3248 DOI:10.1007/s11256-07-0352-0 0220NE AND PLANT LIFE: THE ITALIAN STATE-OF-THE-ART

Ozone flux in plant ecosystems: new opportunities for long-term monitoring networks to deliver ozone-risk assessments

Silvano Fares¹ · Adriano Conte¹ · Abad Chabbi^{2,3}

At increasing ground levels of ozone, the slope between GPP and stomatal ozone deposition decreases



Photosynthesis uncoupling from stomatal conductance ay high levels of O3 concentrations

Fares et al. 2013 Glob. Chan. Biol.

The FREQUENCY domain: Usage of Wavelet coherence analysis to highlight regions of significant temporal correlations in a pine forest

- Temporal correlation between GPP (residuals), ozone concentration and stomatal ozone flux exists
- High correlation at daily scale (period ~ 1) was observed
- At the higher GPP we often do not reach the highest covariance between GPP and stomatal ozone deposition...



Can we predict GPP using multiple regression linear and nonlinear models?

Multiple regression linear model: (GPP = b1P + b2Q + b3R...+bnN)

	Blodgett					Lindcove				Castelporziano					
	Case 1														
	Predictors	beta	multiple R ²	F	total		beta	multiple R ²	F	total		beta	multiple R ²	F	total
	PAR (umolm ⁻² s ⁻¹)	-0.722	0.489	46407.180		PAR (umolm ⁻² s ⁻¹)	-0.431	0.098	470.028		Soil moisture (%)	-0.414	0.115	176.796	
_	VPD (kpa)	0.457	0.492	210.360		VPD (kpa)	0.493	0.156	299.663		PAR (umolm ⁻² s ⁻¹)	-0.438	0.209	159.452	
4 case	Ta (°C) Soil moisturo (%)	-0.350	0.499	680.680		Ta (°C) Soil moisturo (%)	-0.236	0.162	29.010		VPD (kpa) Ta (°C)	0.089	0.215	10.667	
	R-sauare	0.087	0.502	520.510	0.5	Son moisture (%)	-0.055	0.105	0.101	0.17	10 (C)	0.081	0.217	5.257	0.22
studies	slope				0.86					0.74					0.77
	df				48399					4338					1351
	F Crist 2				12198					211					94
	Case 2	0.460	0.482	27255 570		$DAD (um a lm^{-2} a^{-1})$	0 252	0.008	470 029		Coil moisture (%)	0 221	0.115	176 706	
Le metili de siene	$PAR(umolm^{-2}s^{-1})$	-0.469	0.483	27355.570		VPD (kna)	-0.253	0.098	470.028 299.663		$FT(mmolm^{-2}s^{-1})$	-0.331	0.115	1/0.790	
vegative sign	Soil moisture (%)	0.072	0.546	213.980		ET (mmolm ⁻² s ⁻¹)	-0.438	0.234	440.230		PAR (umolm-2 s-1)	-0.323	0.233	32.896	
f prodictor	VPD (kpa)	0.375	0.547	71.590		Та (° С)	0.115	0.235	5.738		VPD (kpa)	0.126	0.245	21.623	
n predictor.	Ta (° C)	-0.352	0.551	312.320		Soil moisture (%)	0.032	0.236	5.394		Ta (° C)	0.121	0.249	7.515	
egative	R-square				0.55					0.24					0.25
icgutive	siope				0.88 29254					0.76					0.78
effect on GPP	F				7192					267					89.52
	Case 3														
	ET (mmolm ⁻² s ⁻¹)	-0.469	0.483	27355.570		PAR (umolm ⁻² s ⁻¹)	-0.254	0.098	471.990		Soil moisture (%)	-0.331	0.115	176.796	
	PAR (umolm ⁻² s ⁻¹)	-0.308	0.542	3771.650		VPD (kpa)	0.277	0.156	298.684		ET (mmolm ⁻² s ⁻¹)	-0.239	0.214	169.705	
	Soil moisture (%)	0.072	0.546	213.980		ET (mmolm ⁻² s ⁻¹)	-0.453	0.234	441.996		PAR (umolm ⁻² s ⁻¹)	-0.323	0.233	32.896	
	VPD (kpa)	0.375	0.547	71.590		[O ₃] (ppb)	0.106	0.237	14.196		VPD(kpa)	0.126	0.245	21.623	
Ctomotol	Ta(°C)	-0.352	0.551	312.320		Ta (°C)	0.103	0.238	4.598		Ta (°C)	0.121	0.249	7.515	
Stomatai	R-square	11.5.	11.5.	11.5.	0 55	Son moisture (%)	0.020002	0.236203	5.5540	0 24	[O ₃] (ppb)	11.5.	11.5.	11.5.	0.25
07000	slope				0.88					0.76					0.78
ozone	df				29254					4332					1350
deposition	F Crac 4				7192					225.84					90
	Case 4	0 720	0 472	21696 420		C (m c ⁻¹)	0.052	0.085	272 101		(m e ⁻¹)	0.247	0.240	422.200	
explains	(ms^{-1})	-0.730	0.473	21080.430		$G_{03}(ms)$	0.053	0.085	272.181		G_{03} (m s)	-0.347	0.240	422.300	
	PAR (umoim 2 1	-0.242	0.525	813 270		VPD (kna)	0.205	0.132	99 428		$PAR(umolm^{-2}s^{-1})$	-0 199	0.200	28 848	
better than	VPD (kpa)	0.252	0.548	446.420		ET (mmolm ⁻² s ⁻¹)	-0.461	0.225	168.336		та (°С)	0.134	0.314	10.790	
07000	Soil moisture (%)	0.062	0.551	131.650		Ta (° C)	0.048	0.226	6.805		ET (mmolm ⁻² s ⁻¹)	-0.056	0.315	2.796	
ozone	Та (°С)	-0.082	0.551065	12.11		Soil moisture (%)	0.143966	0.227684	4.8459		VPD (kpa)	n.s.	n.s	n.s	
concentration	R-square				0.55					0.23					0.315
	slope				0.89					0.79 2027					0.79 1222
GPP decrease!	F				4947					2957 144					1552

Statistical analysis to estimate ozone effects on GPP

Random Forest Analysis of the effects on GPP at three Mediterranean-type ecosystems: Pinus ponderosa, Citrus sinensis, Quercus ilex



Long-term continuous eddy-covariance measurements (>9 years at 30 min resolution) at three Mediterranean-type sites showed that Up to 12–19% of the carbon assimilation reduction is explained by higher stomatal ozone flux!

Global Change Biology

Global Change Biology (2013) 19, 2427-2443, doi: 10.1111/gcb.12222

Tropospheric ozone reduces carbon assimilation in trees: estimates from analysis of continuous flux measurements

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Long-term measurements may support the training and application of Neural Network analysis



Neural Network Analysis to Evaluate Ozone Damage to Vegetation Under Different Climatic Conditions

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Refining new metrics for ozone-risk assessment with EC data, is it possible?

Evaluation of reducing factors for Photosynthesis and stomatal conductance $F_{pO3} e F_{cO3}$

Ball, Woodrow & Berry (1987) model nested in the AIRTREE model:

 $g_{s} = g_{0} + m \frac{A_{n} * RH}{C_{s}} \qquad \qquad A_{n} = A_{n} * F_{po_{3}}$ $g_{s} = g_{s} * F_{co_{3}}$

 $F_{GSO_3} = a_{GS} * POD_Y + b_{gS}$ $F_{AO_3} = a_A * POD_Y + b_A$ $POD = CEO_3 * gS * K_{O3} * 3600 * 10-6$ $CEO_3 = [O_3] * H * D$

Where a and b are slope and intercept of the regression line between CUO and gs and An, respectively. CEO₃ is the cumulative ozone concentration (i.e. SUM00, AOT00 etc.).

- ✓ POD 3 to 5 works best for Holm oak (ozone resistant).
- ✓ POD 0-1 works best for Pinus Ponderosa (ozone sensitive).

5 to 10 % reducion of GPP by ozone!

c .	Phot	osynthesis	Conductance				
Species	Slope (ap)	Intercept (b _p)	Slope (a _c)	Intercept (b _c)			
Q.ilex	-0.0003	0.7930	-0.0009	0.8572			
P.ponderosa	-0.0005	0.9152	-0.0007	1.0671			



Fares et al. STOTEN 2019

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Thanks for your attention!

