

Relaxed eddy accumulation, a new technique for measuring emission and deposition fluxes of volatile organic compounds by capillary gas chromatography and mass spectrometry

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Abstract

The possibility afforded by a new relaxed eddy accumulation system in the determination of emission and deposition fluxes of volatile organic compounds (VOCs) by chromatographic techniques will be presented. The system, especially designed to limit sampling artifacts, uses adsorption traps filled with solid sorbents as reservoirs for VOC collection. Enriched compounds were analyzed by capillary GC and positive identification and quantification of eluted compounds was achieved by mass-spectrometric detection. The method has been used to quantify the emission and deposition of both biogenic and anthropogenic VOCs over a Mediterranean forest ecosystem located in Central Italy. For the first time, both daily and seasonal trends of anthropogenic and biogenic VOCs will be reported. The consistency of monoterpene fluxes with predictions based on the knowledge of VOC emission from the dominant vegetation species will be tested. Data have been used to develop a novel algorithm to predict the seasonality of biogenic emission from the forest ecosystem.

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1. Introduction

In the last 10 years, intensive work has been devoted to measure emission and deposition of those trace gases that play a key role in affecting the radiative forcing of the earth (CO_2 , CH_4 , N_2O , O_3) and the oxidation capacity of the atmosphere (VOC, NO_x , O_3) [1]. In particular, research has been

focused on the biosphere–atmosphere exchange of carbon compounds in order to quantify the net amount of CO_2 removed from the atmosphere by forest ecosystems. Since terrestrial vegetation has been identified as an important sink for atmospheric CO_2 , the identification and quantification of potential losses of this gas in the environment is of great relevance for the global carbon budget. The quantification and fate of the fraction of assimilated carbon that is re-emitted from forest ecosystems as volatile organic compounds, which are mainly isoprenoids [2], represents, today, an important part of this

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research [3]. In addition to be a net sink for assimilated CO₂, biogenic volatile organic compounds (VOCs) can act as precursors of ozone and secondary aerosols when sufficient amounts of NO_x are present in air [4]. Present figures of VOC emission at local and global scale are affected by large uncertainties due to the difficulty to quantify fluxes from forest ecosystems.

A direct determination of emission and deposition fluxes through a micrometeorological technique called eddy correlation (EC) [5,6] is, in fact, possible only for those trace gases for which fast and sensitive sensors are available. Fast response is needed because eddy covariance is the method used for flux determination. With this technique, the flux is obtained by averaging over a long period of time (from 5 to 30 min) the instantaneous product between the vertical wind speed, w , and the aerometric concentrations C_g of the trace gas of interest ($F = \bar{w}\bar{C}_g$). By considering the frequency of the eddies in air, sensors capable to work at frequencies ranging between 1 and 10 Hz [5,6] are needed for the determination of trace gas fluxes by EC. Since no sensors of this type are available for the determination of VOCs in air, other micrometeorological techniques need to be used for measuring the fluxes of these compounds. Among them, the most recent one is relaxed eddy accumulation (REA). According to the REA theory, originally proposed by Desjardins [7], and later modified by Businger and Oncley [8], the flux of a trace gas in the atmosphere can also be obtained by collecting the updraft and downdraft air into two separate reservoirs at a rate which is proportional to the vertical wind speed. This is only possible, however, when stationarity conditions are established over the site. Such conditions are met when 10 to 30 min-averaged values of the vertical wind speed closely approach to zero ($\bar{w} = \text{ca. } 0$). In terrestrial ecosystems, this usually happens during daytime hours when a rather strong turbulence is generated over the forest canopy. Under these conditions, it is possible to efficiently separate the updraft and downdraft components of the air and store the trace gases associated to them into different reservoirs. By calling \bar{C}_{UP} and \bar{C}_{DOWN} the concentrations of a trace gas into the reservoirs in which the updraft and downdraft air is accumulated, the net

flux F from the terrestrial ecosystem can be calculated using the following equation:

$$F = \beta\sigma(\bar{C}_{\text{UP}} - \bar{C}_{\text{DOWN}}) \quad (1)$$

in which β is a dimensionless empirical coefficient having a constant value of ca. 0.56 and σ is the standard deviation of the vertical wind speed. By expressing the concentrations in proper units, the application of Eq. (1) directly provides the flux of a trace gas in mg m⁻² h⁻¹ or, if necessary, in mg C m⁻² h⁻¹, where mg C stands for milligram of carbon.

According to the REA theory, the capability of efficiently separate the updraft and downdraft components of the air is strictly dependent on the vertical wind speed and representative values of \bar{C}_{UP} and \bar{C}_{DOWN} are only obtained if a specific value of w is used to allow the access of the air into the reservoirs. Repeated experiments performed with gases (such as CO₂ and H₂O) for which REA sampling can be performed in parallel with the eddy correlation technique [6–9] have shown that reliable fluxes of a trace gas are obtained by REA if the access to the reservoirs takes place when the vertical wind is above $+0.6\sigma$ (updraft air) or below -0.6σ (downdraft air). The various steps used by REA for the conditional sampling of a trace gas are illustrated Fig. 1. To perform REA sampling, it is thus required that instantaneous data of the vertical wind speed are continuously acquired with a fast sensor (usually a sonic anemometer) and transferred into a personal computer where values of σ and of the vertical wind thresholds are regularly calculated and updated. Once defined the thresholds, the computer must compare the instantaneous value of the wind speed with them in order to open the valves whenever w exceeds the calculated thresholds. To reduce the errors in the calculation of F , it is essential that the transfer time of the air into the reservoirs is of the same order of magnitude of the time between two consecutive switches.

Until recently, the REA geometry reported in Fig. 1 has been the only one used for the determination of trace gases over terrestrial ecosystem [6]. The air is aspirated by a pump whose inlet is located as close as possible to the wind sensor. The pump outlet is

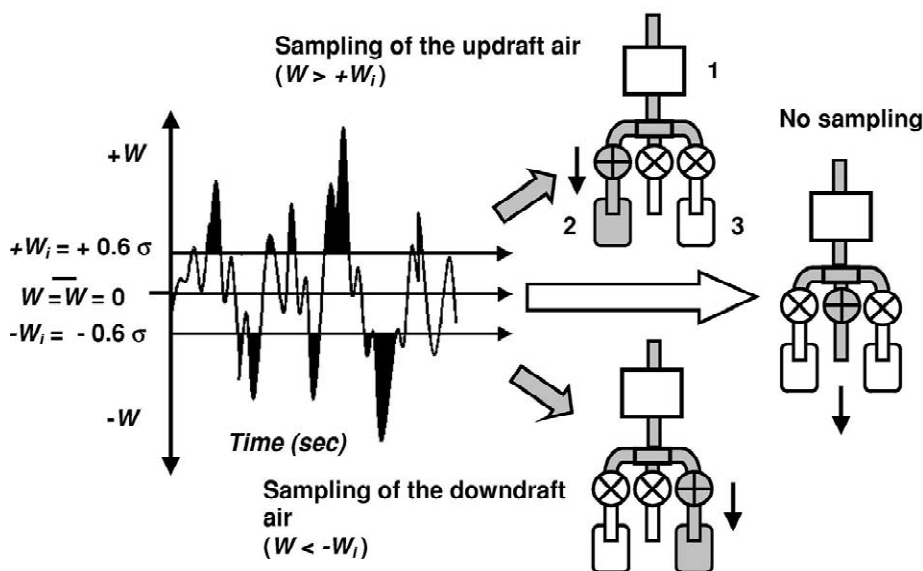


Fig. 1. Schematic diagram showing the working mechanism of conditional sampling with the REA technique. (1) Aspirating pump, (2) reservoir accumulating the updraft air, (3) reservoir accumulating the downdraft air.

connected to three different lines whose access is controlled by fast valves. While the outlet of the updraft and downdraft lines are connected to PTFE bags (or passivated canisters) for the storage of the sample, the waste line is connected with the open air.

While this type of REA systems are fully adequate for measuring fluxes of inert compounds present in air at ppmv levels (such as CO_2 , CH_4 and water vapor), they can be subjected to severe limitations when used with very reactive VOCs present in air at trace levels (ppbv–pptv). The first limitation is represented by the fact that compounds must pass through the pump, lines and valves before they reach the reservoirs. This can give rise to partial losses of the sample due to adsorption, partition or decomposition processes. Even if inert materials are used, water can be partly deposited on the membrane of the pump or on the connecting lines and it can selectively uptake polar compounds. The second limitation arises from the fact that compounds accumulated inside the PTFE bags or passivated canisters remain in contact with atmospheric oxidants (such as ozone and OH radicals) for 30 min to 1 h before they are analyzed. This time is long enough to cause a substantial oxidation of the most reactive compounds

and convert them into secondary products. In addition to this, the sample accumulated in PTFE bags or passivated canisters cannot be directly analyzed and must be enriched on traps filled with solid sorbents before to be injected into the GC column by thermal desorption.

To limit the artifacts associated with the REA system illustrated in Fig. 1, a different geometry has been recently proposed for the measure of VOC fluxes from forest ecosystems [9]. It is illustrated in Fig. 2a. The main advantage of this system is that VOC are directly accumulated into the reservoirs without passing through the pump, lines and valves. Since adsorption traps are used as reservoirs, the sampling and enriching steps are performed at once and VOCs can be directly analyzed after sampling. With this geometry, the dead volume is much more limited because it is basically represented by the internal volume of the lines connecting the outlet of the traps with the valves. It can be drastically reduced by using short (4–5 cm) stainless steel tubes having an internal diameter of 1 mm [9]. This type of geometry (that can be called *reversed geometry*) has been successfully used to measure monoterpene fluxes over a pine-oak forest of Central Italy [9].

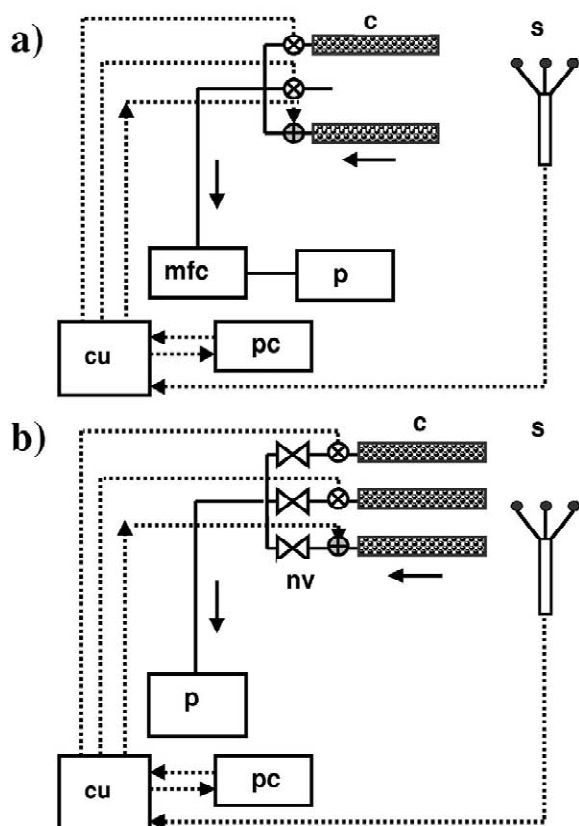


Fig. 2. Schematic diagram of the REA systems using the reversed geometry. Solid lines are used to indicate the pneumatic lines, dotted lines are used to indicate the electric lines. (a) Instrument used in previous studies; (b) instrument used in the present study. Letters indicate the various parts of the two instruments; c = adsorption traps, cu = central unit including the interface with the computer, mfc = mass flow controller, nv = needle valves, p = aspirating pump, pc = personal computer, s = sonic anemometer.

Based on the experience gained through these experiments, an implemented version of the original system has been developed. It has been tested for more than one year in a Mediterranean forest ecosystem. By combining adsorption traps with capillary GC connected to mass spectrometry, unambiguous identification of biogenic and anthropogenic VOCs has been achieved. Thanks to this technique, diurnal and seasonal variations of different VOCs has been measured over the site. Data obtained will be presented and critically discussed.

2. Experimental

2.1. The REA design

Fig. 2b reports a schematic diagram of the REA system used in this investigation. With respect to the original design [9], the mass flow controller was removed and the constancy of the flow-rate through the sampling lines was achieved by inserting a needle valve in each one of them. Needle valves were placed very close to the switching valves and connected to them using narrow bore (1 mm I.D.) stainless steel tubes. To minimize the differences in resistance through the various lines and allow a better control of the flow-rates, a trap was also inserted in the waste line (dummy trap).

With these modifications, it was possible to drastically cut the cost of the instrumentation and, more importantly, to limit the pressure problems occurring at high sampling frequencies (low σ values). With the system reported in Fig. 2a, a built up of pressure in the pneumatic circuit was indeed observed anytime the sampling frequency exceeded the capability of the mass flow controller to adjust the flow-rates through the lines. Since substantial portions of the sample were allocated in the wrong reservoir, this effect was a source of errors in the measure of VOC fluxes when low thresholds were needed in the REA sampling. Tests performed in the field showed that overpressure problems were very limited with the system shown in Fig. 2b and a correct sampling was achieved at high frequencies in the range of flow-rates used by the traps (50 to 300 mL min⁻¹). The constancy of the flow-rate through the lines was checked with an electronic flow meter whose reading was continuously displayed in the screen of the personal computer.

To locate the sampling inlet as closed as possible to the wind sensor, the traps, the switching valves and the needle valves were all placed in a sampling head that could have been lifted to any height above the emission source. The sampling head was connected to a control unit and an aspirating pump, both placed at ground level, using tubes and electric cables 10 m long. Using a small elevator it was possible to locate the traps very close to the wind sensor (30 cm). The sampling head was cylindrically

shaped in order to limit the interference with the wind sensor. It was made by an aluminum tube 25 cm long and 4 cm wide. Traps were located in a compartment separated from the one containing the fast response valves and the needle valves. In this way, they were efficiently protected by the sun and by the heat generated by the valves. The trap inlets emerged from the upper part of the compartment through a conical head made by aluminum. To prevent the collection of rain and dust, short (3 cm × 0.5 mm I.D.) L-shaped glass tubes were placed at the trap inlet. The cylindrical housing was equipped with a small “wing” aligned with the main axis of the tube. Using this simple device, the sampling head, that was free to rotate along the main axis, was able to follow the direction of the horizontal wind speed. This made it possible to fix the traps in such a way that the direction of the air flow was always perpendicular to that of the horizontal wind. A sonic anemometer (Gill Instrument, Lymington, UK) was used as a wind sensor. An interface was developed to transfer the data from the sonic anemometer to the computer and to send the signals to the actuating valves. The system was able to calculate the σ values and to update the thresholds to be used for conditional sampling every 3 min.

2.2. Description of the sampling site

Flux measurements of biogenic and anthropogenic VOCs were performed in an oak (*Quercus ilex* L.) forest located inside the presidential estate of Castelporziano (Rome, Italy) having a total surface of 6000 hectares. The area was selected because of the wide number of Mediterranean ecosystems present in it and the low changes to which the forest composition was subjected since the Roman empire. Although the presidential estate is a restricted area, a consistent number of people is permanently living in it. Most of them are farmers managing the land and the forest to prevent damages caused by accidental fires and wild animals. The human presence in the site and the activities related to the forest management could have occasionally generated the emission of anthropogenic VOCs.

The REA system was placed 4 m above the canopy, on the top of a 12-m tower equipped with

sensors for the measure of meteorological parameters and with apparatuses for measuring water, CO₂ and latent heat fluxes by eddy correlation. With this arrangement, a fetch (i.e. the distance around the tower that was sensed by the REA system) was estimated to range from 300 to 750 m as a function of the stability conditions occurring over the canopy. Due to the vicinity of the sea and the flat configuration of the terrain, the site was experiencing moderate to strong advection and average values of the fetch larger than 500 m were estimated to occur for most of the time. VOC fluxes were measured from February 1997 to June 1998 by collecting three REA samples twice a week between 11:00 a.m. and 2 p.m.. Daily trends were also recorded for each season. They were measured in days when meteorological conditions representative of the whole season were observed.

2.3. Traps used for VOC collection and their analysis by GC-MS

REA samples were enriched on glass tubes (15 cm × 0.3 cm I.D.) filled with a bed of Carbopack C (34 mg) set in series with a bed of Carbopack B (170 mg). All packing materials were supplied by Supelco (Bellefonte, PA, USA). The particle size was ranging between 20 and 40 mesh. Air volumes ranging from 2 to 4 L were usually accumulated in the up and down traps. At the flow-rate used (250–300 mL min⁻¹), collection times of the order of 30 min to 1 h were necessary to get the amount of material suitable for the analysis. This sampling time was necessary because only 60% of the total volume were actually sampled in the up and down reservoirs. The rest was enriched in the dummy trap. The analysis of volumes collected in the up and down reservoirs was also very important as it provided essential information to check if the stationarity conditions required by the REA theory ($\bar{w} = ca. 0$) were met during sampling. As a general guideline, were considered good samples for flux determination only those in which the difference between the volumes collected in the up and down reservoirs were smaller than 15%. Traps used allowed to determine the fluxes of all VOCs having volatility lower than *n*-pentane [10]. They were preferred to

the ones having stronger adsorbents because preliminary investigations carried out with branch enclosures [10–12] clearly indicated that no substantial release of isoprene occurred from the vegetation species responsible for the emission of VOCs in the ecosystem investigated. No ozone scrubbers were used to prevent possible decomposition of biogenic VOCs inside the adsorbent. Even though the use of ozone scrubbers would have allowed a more quantitative sampling of the most reactive monoterpenes [13], it would have prevented a quantitative evaluation of semi-volatile polar compounds such as carbonyls, alcohols and acids [14]. The determination of carbonyl compounds was considered particularly important for the carbon budget of VOCs because these components, which are ubiquitous in combustion sources, could also be released by the vegetation or formed over the canopy surface by reaction of the leaf surface with tropospheric ozone [15]. Interest on these components was increased by recent studies [16] which have unambiguously proven that the high concentrations of semi-volatile carbonyls observed in forest areas are not generated by sampling artifacts, as it was believed for long time, but they were actually present in the atmosphere.

Before use, tubes were conditioned at a temperature of 300 °C under a mild flow of inert gas (helium) and sealed with metal connectors. They were stored in tight glass containers to prevent contamination during transport from the laboratory to the site. After sampling, tubes were flushed with 200 mL of helium to remove oxygen and water and CO₂ from the surface. They were then sealed and stored in tight glass containers. Traps were kept in the refrigerator until they were analyzed. Analysis was performed no later than 2 days after sampling. Tubes were thermally desorbed using a Chrompack TCT/PT1 CP4001 desorption unit. Compounds were completely released by carbon adsorbents by increasing the temperature of the traps from 25 to 235 °C in 2.5 min. They were first cryofocused on a silica liner maintained at –150 °C and then transferred into the GC column by heating the liner to 200 °C in 30 s. The separation was accomplished on a 60 m capillary column (0.32 mm I.D.) internally coated with a thin film (0.25 μm) of DB-1, a dimethylethylpolysiloxane polymer. J&W (Folsom, CA, USA) supplied the column. The column was

maintained at 5 °C for 3 min, programmed to 50 °C at 3 °C min⁻¹ and then to 220 °C at 5 °C min⁻¹. A Hewlett-Packard (Palo Alto, CA, US) gas chromatograph model 5890 connected to a quadrupole mass spectrometer (Model 5970) supplied by the same company was used for the analysis. The mass spectrometer was operated in the scan mode. Selective identification of monoterpenes was achieved through the analysis of selected ions and the elution sequence determined by analyzing dilute liquid solutions of pure compounds into the traps. Subtraction techniques were used for quantifying coeluted components [10]. Weekly calibrations were performed to check the sensitivity and the linearity of the detector.

3. Results and discussion

The ability of the REA system to measure fluxes that were representative of the biogenic emission from the forest ecosystem investigated was tested by looking at the results that obtained with isoprenoid compounds emitted by vegetation. The first step was to check that the fluxes measured by our REA system were fully consistent with *Quercus ilex* L. emission in terms of composition and dependence from environmental factors. This was possible because the composition and emission behavior of this oak species were both well known from previous investigations. Enclosure studies performed at leaf and branch level [10–12,17] have unambiguously shown that *Quercus ilex* L. behaves differently from other oak species present in Europe, North America and Asia because it does not emit isoprene but only monoterpenes. The emission is triggered by light and temperature [11,12,17]. Studies conducted with ¹³C-labeled CO₂ have shown that the biosynthesis and emission of monoterpenes in *Quercus ilex* L. leaves are as fast as those of isoprene produced by other oaks [18]. In contrast with the mechanism used by coniferous trees, synthesized monoterpenes are not stored in specialized organs, but they are rapidly released through the stomata. Because of this, short term variations of *Quercus ilex* L. emission can be described by the same light and temperature dependent algorithm followed by isoprene emitting oaks [11,12]. The algorithm originally developed by

Guenther et al. [19] (also called G93 algorithm), states that:

$$E = E^\circ C_T C_L \quad (2)$$

where E is the monoterpene emission in mg m^{-2} (of leaf area) h^{-1} , E° is the so-called basal emission (i.e. the emission measured at 30°C and $1000 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ of the photosynthetic active radiation), also expressed in mg m^{-2} (of leaf area) h^{-1} , and C_T and C_L are empirical terms having the following form:

$$C_L = \frac{\alpha c_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \quad (3)$$

$$C_T = \frac{\exp\left(\frac{c_{T1}(T - T_s)}{RTT_s}\right)}{1 + \exp\left(\frac{c_{T2}(T - T_M)}{RTT_s}\right)} \quad (4)$$

In which Q is the photosynthetic active radiation (PAR) in $\mu\text{mol photons m}^{-2} \text{s}^{-1}$, T is leaf temperature in K, T_s is leaf temperature in K at standard condition (303 K), R is the gas constant in $\text{J K}^{-1} \text{mol}^{-1}$ (8.314) and the other terms are empirically determined coefficients having the following values: $\alpha = 0.027$, $c_{L1} = 1.066$, $c_{T1} = 95\,000 \text{ J mol}^{-1}$, $c_{T2} = 230\,000 \text{ J mol}^{-1}$ and $T_M = 314 \text{ K}$.

For vegetation species whose emission is triggered by the light, is possible to correlate canopy fluxes with leaf emission through the following simplified equation:

$$F = ELAI\rho\gamma_s \quad (5)$$

where the LAI is the leaf area index which converts the surface of forest into that of the emitting foliage, ρ is factor accounting for the part of the canopy that is actually exposed to sunlight and γ_s is a density factor accounting for the contribution of a given vegetation species to the overall emission. Since in our case, the flux is entirely determined by one vegetation species ($\gamma_s = 1$), it is possible to directly translate the emission into fluxes and we can write

$$F = F^\circ C_L C_T \quad (6)$$

where F° is the monoterpene flux measured when the portion of the canopy fully exposed to sunlight reaches a temperature of 30°C under light saturation

conditions ($\geq 1000 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$). By considering that in our case the LAI was 3.7 and the exposed part of the canopy about 20% of the total emitting biomass (close canopy), the expected basal flux was roughly estimated to be 72% of leaf basal emission. By knowing that the basal monoterpene emission (E°) of *Quercus ilex* L. measured in Castelporziano during summer is ca. 3.24 mg m^{-2} (leaf surface) h^{-1} [20], F° should be in the range of $2.34\text{--}2.88 \text{ mg m}^{-2} \text{h}^{-1}$ and diurnal variations of F should follow Eq. (6).

Before to test the consistency of monoterpene fluxes with theoretical predictions, it was important to check if the aerometric composition of monoterpenes reflected the one produced by *Quercus ilex* L. emission. Since emission studies carried out in the Castelporziano with branch enclosures were all performed in the summer season, the consistency between the composition of monoterpenes in air and that generated by the biogenic emission was checked by using REA data collected between July and August 1997. Accurate values of the percent monoterpene composition in air were obtained by analyzing air samples by reconstructed mass chromatography. The most used ions for monoterpene identification and quantification were the molecular ion (m/z 136), the fragment at m/z 93 (base peak) and the ion at m/z 67. In the case of overlapping compounds, subtraction techniques and additional ions were also used.

Fig. 3a show the total ion current (TIC) profiles that were recorded during the analysis of VOC collected in the up and down reservoirs during the REA sampling performed around noon of 31 July 1997. Fig. 3b reports the corresponding monoterpene profiles obtained by plotting the signal generated the ion with m/z 93. The content of overlapping compounds (namely compounds 12, 13 and 14 in Fig. 3b) was determined using different approaches. While the signals generated by ion with m/z 154 were used to quantify 1,8-cineol, subtraction techniques were used to quantify β -phellandrene in the presence of limonene.

In Table 1 are summarized the difference in percent monoterpene composition measured in air and in the emission source. The emission composition used in the table was taken from ref. [12]. It refers to a study performed in Castelporziano using

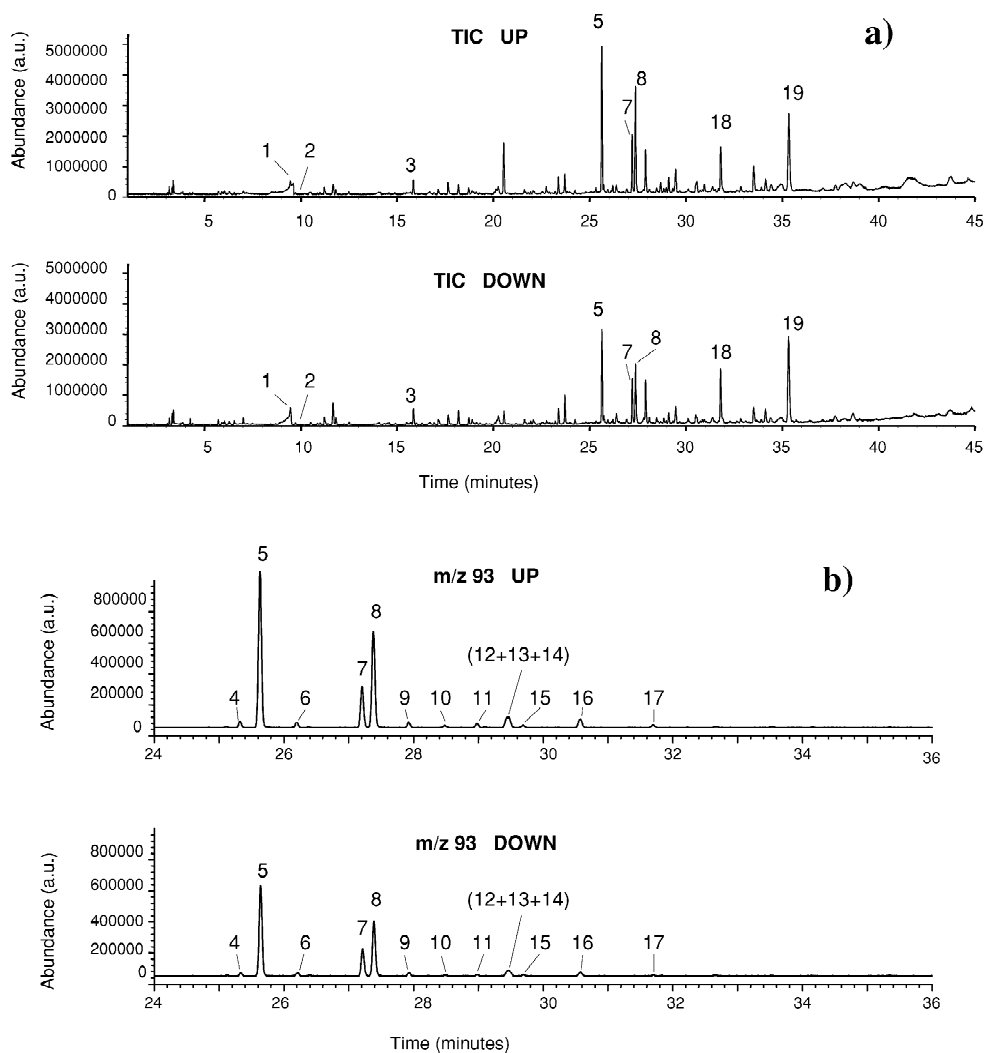


Fig. 3. (a) Typical total ion current (TIC) profiles obtained by submitting to GC–MS determination the up and down samples collected with the REA system; (b) selected ion current profiles obtained by plotting the ion generated by the fragment with m/z 93. Numbers refer to: 1=benzene, 2=carbon tetrachloride, 3=toluene, 4= α -thujene, 5= α -pinene, 6=camphene, 7=sabinene, 8= β -pinene, 9=myrcene, 10= α -phellandrene, 11= α -terpinene, 12= β -phellandrene, 13=1,8-cineol, 14=limonene, 15=*cis*- β -ocimene, 16= γ -terpinene, 17= α -terpinolene, 18=nonanal, 19=decanal.

branch cuvettes flushed with ambient air. Even though these emission values did not differ too much (<10%) from those obtained using air free from ozone, they were used for our evaluation as they were more representative of the real situation experienced by the plant in the field. As it can be seen from the table, differences observed were rather

small and they confirmed that aerometric concentrations of monoterpenes in the site were essentially determined by *Quercus ilex* L. emission. They showed also that no substantial losses of monoterpenes occurred in the REA system because of chemical reactions in the atmosphere [9,21] or in the trapping materials [13].

Table 1

Average percent composition of monoterpenes in air and in *Quercus ilex* L. emission. Air samples were collected by the REA technique in summer 1997 whereas emission samples were collected from branch enclosures installed in Castelporziano in the Summer of 1994

Compound	Enclosure ^a		REA	
	Average (%)	SD (%)	Average (%)	SD (%)
Tricyclene	0.2	0.2	0.4	0.4
α -Thujene	1.9	0.4	1.2	0.3
α -Pinene	32.3	4.0	36.9	5.3
Camphene	3.1	1.0	2.3	0.5
Sabinene	8.8	3.0	10.6	2.0
β -Pinene	22.2	2.1	27.8	1.9
Myrcene	2.4	0.2	3.5	1.6
α -Pellandrene	1.0	0.5	0.3	0.2
α -Terpinenep	2.7	0.6	1.3	0.4
<i>p</i> -Cymene	4.2	1.0	2.6	0.6
1,8-Cineool	8.2	2.0	2.4	1.9
β -Phellandrene	1.0	0.5	1.5	0.8
Limonene	4.1	2.0	6.7	5.8
<i>cis</i> - β -Ocimene	–	–	–	–
<i>trans</i> - β -Ocimene	–	–	–	–
γ -Terpinene	4.5	2.0	1.9	0.5
Terpinolene	1.8	0.8	0.5	0.4
Linalool	0.4	0.1	–	–
4-Terpinenol	1.2	0.8	–	–

^a Data taken from ref. [12].

Also close to the expectation ($2.88 \text{ mg m}^{-2} \text{ h}^{-1}$) was the value of F° that was measured during the summer season when the portion of the canopy exposed to sunlight reached 30°C . Using this experimental value and the data of temperature and photosynthetic active radiation recorded during 31 July 1997, daily profiles of monoterpene fluxes measured by REA were compared with those predicted by using Eq. (6). Data reported in Table 2 show that, within the experimental errors, a good agreement was found between measured and calculated fluxes. In this table are also indicated in brackets the emission values in $\text{mg C m}^{-2} \text{ h}^{-1}$. Such values have been inserted into the table because they are extremely useful to assess the net carbon budget of the forest ecosystem.

When the G93 algorithm was used to predict the seasonal variation of monoterpene fluxes from the *Quercus ilex* L stand, large deviations were observed

between predictions and observations. As can be seen from Table 3, values obtained by using the G93 algorithm largely exceeded the measured values during the spring and winter season. This suggested that changes in the basal emission (and hence in the basal flux) could have occurred in *Quercus ilex* L. leaves and an additional term accounting for the seasonality of F° should have been introduced in the G93 algorithm. A regression analysis performed on the available data sets showed that seasonal variations of monoterpene fluxes were better described if the following seasonality term was introduced in Eq. (6):

$$C_s = \exp\left(\frac{(a-t)^2}{2b^2}\right) \quad (7)$$

in which t is the Julian day and a and b are two empirical terms having a value of 170.538 and 75.033, respectively. In Table 3, observed monoterpene fluxes are compared with the ones obtained by introducing the correction term C_s in Eq. (6).

The ability of REA fluxes to represent the seasonal variations of *Quercus ilex* L. emission has been fully confirmed by a recent laboratory study [22] in which the basal emission of several leaves has been measured from sprout to abscission. According to this study, a strong seasonality in the basal monoterpene emission was observed in the two years in which *Quercus ilex* L. leaves were investigated. Although slightly different seasonality terms were derived for young and old leaves (the average life of *Quercus ilex* L. leaves is less than two years), the correction term necessary to describe variations of a 1/1 combination of old and young leaves was basically the same as to that of Eq. (7).

Once proved that the REA system provided reliable value of monoterpene fluxes, research on VOC exchange over the forest ecosystem was extended to those components (arenes and alkanals) whose fluxes were comparable to those of monoterpenes released by the *Quercus ilex* L. stand. In addition to these compounds, fluxes of CCl_4 were also investigated. Since this halogenated component is only produced by man-made sources, a homogeneous distribution was expected in the boundary layer when no anthropogenic activities were performed inside the fetch seen by the REA system. Under these conditions,

Table 2

Daily variations of canopy fluxes of total monoterpenes and α -pinene ($\text{mg m}^{-2} \text{h}^{-1}$) measured by REA and calculated using the light and temperature algorithm (G93)^a

Sampling time		Measured			Calculated using the G93 algorithm		
Start	End						
Total monoterpenes							
7:30	8:30	0.94	(0.83)	± 0.01	0.44	(0.39)	± 0.05
9:30	10:30	2.17	(1.92)	± 0.01	1.50	(1.32)	± 0.18
10:25	11:25	2.42	(2.14)	± 0.01	1.75	(1.55)	± 0.21
11:40	12:40	3.13	(2.76)	± 0.01	3.37	(2.97)	± 0.40
13:00	14:00	3.07	(2.71)	± 0.01	3.27	(2.88)	± 0.39
14:10	15:10	2.66	(2.34)	± 0.01	2.95	(2.60)	± 0.35
15:25	16:25	2.11	(1.86)	± 0.01	2.69	(2.37)	± 0.32
16:35	17:35	2.19	(1.93)	± 0.01	2.36	(2.09)	± 0.28
17:45	18:45	0.86	(0.76)	± 0.01	1.46	(1.28)	± 0.17
18:55	19:55	0.27	(0.24)	± 0.01	0.49	(0.43)	± 0.06
α -Pinene							
7:30	8:30	0.39	(0.35)	± 0.01	0.16	(0.14)	± 0.02
9:30	10:30	0.91	(0.80)	± 0.01	0.55	(0.43)	± 0.07
10:25	11:25	0.95	(0.84)	± 0.01	0.65	(0.57)	± 0.08
11:40	12:40	1.29	(1.14)	± 0.01	1.25	(1.10)	± 0.15
13:00	14:00	1.36	(1.20)	± 0.01	1.21	(1.07)	± 0.15
14:10	15:10	1.11	(0.98)	± 0.01	1.09	(0.96)	± 0.13
15:25	16:25	0.71	(0.63)	± 0.01	0.99	(0.88)	± 0.12
16:35	17:35	0.88	(0.77)	± 0.01	0.87	(0.77)	± 0.10
17:45	18:45	0.38	(0.34)	± 0.01	0.54	(0.48)	± 0.06

^a Data were collected in the *Quercus ilex* L. stand of Castelporziano (Rome, Italy) in 31 July 1997. In brackets are reported the corresponding fluxes expressed in $\text{mg C m}^{-2} \text{h}^{-1}$. Basal emissions of 2.88 and 1.07 $\text{mg m}^{-2} \text{h}^{-1}$ were used for the calculation of total monoterpenes and α -pinene, respectively. The corresponding values in $\text{mg C m}^{-2} \text{h}^{-1}$ were 2.54 (total monoterpenes) and 0.94 (α -pinene).

very small fluxes (equal or lower than $\pm 0.01 \text{ mg m}^{-2} \text{h}^{-1}$) should have been measured for this component.

Data reported in Table 4 show that not always fluxes of CCl_4 were consistent with the lack of anthropogenic sources inside the forest. Unusually high positive fluxes were indeed measured in February and April 1997. The fact that they were mirrored by high positive fluxes of benzene and toluene was taken as an indication that anthropogenic emission was taking place near the sampling site. The arene composition strongly supported these conclusions. It was found that the ratios between the fluxes of toluene and benzene measured in the first 3 months of the year closely approached those typically observed in fresh anthropogenic emission. Ratios ranging from 4 to 2 are in fact quite close to those measured in combustion sources not consumed by photochemical processes. Since these sources also contain semi-volatile carbonyls in a variable amount (semi-volatile carbonyls have been found in the

emission of gasoline and diesel engines and biomass burning), it is not surprising that the highest fluxes of nonanal and decanal were also recorded in this period. The most likely sources for these components are man-made activities linked to the management of the forest. Indeed, this is the time of the year in which dead trees are cut and short vegetation inside the forest is harvested and burned.

This explanation is supported by the drastic decay in the fluxes of arenes and CCl_4 observed in the summer months. In this part of the year, an almost homogeneous distribution of CCl_4 in the atmospheric boundary layer was coupled with rather small fluxes of arenes characterized by toluene–benzene ratios equal or lower than 0.5. These values are typical of anthropogenically polluted air masses that were subjected to severe aging before reaching the site.

The lack of fresh anthropogenic emission was only partly confirmed by the data of semi-volatile carbonyls as they showed an increase in fluxes during the month of August. The decoupling of arene, CCl_4

Table 3

Seasonal variations of canopy fluxes of total monoterpenes and α -pinene ($\text{mg m}^{-2} \text{h}^{-1}$) measured by REA and calculated using the original light and temperature algorithm (G93) and the one corrected for the seasonality (for the equations see the text)^a

	Measured			G93 corrected for seasonality			G93 non-corrected		
Total monoterpenes									
February	0.01	(0.01)	± 0.01	0.01	(0.01)	± 0.01	0.24	(0.21)	± 0.04
March	0.04	(0.03)	± 0.01	0.05	(0.04)	± 0.01	0.38	(0.33)	± 0.06
April	0.07	(0.06)	± 0.01	0.15	(0.13)	± 0.02	0.58	(0.51)	± 0.08
May	0.36	(0.32)	± 0.01	0.60	(0.53)	± 0.08	1.35	(1.20)	± 0.18
June	–	–		1.34	(1.18)	± 0.10	2.00	(1.76)	± 0.23
July	2.37	(2.09)	± 0.01	1.85	(1.63)	± 0.12	2.12	(1.87)	± 0.24
August	3.07	(2.70)	± 0.01	3.08	(2.72)	± 0.20	3.11	(2.74)	± 0.29
September	1.56	(1.38)	± 0.01	2.14	(1.89)	± 0.15	2.20	(1.94)	± 0.24
October	0.72	(0.64)	± 0.01	1.11	(0.98)	± 0.11	1.34	(1.18)	± 0.20
November	0.18	(0.16)	± 0.01	0.28	(0.24)	± 0.05	0.45	(0.40)	± 0.05
December	0.04	(0.03)	± 0.01	0.08	(0.07)	± 0.02	0.20	(1.17)	± 0.03
1998									
January	–	–		0.04	(0.03)	± 0.01	0.18	(0.16)	± 0.03
February	–	–		0.01	(0.01)	± 0.01	0.21	(0.19)	± 0.04
March	0.04	(0.03)	± 0.01	0.06	(0.05)	± 0.02	0.47	(0.41)	$0.07 \pm$
April	0.04	(0.03)	± 0.01	0.15	(0.13)	± 0.02	0.59	(0.52)	± 0.06
May	–	–		0.87	(0.77)	± 0.10	1.95	(1.72)	± 0.23
June	1.49	(1.31)	± 0.01	1.49	(1.31)	± 0.10	2.81	(2.48)	± 0.24
α -Pinene									
February	0.01	(0.01)	± 0.01	<0.01	(<0.01)	± 0.01	0.09	(0.08)	± 0.01
March	0.01	(0.01)	± 0.01	0.02	(0.02)	± 0.01	0.14	(0.12)	± 0.02
April	0.01	(0.01)	± 0.01	0.06	(0.05)	± 0.01	0.21	(0.19)	± 0.03
May	0.11	(0.10)	± 0.01	0.22	(0.20)	± 0.04	0.50	(0.44)	± 0.07
June	–	–		0.50	(0.44)	± 0.04	0.74	(0.65)	± 0.09
July	0.85	(0.75)	± 0.01	0.69	(0.60)	± 0.08	0.78	(0.69)	± 0.09
August	1.22	(1.08)	± 0.01	1.14	(1.00)	± 0.06	1.15	(1.01)	± 0.11
September	0.63	(0.56)	± 0.01	0.79	(0.70)	± 0.04	0.81	(0.72)	± 0.09
October	0.30	(0.27)	± 0.01	0.41	(0.36)	± 0.04	0.49	(0.44)	± 0.07
November	0.07	(0.06)	± 0.01	0.10	(0.09)	± 0.02	0.17	(0.15)	± 0.02
December	0.01	(0.01)	± 0.01	0.03	(0.03)	± 0.01	0.07	(0.06)	± 0.01
1998									
January	–	–		0.01	(0.01)	± 0.01	0.07	(0.06)	± 0.01
February	–	–		<0.01	(<0.01)	± 0.01	0.08	(0.07)	± 0.01
March	0.02	(0.01)	± 0.01	0.02	(0.02)	± 0.01	0.17	(0.15)	± 0.03
April	0.01	(0.01)	± 0.01	0.06	(0.05)	± 0.01	0.22	(0.19)	± 0.02
May	–	–		0.32	(0.28)	± 0.03	0.72	(0.64)	± 0.09
June	0.56	(0.50)	± 0.01	0.62	(0.55)	± 0.04	0.93	(0.82)	± 0.08

^a In brackets are reported the corresponding fluxes expressed in $\text{mg C m}^{-2} \text{h}^{-1}$. Basal emissions of 2.88 and 1.07 $\text{mg m}^{-2} \text{h}^{-1}$ were used for the calculation of total monoterpenes and α -pinene, respectively. The corresponding values in $\text{mg C m}^{-2} \text{h}^{-1}$ were 2.54 (total monoterpenes) and 0.94 (α -pinene).

and semi-volatile carbonyls suggested that other sources than those associated with anthropogenic emissions were responsible for the observed emission of nonanal and decanal in this particular month. Since August is the month of the year when the highest levels of ozone are reached in Central Italy, it is possible that positive fluxes of semi-volatile

carbonyls were generated by ozonolysis reactions occurring at the leaf surface [15]. It is also possible that increased emission of nonanal and decanal was coming from the short vegetation growing below the trees. It has been reported that shrubs can emit these components during the senescence period that usually occurs in late summer [23]. Whichever the source

Table 4
Seasonal variations of VOC fluxes over the *Quercus ilex* L. stand of Castelporziano measured in the year 1997^a

Most abundant monoterpenes															
	α -Pinene			β -Pinene			Sabinene			Limonene		β -Phellandrene			
February	0.01	(<0.01)	± 0.01	<0.01	(<0.01)	± 0.01	<0.01	(<0.01)	± 0.01	-0.01	(<-0.01)	± 0.01	<0.01	(<0.01)	± 0.01
March	0.01	(0.01)	± 0.01	<0.01	(<0.01)	± 0.01	<0.01	(<0.01)	± 0.01	0.02	(0.02)	± 0.01	<0.01	(<0.01)	± 0.01
April	0.01	(0.01)	± 0.01	0.01	(0.01)	± 0.01	0.01	(0.01)	± 0.01	0.01	(0.01)	± 0.01	<0.01	(<0.01)	± 0.01
May	0.11	(0.10)	± 0.01	0.10	(0.08)	± 0.01	0.03	(0.03)	± 0.01	0.06	(0.05)	± 0.01	<0.01	(<0.01)	± 0.01
June	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
July	0.85	(0.75)	± 0.01	0.59	(0.52)	± 0.01	0.22	(0.19)	± 0.01	0.14	(0.12)	± 0.01	0.06	(0.05)	± 0.01
August	1.22	(1.08)	± 0.01	0.88	(0.78)	± 0.01	0.30	(0.26)	± 0.01	0.11	(0.09)	± 0.01	0.07	(0.06)	± 0.01
September	0.63	(0.56)	± 0.01	0.39	(0.34)	± 0.01	0.10	(0.09)	± 0.01	0.08	(0.07)	± 0.01	0.04	(0.03)	± 0.01
October	0.30	(0.27)	± 0.01	0.21	(0.19)	± 0.01	0.07	(0.07)	± 0.01	0.02	(0.02)	± 0.01	0.01	(0.01)	± 0.01
November	0.07	(0.06)	± 0.01	0.03	(0.03)	± 0.01	<0.01	(<0.01)	± 0.01	0.03	(0.02)	± 0.01	0.01	(0.01)	± 0.01
December	0.01	(0.01)	± 0.01	0.01	(0.01)	± 0.01	<0.01	(<0.01)	± 0.01	0.02	(0.01)	± 0.01	<-0.01	(<-0.01)	± 0.01
Other VOCs															
	Benzene			Toluene			Nonanal			Decanal		CCl ₄			
February	0.22	(0.20)	± 0.01	0.18	(0.16)	± 0.01	-0.84	-(0.64)	± 0.01	-1.59	-(1.22)	± 0.01	0.05	(<0.01)	± 0.01
March	0.03	(0.02)	± 0.01	0.06	(0.05)	± 0.01	0.29	(0.22)	± 0.01	0.43	(0.33)	± 0.01	0.01	(0.01)	± 0.01
April	0.39	(0.36)	± 0.01	0.77	(0.70)	± 0.01	0.72	(0.55)	± 0.01	0.87	(0.67)	± 0.01	0.11	(<0.01)	± 0.01
May	0.06	(0.06)	± 0.01	0.02	(0.02)	± 0.01	0.31	(0.24)	± 0.01	0.24	(0.19)	± 0.01	0.02	(<0.01)	± 0.01
June	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
July	0.02	(0.02)	± 0.01	0.01	(0.01)	± 0.01	-0.06	-(0.04)	± 0.01	0.16	(0.13)	± 0.01	0.02	(<0.01)	± 0.01
August	0.02	(0.02)	± 0.01	0.01	(0.01)	± 0.01	0.14	(0.10)	± 0.01	0.32	(0.25)	± 0.01	<-0.01	(<0.01)	± 0.01
September	0.07	(0.06)	± 0.01	-0.01	-(0.01)	± 0.01	0.02	(0.01)	± 0.01	0.01	(0.01)	± 0.01	0.01	(<0.01)	± 0.01
October	0.04	(0.03)	± 0.01	0.05	(0.04)	± 0.01	<-0.01	(<-0.01)	± 0.01	<-0.01	(<-0.01)	± 0.01	0.01	(<0.01)	± 0.01
November	0.06	(0.06)	± 0.01	0.13	(0.12)	± 0.01	0.16	(0.12)	± 0.01	0.23	(0.18)	± 0.01	0.03	(<0.01)	± 0.01
December	0.12	(0.11)	± 0.01	0.52	(0.48)	± 0.01	0.06	(0.15)	± 0.01	0.03	(0.01)	± 0.01	<0.01	(<0.01)	± 0.01

^a Data are given in $\text{mg m}^{-2} \text{h}^{-1}$. In brackets are reported the values in $\text{mg C}^{-2} \text{h}^{-1}$.

of semi-volatile carbonyls in August is, it seems to be associated with vegetation processes and not related to anthropogenic emissions.

4. Conclusions

The study conducted in the Mediterranean forest ecosystem has clearly shown that the REA technique, in combination with GC–MS, can be successfully used to investigate emission and deposition processes of VOCs in the troposphere. By considering that more than 300 components present in air samples can be identified by GC–MS [17], the proposed technique has a great potential for investigating the exchange of organic compounds between the earth surface and the atmosphere. By extending the retention capabilities of the adsorption traps, the REA technique shown in Fig. 2b has been successfully used for measuring the isoprene fluxes from a primary tropical rainforest of the Amazon basin [24]. Values as high as $2.88 \text{ mg m}^{-2} \text{ h}^{-1}$ were detected for this component at the end of the dry season. In such a pristine environment, where no anthropogenic emissions occurs outside the burning period, isoprene emission was concurrent with strong deposition of arenes and carbonyl compounds.

The potential of REA can be further expanded if other collection systems (such as filters, liquid solutions, denuders and other chemically coated devices) than adsorption traps are used for the accumulation of the sample and different high-resolution separation techniques (such as liquid chromatography or capillary electrophoresis) are exploited for the analysis. With such combinations it would be also possible to measure fluxes of biogenic and anthropogenic compounds dispersed in suspended particles and aerosols.

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