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Article

Temporal and spatial variability of volatile organic compounds in the forest atmosphere

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Abstract: Forest healing effects are increasingly valued for their contribution to human psychological and physiological health, motivating further advances aimed at improving the knowledge of the relevant forest resources. Biogenic volatile organic compounds, emitted by the plants and accumulating in the forest atmosphere, are essential contributors to the forest healing effects, and represent the focus of this study. Using a photoionization detector, we investigated the high frequency variability, in time and space, of the concentration of total volatile organic compounds, on a hilly site, as well as along forest paths and long hiking trails on Italian northern Apennines. The scale of concentration variability was found to be comparable to absolute concentration levels, within time scales of less than one hour, and spatial scales of several hundred meters. During daylight hours, the concentration peaked from noon to early afternoon, followed by early morning, with lowest levels in late afternoon. Based on a conceptual model, these results were related to meteorological variables, including the atmospheric vertical stability profile. Moreover, preliminary evidence pointed to higher concentration of volatile organic compounds in forests dominated by conifer trees, in comparison with pure beech forests.

Keywords: bioactive compounds; forest air; forest bathing; forest therapy; hiking trails; human health; monoterpenes; stress; volatile organic compounds.

1. Introduction

A recent Australian study showed that the improvement of the mental health of visitors of the national protected areas translated into savings of about 7.5% of the aggregate costs of poor mental health, in turn amounting to about 10% of global domestic product (GDP) [1]. The annual health services value of Australia's national parks was estimated at the level of about US$100 billion, *i.e.*, about 7.5% of Australia's GDP, 1.6 times the entire annual turnover of Australia's tourism industry, and two orders of magnitude larger than the aggregate annual budget of Australia's national parks agencies [1]. The global projection showed that this specific ecosystem service value amounted to at least US$6 trillion per year, or about 8% of global gross national product (GNP) in 2017. These figures are more than sufficient to motivate any contribution to increase the efficiency, and possibly to widen

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the scope, of natural and protected areas about the improvement of human health, either mental or physiological.

Plenty of recent evidence supports the value attributed to accessible natural areas. Physiological measurements integrated with psychological analyses demonstrated the significant positive effects on mental health, especially in people with depressive tendencies [2–4]. Even pure psychological studies confirmed remarkable improvements in mood, decrease in the anxiety and stress levels [5–7], and a decreased risk of psychosocial stress-related diseases [8–10].

Attention continued to grow in recent years towards using the forest environment not only for leisure but also for health purposes [11]. Forest bathing, or forest therapy, derived from the Japanese *Shinrin-Yoku*, is a kind of forest recreation, either assisted by specialists or not, traditionally practiced in Japan for improving physical and mental health, as well as a remedy for stress [12]. The term *Shinrin-yoku* was coined by the Japanese Ministry of Agriculture, Forestry, and Fisheries in 1982 [13], to define the practice of walking in the woods immersing oneself in nature by mindfully using all five senses [6].

Several elements of the forest environment can positively affect the human psychological and physiological conditions. Indeed, forest healing effects can arise from visual, olfactive, auditory, and tactile stimulations, related to elements such as aromatic volatile substances (phytoncides) and the scent of wood, the sound of stream water, and the landscape [12,14]. Even the only visual stimulation with forest imagery showed psychologically and, often, physiologically positive effects [15], including children [16], with a significant dependence on the presented landscape, for example, natural areas with some artifacts suggesting accessibility showed higher effectivity [17]. Likely, the rather surprising effects from simple imagery derived from the human ancestral habit to live in natural environment [12].

On the physiological side, the forest environment showed anti-hypertensive effects [9,18,19], and promoted the regularization of the hearth rate variability [13,20], including in middle-aged and elderly individuals [21]. The psychological effects found a physiological correspondence in the reduction of stress hormones, such as adrenaline, noradrenaline, and cortisol [20,22,23].

Forest therapy showed efficacy in increasing the numerosity and activity of human natural killer cells, improving the immune system [24,25], with positive clinical and immunological effects in children affected by allergic diseases such as asthma and atopic dermatitis [26]. In diabetic patients, forest therapy was shown to decrease the blood glucose levels [27].

Based on the above-mentioned health effects, forest therapy was attributed a specific role in medical prevention. Healthcare programs based on forest therapy were developed in some countries [28], and recently recommended on a large scale, based on sound economic bases [1].

The natural inhalation of essential oils extracted from different trees, such as the monoterpenes (MTs) α-pinene and *d*-limonene, was attributed a distinct and important role with regards to increasing the numerosity and activity of human natural killer cells [24]. Indeed, it has been long known that MTs, while sparingly soluble in water, are soluble in blood and lipophilic tissues [29]. *In vivo* tests confirmed that the remarkable uptake of inhaled α-pinene in human body and blood circulation [30]. More recently, similar results were achieved in field tests, analyzing the serum of people walking in a conifer forest [31].

An extensive review of *in vitro*, *in vivo* and clinical studies, allowed to establish that the biological activities of the same essential oils, emitted by forest trees and accumulating in the forest air, denominated as biogenic volatile organic compounds (BVOCs), support the benefits of forest bathing [32]. Notably, different MTs, altogether constituting about 90% of the essential oils, showed significant specializations with regard to healing effects, such as antioxidant [33], anti-inflammatory, anti-tumorigenic [34,35], and neuroprotective [36–38].

BVOCs, low-molecular-weight compounds [39], are emitted by plant parts above and below the ground, as well as from leaf litter, soil microbes and insects, and show important functions for protection, defense and communication among plants, as well as between plants and other organisms [40]. All plant organs from flowers to roots can generate and release BVOCs [41], with leaves generally producing the highest emission rates [42].

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Overall, the most abundant BVOCs are isoprene (about 50% of the total global BVOCs per year) and MTs (about 15%) [43]. Terpenes, that consist of multiple isoprene units, are the largest class of organic compounds produced by various plants, with isoprene and MTs (two isoprene units), which are quite volatile, being the major components of forest aerosols [42].

Based on decades of studies, reliable catalogues of the BVOC emission potential of leaves and needles of major European forest tree species are nowadays available. Notably, trees able to store MTs, such as conifer species, are not necessarily the highest potential emitters, with deciduous trees typical of mountainous forests in European temperate areas, such as beech (*Fagus sylvatica*) and chestnut (*Castanea sativa*), greatly exceeding, at least potentially, widespread conifer species such as Norway spruce (*Picea abies*) and silver fir (*Abies alba*) [44]. However, some studies showed that conifers can be important emitters, as well as the respective typical MTs, among which α-pinene and d-limonene often stand out, are endowed with recognized and important biological activities [31].

Beyond the large differences among forest tree species, the study of the variability of BVOC emission rates are hindered by their high reactivity with other compounds in the atmosphere, and by the high variability of biosynthesis and emission mechanisms, leading to remarkable intraspecific differences in terpene emission, with regard to both total emissions and chemical profile [45]. Emission rates from leaves depend on several factors, such as physiological (age and developmental stage of plant), and physicochemical, *i.e.*, related to temperature, stomatal openness and leaf structure [46].

Temperature and light (radiation) were shown to be key environmental mechanisms for the synthesis and emission of BVOCs. Generally, isoprene emission is high dependent on light, as well as on temperature, due to its high volatility [46]. MTs emission may show different sensitivity to light and temperature, also depending on the presence or absence of storage structures [47]. In plants with BVOC storage compartments, the emissions are basically temperature-dependent, because temperature is able to volatilize compounds from stored pools, whereas in plants not storing BVOCs, the emissions rate is light and temperature dependent [48,49]. Temperature variability affects also the VOC fluxes from the forest floor [50].

A recent study performed by the Korea's National Center for Forest Therapy focused on the variability of BVOCs concentration in the atmosphere of a *Pinus densiflora* forest, on a fixed site, during daylight hours (one hour measurements starting at 8 am, noon, and 5 pm), and once a month for a year [51]. The study was motivated by the consideration of BVOCs as one of the important resources of forest therapy, due to their wide-spectrum healing effects, and was carried out by means of absorbent tubes and subsequent desorption and gas chromatographic analysis.

A remarkable seasonal variability was found, with the concentration of total BVOCs highest in summer, followed by spring and fall, and lowest in winter. In summer, the relative concentration of α-pinene was also highest, showing that not only total BVOCs but also individual components may change seasonally. On a daily basis, BVOC concentrations were found to be increase from 8-9 am to 12 am–1 pm, and again, marginally, up to 5 pm, somehow contrary to previous studies, which found higher concentrations at sunrise and sunset. However, admittedly, the discrete sampling prevented from drawing definitive conclusions.

This study presents the results of few high frequency monitoring campaigns of total volatile organic compounds (TVOC) concentrations both on fixed sites and along paths (a forest path and few hiking trails), far from anthropogenic sources, each campaign carried out for several hours during daylight. Beyond the representativeness of the measurements of TVOCs with regard to BVOCs, such relative remoteness was deemed to minimize the reaction of terpenes with anthropogenic pollutants that, in contaminated environments such as urban forests, might enhance photochemical pollution [45], possibly offsetting the BVOCs related health benefits. No other previous studies investigated the variability of the concentration of TVOCs, or BVOCs, in the forest air with such a temporal and spatial detail, let alone along long paths (tens of km), spanning different elevations, climates, and forest compositions.

2. Materials and Methods

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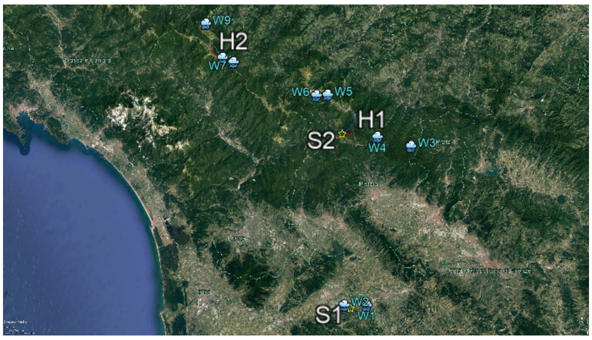
2.1. Measurement of volatile arganic compounds

TVOCs in the forest atmosphere were measured by means of a portable (0.72 kg) photoionization detector (PID, model Tiger VOC detector, Ion Science Ltd, Fowlmere, Royston, UK), with detection limits from 0.001 ppm (1 ppb) to 20,000 ppb. The PID was equipped with a pump, aspiring the ambient air at a rate of 220 mL/min, and an ultraviolet, 10.6 eV lamp allowing the ionization of organic substances in the aspired air, among which all MTs found in BVOCs. The resulting electric current flowing between two electrodes was measured and amplified, and transformed into a concentration level of the ionized substance or group of substances.

Factory's calibration was performed at the temperature of 21.5±0.1°C and atmospheric pressure, with respect to the substance isobutylene, with estimated measurement uncertainty of ±2%. The concentration of other substances was derived after the application of a response factor that, for TVOC, was equal to 1. While practically immediate, this detection method did not allow the identification of single compounds in TVOCs, which would require a gas chromatograph. This issue is discussed further in Section 4.

2.2. Study sites and weather stations

Figure 1(a-c) show the location of the study sites in a broad geographical context, across Tuscany and Emilia-Romagna regions, Italy, labeled as S1 (hilly site), S2 (forest path), both represented by yellow stars, H1 and H2 (hiking trails), represented by red and blue lines. The considered weather stations (W1 to W9) are represented too. Figure 1(b) shows the detail of area S1 (hilly site), and Figure 1(c) shows the detail of areas S2 (forest path), H1 and H2 (hiking trails).



(**a**)

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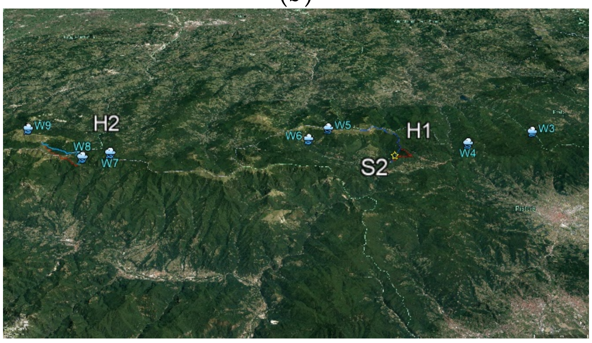

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(c)

Figure 1. (**a**) Study sites and weather stations in a broad geographical context (central and northern Tuscany, Italy); (**b**) Detail over the study site S1; (**c**) Detail over the study sites S2, H1 and H2. S1 and S2 are represented by yellow stars. H1 and H2 are represented by red and blue lines.

Table 1 shows the list of the study sites and the weather stations, along with the respective geographical coordinates (for weather stations), elevation, and data collected.

Table 1. List of study sites and weather stations.

ID	Type	Lat	Lon	Elevation	Data
S1 [1]	Hilly site	43°41'21.16"	10°50'08.38"	61 m a.s.l.	TVOC
W1	Weather station	43°40'48.00"N	10°53'00.40"E	117 m a.s.l.	W, GR [4]
W2	Weather station	43°40'48.00"N	10°49'00.80"E	102 m a.s.l.	T
S2 [2]	Forest path			960-1150 m a.s.l.	TVOC
H1 [2]	Hiking trail			960-1855 m a.s.l.	TVOC
W3	Weather station	44°01'12.00"N	11°01'00.80"E	950 m a.s.l.	GR
W4	Weather station	44°02'24.00"N	10°55'00.20"E	785 m a.s.l.	W
W5	Weather station	44°07'48.00"N	10°46'00.80"E	1716 m a.s.l.	T, W, RH
W6	Weather station	44°07'48.00"N	10°44'00.40"E	1000 m a.s.l.	T
H2 [3]	Hiking trail			1312-1816 m a.s.l.	TVOC
W7	Weather station	44°12'00.00"N	10°29'00.40"E	1637 m a.s.l.	T, W, GR
W8	Weather station	44°12'36.00"N	10°27'00.00"E	1297 m a.s.l.	T
W9	Weather station	44°16'55.56"N	10°24'00.10"E	2057 m a.s.l.	T, W

[1] Meteorological data from weather stations W1 and W2. [2] Meteorological data from weather stations W3, W4, W5 and W6. [3] Meteorological data from weather stations W7, W8 and W9. [4] Meteorological data abbreviations and units: T, air temperature 2 m above ground (°C); W, wind intensity 10 m above ground (ms^{-1}); RH, relative humidity 2 m above ground (%); GR, global radiation (Wm^{-2}).

All weather data were collected every 15 min and consisted of the average over the previous 15 min. The weather stations W1 to W8 belonged to the monitoring network of the Regional Functional Center for Weather – Hydrological Monitoring, Tuscany, Italy (http://cfr.toscana.it/). Weather station W9 belonged to the monitoring network of the "Reggio Emilia Meteo" association (http://www.reggioemiliameteo.it/), and the respective data (temperature and wind) were retrieved from the public web site.

2.3. TVOC, geographical and meteorological data: measurement, logging and merging

The measurement sessions on the fixed site S1 were carried out with PID's pump placed 1.2±0.1 m above the ground, such height corresponding approximately to the height of the nose of a 1.75 m tall person sitting on a chair. The measurement sessions along pathways (S2, H1 and H2) were carried out with the PID fixed on the backpack. The pump was again 1.2±0.1 m above the ground, and the paths were always traveled on foot, in order to avoid any contamination from engine exhaust gases. However, most of the routes could not be traveled by other means.

The PID logged data every 2 sec, with each data string consisting of the time of measurement and TVOC concentration level in ppm unit (mg/kg). For each measurement session, the lowest detected concentration (which could be positive or negative, due to the factory calibration used), was subtracted from all the other data, in order to remove, as far as possible, the background TVOC concentration level. Such background level likely included BVOC too, thus the resulting TVOC concentration levels could be considered as lower estimates of the actual BVOC concentration levels, especially due to the remoteness of the considered sites from any anthropogenic source.

While, in principle, changes of the levels of anthropogenic VOCs during time spans of few hours could not be ruled out, for example due to changes in the atmospheric vertical stability, or to changes in the emission rates from anthropogenic sources, the above-mentioned remoteness should keep such uncertainty at comparatively low levels. This topic is further discussed in Section 4. Finally, since this study aimed at a preliminary assessment of the relative variability in time and space of BVOC concentration levels within the forest atmosphere, the accurate assessment of the respective absolute concentration levels remains outside the scope.

Limited to the measurements along pathways, continuous geographic localization was performed by means of a Global Positioning System (GPS) software installed in a commercial smartphone (Open GPX Tracker, https://apps.apple.com/it/app/open-gpx-tracker/id984503772), with data logging every 7 sec, including the time of measurement, latitude and longitude. The height above sea level (a.s.l.) was assigned to each geographical point, based on the dataset of the National Aeronautics and Space Administration, Shuttle Radar Topography Mission (NASA's SRTM), 30 m horizontal resolution, by means of an online conversion software (GPS Visualizer, https://www.gpsvisualizer.com/convert_input). The PID and the smartphone were synchronized, then TVOC and geographical data were merged based on the respective measurement times, with TVOC data interpolated to the time points of the GPS data.

In order to assign to each TVOC data point, at any time, a complete set of meteorological data (temperature, global radiation and wind intensity), the data collected at the weather stations were interpolated as follows. At local elevations below or above the range of elevations of the considered stations, the air temperature measured at the nearest weather station was interpolated based on the local elevation, according to the standard vertical gradient in the lower troposphere of -0.6°C/100 m [52]. Otherwise, a linear interpolation to the local elevation was performed, based on data collected at the weather stations located at the closest elevations below and above the local one.

The wind intensity was linearly interpolated to the local elevation, based on two the weather stations located at elevations closest the local one. Global radiation data were available only at a single weather station for each study site. However, due to the observed low-level cloudiness around the ridge along the H1 hiking trail, the global radiation at elevations above 1600 m a.s.l. was corrected to a random level between 0 and 100 Wm^{-2} whenever the relative humidity at the weather station W5 was at the level of 95% or above. While this was a somehow arbitrary choice, adopted for representation purposes, the correction was imposed by the relative remoteness of the weather station W5 (measuring the global radiation), its location far below the mountain ridge, and the local character of the cloudiness over the ridge itself. The choice of adopting a random level between 0 and 100 Wm^{-2} – a range representative of cloudy conditions – was adopted for graphical representation purposes; however, knowing the exact level below 100 Wm^{-2} was practically useless for the purposes of this study. As discussed in Section 4, more accurate meteorological data will be needed in order to derive quantitative relationships between TVOC concentrations and meteorological data.

3. Results

3.1. Hilly site

3.1.1. Clear and calm days

Figure 2(a)-(c) show the TVOC concentration and weather data series for the hilly site, labeled as site S1 in Table 1, during days with generally clear skies, low wind (average wind intensity over 15 min lower than 3 m/s), and relatively high temperatures. TVOC concentration, temperature and global radiation are shown in Figures 2(a), 2(b) and 2(c), respectively.

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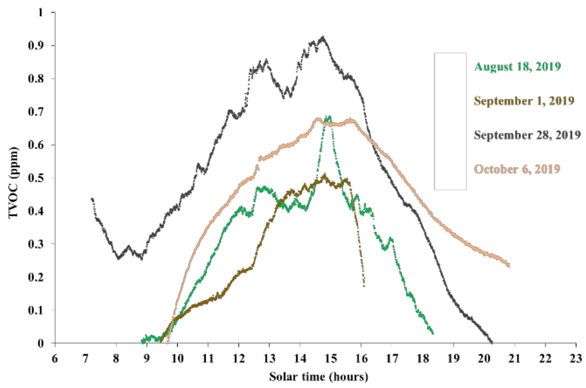
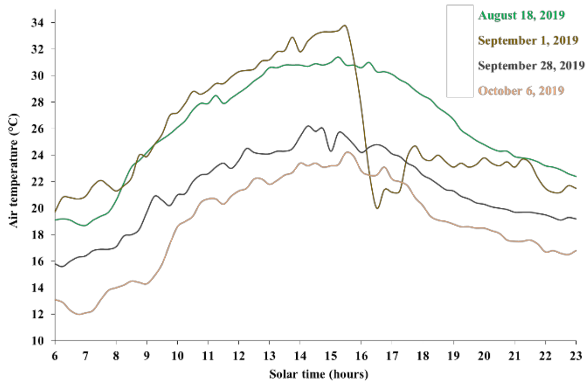


(**a**)



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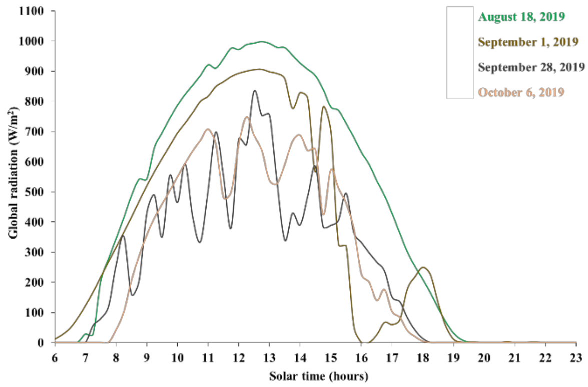

(**c**)

Figure 2. Data on site S1, during generally clear and calm days: (**a**) TVOC concentration; (**b**) Air temperature; (**c**) Global radiation.

The relative changes of the TVOC concentration, during any given day, spanned the range 0.5 to more than 0.9 ppm, *i.e.*, around the magnitude of the highest concentration levels commonly observed in the forest air [31]. During any given day, TVOC relative concentration appeared to peak during the time period 1-2 pm to 4 pm, solar time, seemingly following the peak air temperature, which lags behind peak radiation, rather than global radiation itself. However, dependence of TVOC concentration on radiation could not be ruled out, for example due to the accumulation and persistence of MTs in the lower atmosphere. Forest in site S1 was locally dominated by both evergreen trees (storing MTs), such as cypress and eucalyptus, and deciduous trees, such as oak and poplar, suggesting dependence on both temperature and radiation [47]. However, looking at different days, no evidence arose about any monotonic relationship between the maximum amplitude of the daily concentration cycle and the peak temperature.

Radiation could play a more remarkable role in late afternoon (approximately, after 4 pm), when air temperature decreased slowly and was still relatively higher than in the morning, while the TVOC concentration dropped much faster than the respective rate of increase observed in the morning.

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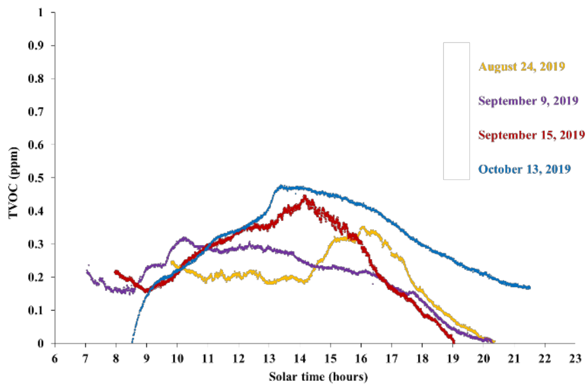
Likely, emissions from deciduous trees dropped quickly with the vanishing radiation. This could be confirmed based on the event occurred on September 1, 2019, when the sudden drop in the TVOC concentration, starting around 3:30 pm, followed the fast decrease of global radiation (related to a sudden storm approaching the site), with a short delay (about 30 min). The air temperature dropped too, however down to approximately the levels shown in the same time period during the days of September 28 and October 6, when the TVOC concentrations did not drop significantly.

Another important factor, contributing to explain the falling concentration in late afternoon, might be the effect of the lowering of radiation levels on the atmospheric vertical stability, especially during clear and calm days, thus on the diffusivity of aerial substances down to the ground. This topic will be discussed further in Section 4.

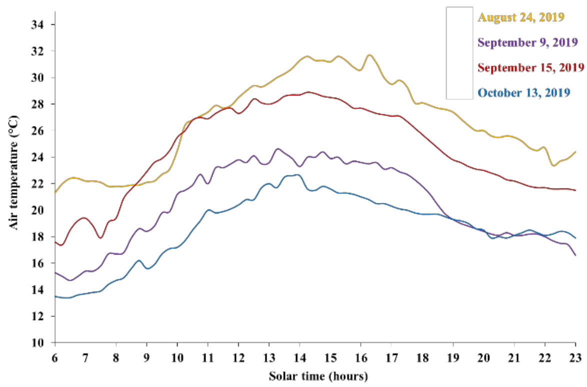
Finally, on September 28, 2019, the initial TVOC concentration (around 7 am) were relatively higher than the following levels, until about 10 am, despite lower radiation and air temperature. This behavior could be suggestive of some relationship between TVOC concentrations and other atmospheric properties, such as, again, the atmospheric vertical stability, which will be discussed further in Section 4.

3.1.2. Other days

Figure 3(a)-(d) show the TVOC concentration and weather data series for the hilly site, labeled as site S1 in Table 1, during days with generally cloudy skies, or lower temperatures, or relatively sustained wind. TVOC concentration, temperature, global radiation, and wind intensity are shown in Figures 3(a), 3(b), 3(c) and 3(d), respectively.



(a)



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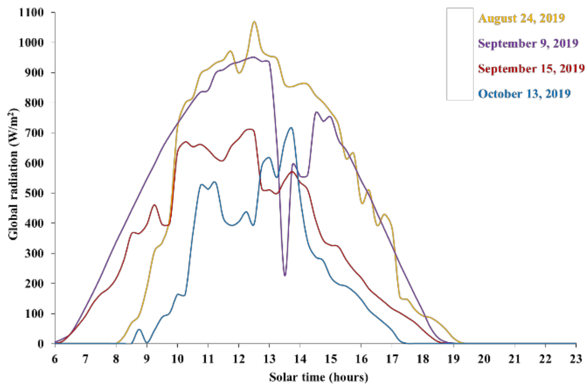

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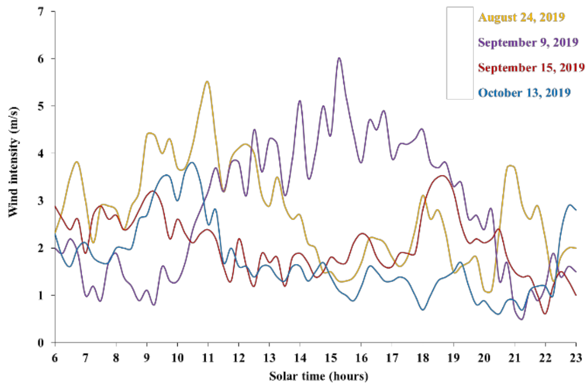

(**d**)

Figure 3. Data on site S1, during generally cloudy, colder or windy days: (**a**) TVOC concentration; (**b**) Air temperature; (**c**) Global radiation; (**d**) Wind intensity.

The relative changes of the TVOC concentration, during any given day, did not exceed 0.5 ppm, *i.e.*, substantially less than on clear and calm days. The global radiation was not much lower than in the clear days, although generally more irregular. The air temperature was generally lower, which – along with frequent drops in radiation – could explain the generally lower levels of the amplitude of TVOC concentration cycles.

On August 24, 2019, the delayed peak in the air temperature, around 4 pm, associates with the peak in TVOC concentration, which could have been favored also by the decreasing wind intensity and the relatively high radiation levels. On September 9, the sudden radiation drop after about 1 pm, and the simultaneous increase in the wind intensity, could have been the drivers of TVOC concentration decline after a weak peak around 10 am, when the wind was low and the radiation already sufficiently high.

During two days, September 9 and September 15, with measurements beginning early enough in the morning, when there was sufficient radiation (contrary to other days), and the wind was low, TVOC concentration was higher in the early morning (7-8 am) than in the following few hours. Again, this evidence possibly points to a relationship between TVOC concentration and the vertical atmospheric stability, which was already noted in Section 3.1.1, and will be discussed further in Section 4.

On the other hand, TVOC concentrations appeared to fall generally less steeply, in the afternoon, than in the clear and calm days considered in Section 3.1.1. Since the solar radiation affects the atmospheric vertical stability more substantially during clear and calm days, this behavior could be again suggestive of an important role played by the atmospheric vertical stability. This topic will be discussed further in Section 4.

3.2. Forest path

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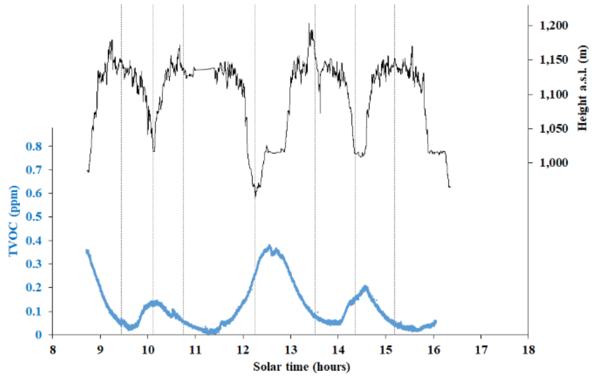
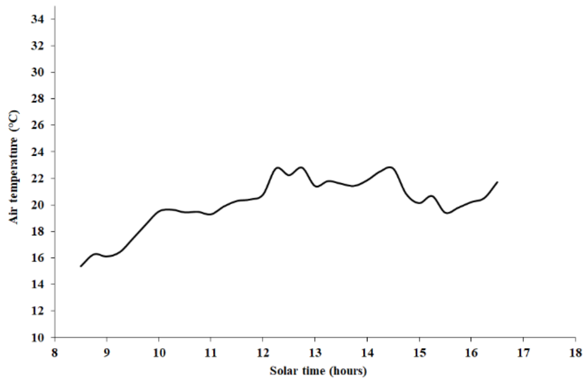
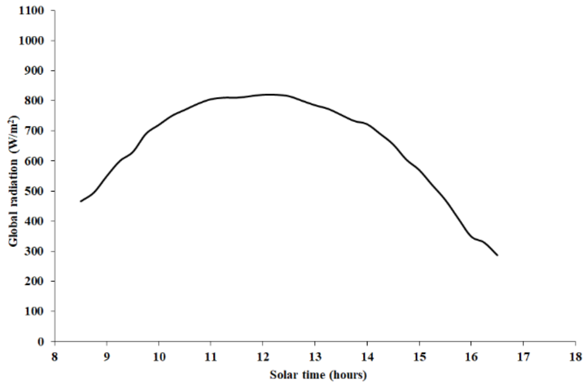
Figure 4(a)-(d) show TVOC concentration and weather data series for the forest path, labeled as site S2 in Table 1, measured on September 11, 2019.



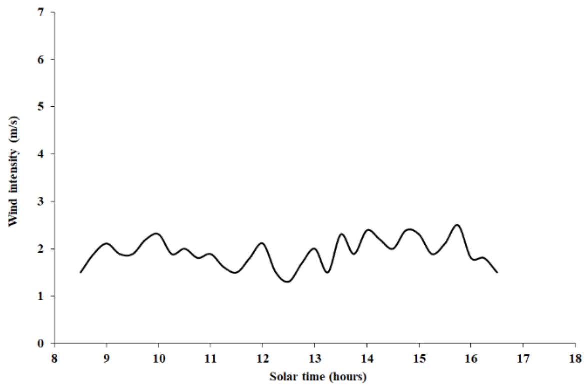
(**a**)



(**b**)



(**c**)



(**d**)

Figure 4. Data along forest path S2, on September 11, 2019: (**a**) Elevation and TVOC concentration; (**b**) Air temperature; (**c**) Global radiation; (**d**) Wind intensity.

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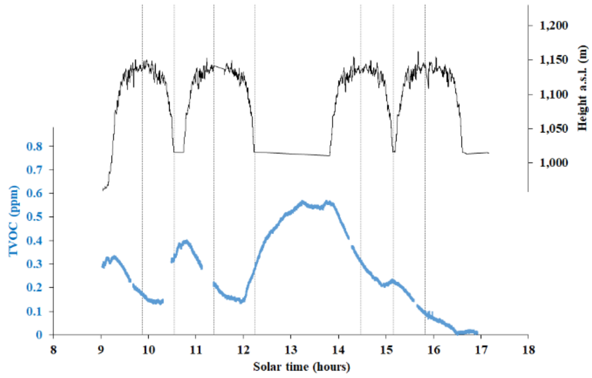
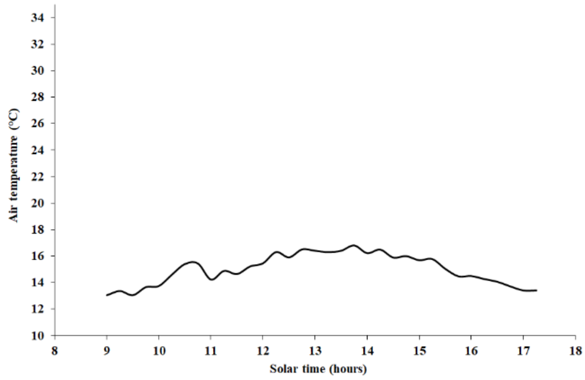
Based on global radiation and air temperature data series, that was a clear and calm day, with very low wind; air temperatures were in the range 16 to 23°C. The cyclical trend of the TVOC concentration, with local peaks around the lowest elevation of the forest path, and local minimums at the highest part of the path, points to a remarkable spatial variability, with a maximum amplitude around 0.4 ppm. Such variability could be related to either the air temperature (decreasing with the elevation at any fixed time), or the plant species and status, the soil emissions, and so on.

The above-mentioned peaks occurred at very different levels. In particular, TVOC concentration peaks were substantially higher in the early morning (before 9 am) and just after 12 am, than around 10 am, 2:30 pm and, even more, 4 pm. Similarly to the behavior observed in Section 3.1, temperature could have driven up TVOC emissions and concentrations during the hottest few hours of the day, while the radiation-driven atmospheric vertical stability could have affected the TVOC concentration levels near the ground in early morning (increase) and late afternoon (decrease).

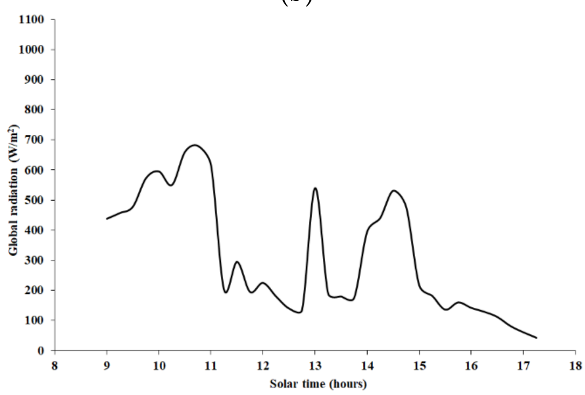
Figure 5(a)-(d) show TVOC concentration and weather data series for the same forest path, labeled as site S2 in Table 1, measured on October 5, 2019.



(a)



(b)



(c)

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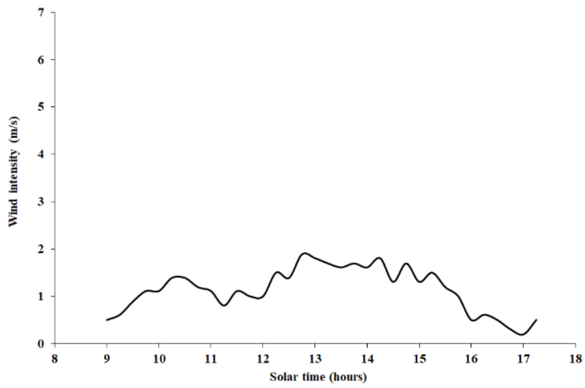


(**d**)

Figure 5. Data along forest path S2, on September 11, 2019: (**a**) Elevation and TVOC concentration; (**b**) Air temperature; (**c**) Global radiation; (**d**) Wind intensity.

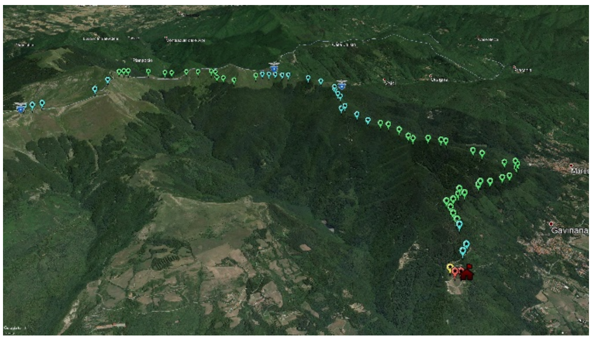
Based on weather data series, that was a calm day, with very low wind, but with alternation of cloudiness and sunny spells, as apparent in the radiation data. The air temperatures spanned the range about 13 to 17°C and no rain was observed during the day.

A cyclical trend of TVOC concentration appeared again, qualitatively very similar to the one observed in Figure 4, with local peaks around the lowest elevation of the forest path, local minimums at the highest part of the path, and maximum amplitude around 0.55 ppm. Such greater amplitude could have been due to the wild changes in radiation.

The absolute peak in TVOC concentration was again observed in early afternoon, in particular between 12:40 am and 2 pm, during a prolonged stop at the lowest site of the route. Interestingly, TVOC concentration increased by more than 0.25 ppm since the arrival at the lowest site, possibly following the sudden spike in radiation, with air temperatures around the peak of day. The second peak in radiation occurred around the highest elevation site of the route (around 2:30 pm), and could have helped to retain a relatively high concentration level. The subsequent fast drop in radiation could explain the substantial absence of further peaks at the lowest site.

3.3. Hiking trails

Figure 6(a)-(e) show TVOC concentration, both superimposed on a topographic map and as a chart, and weather data series, for the uphill part of the hiking trail labeled as H1 in Table 1, measured on October 12, 2019. The lowest TVOC concentration level in Figure 6(a) is above zero because the offset was computed over the whole day, *i.e.*, over the entire hiking trail, including the downhill part, which is described below. The first part of the route, labeled as A in Figure 6(b), coincided with the forest path (site S2 in Table 1) analyzed in Section 3.2.



(**a**)

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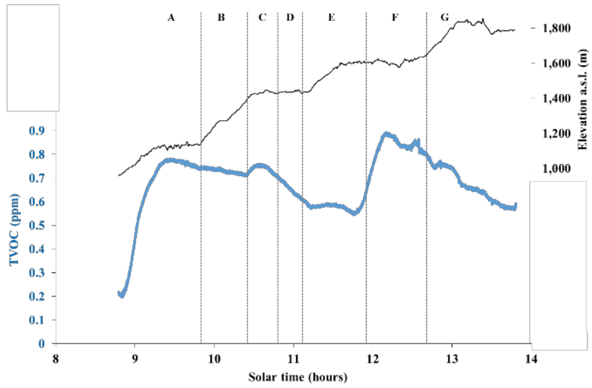
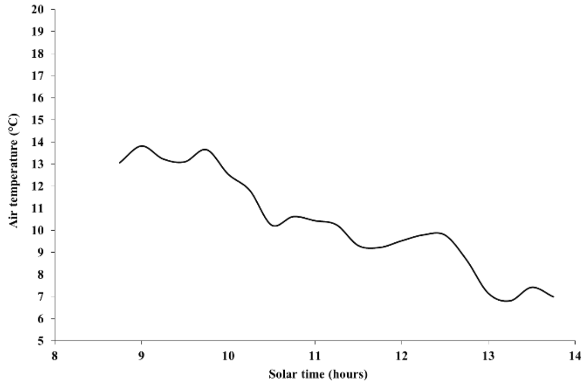
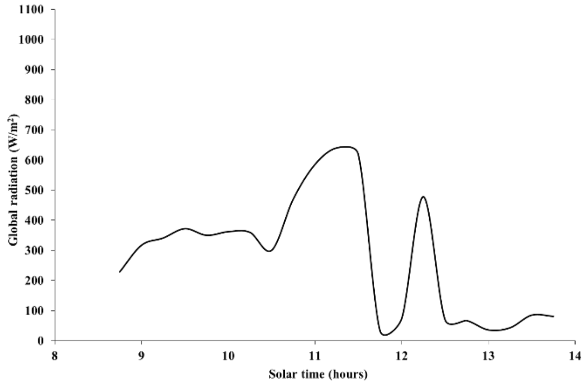


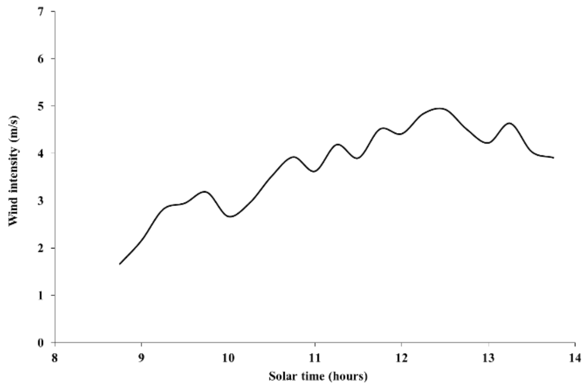
(**b**)



(**c**)



(**d**)



(**e**)

Figure 6. Data along the uphill part of the hiking trail H1, on October 12, 2019: (**a**) TVOC concentration classes on a topographical map (red, 0-0.225 ppm; yellow, 0.225-0.450 ppm; blue, 0.450-0.675 ppm; green, 0.675-0.892 ppm) , with the red colored house representing the site “Pian dei Termini”, and the symbols with blue shield surmounted by an eagle representing mountain refuges, managed by the Italian Alpine Club; (**b**) Elevation and TVOC concentration; (**c**) Air temperature; (**d**) Global radiation; (**e**) Wind intensity.

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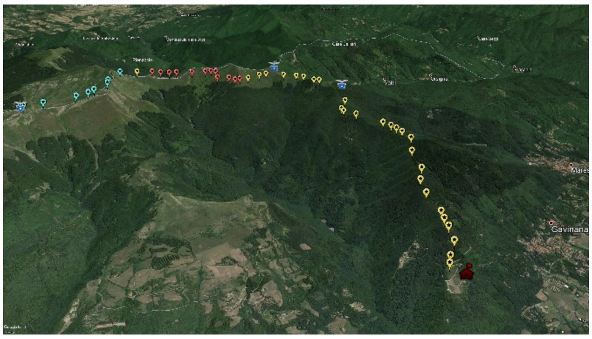
TVOC concentration increased by nearly 0.6 ppm along part A of the route (forest path, site S2 in Table 1, with dominance of chestnut, ash, black pine and silver fir trees), approximately during 9 to 9:45 am, which occurred with low wind, relatively high air temperatures, and moderate radiation. This situation could have mimicked early morning conditions in summer.

Along part B of the route, steeply rising from about 1150 to 1450 m a.s.l., and mostly dominated by beech and silver fir trees, the TVOC concentration remained on comparatively high levels. During approximately 9:45 to 10:30 am, the global radiation was still moderate, the air temperature decreased by about 3°C, and the wind intensity was still low, similarly to part A of the route. The subsequent small local peak in the TVOC concentration, along part C of the route, occurred along with a local minimum of both radiation and air temperature, possibly reinforcing the hypothesis that early morning-like vertical atmospheric stability could favor relatively high TVOC concentrations near the ground. This hypothesis will be discussed further in Section 4. As well, the change in the forest vegetation changes, with beech becoming dominant over fir trees, could have played a role.

Along parts D and E of the route, with elevation eventually reaching about 1600 m a.s.l., and the trail emerging outside a pure beech forest and reaching a mountain grassland, TVOC concentration gradually dropped to a minimum. During these parts of the route (around 10:45 to 11:45 am), the wind intensity increased as the mountain ridge was approached, the radiation reached the daily peak (over 600 Wm^{-2}), and the air temperature changed slightly. Although the relatively high radiation levels should have favored the BVOC emissions from beeches, the neutral to unstable vertical atmospheric profile could have diluted the VOCs across a deeper atmospheric layer, thus lowering the TVOC concentrations near the ground. Moreover, the change from mixed beech – fir tree forest to pure beech forest could have contributed to the observed drop under the specific meteorological conditions.

The absolute peak in TVOC concentration, observed along part F of the route (around 12 to 12:45 am), is harder to explain. Most of the route crossed a mountain grassland, only occasionally reentering the forest, air temperature did not change remarkably, while radiation oscillated wildly between nearly zero (ridge inside low clouds), and almost 500 Wm^{-2}. Notably, the southwesterly wind intensity increased up to the daily maximum of 5 ms^{-1}, which might suggest the advection of BVOCs from the nearby forest, and the respective accumulation near the ground, on the upwind side of the ridge. The same factors could as well explain why the TVOC concentration dropped by only about 0.3 ppm, well below what one could have expected, along part G of the route (12:45 am to 1:45 pm), entirely developing around the ridge and on mountain grasslands, with very low radiation, and air temperatures at the daily minimum (around 7°C).

Figure 7(a)-(e) show TVOC concentration, both superimposed on a topographic map and represented as a chart along with the local elevation, and weather data series, for the downhill part of the hiking trail labeled as H1 in Table 1, again measured on October 12, 2019. The latter part of this route was slightly different from the uphill path, while eventually getting to the same site, and is labeled with a different letter (H).



(a)

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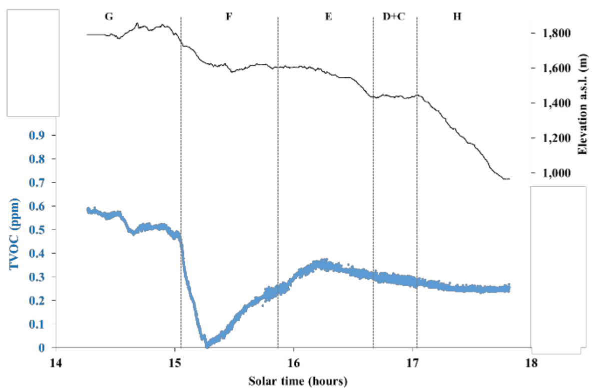
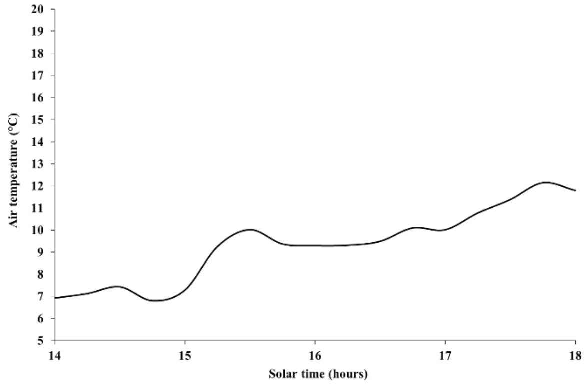
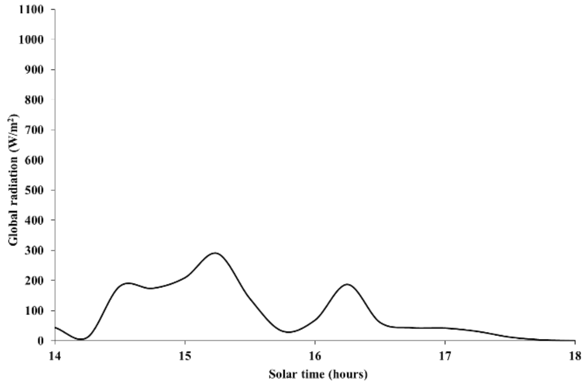


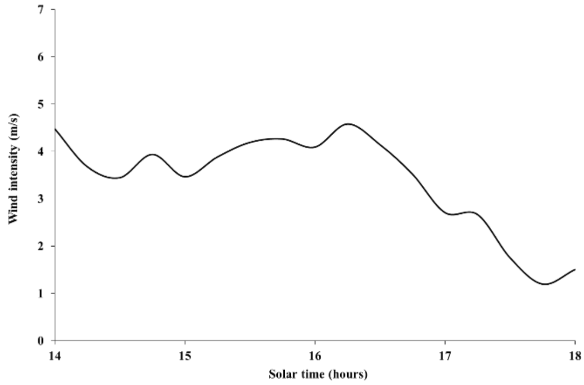
(**b**)



(**c**)



(**d**)



(**e**)

Figure 7. Data along the downhill part of the hiking trail H1, on October 12, 2019: (**a**) TVOC concentration classes on a topographical map (red, 0-0.225 ppm; yellow, 0.225-0.450 ppm; blue, 0.450-0.675 ppm; green, 0.675-0.892 ppm), with the red colored house representing the site “Pian dei Termini”, and the symbols with blue shield surmounted by an eagle representing mountain refuges, managed by the Italian Alpine Club; (**b**) Elevation and TVOC concentration; (**c**) Air temperature; (**d**) Global radiation; (**e**) Wind intensity.

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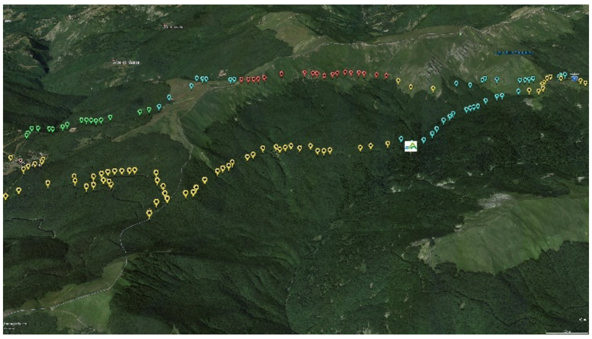
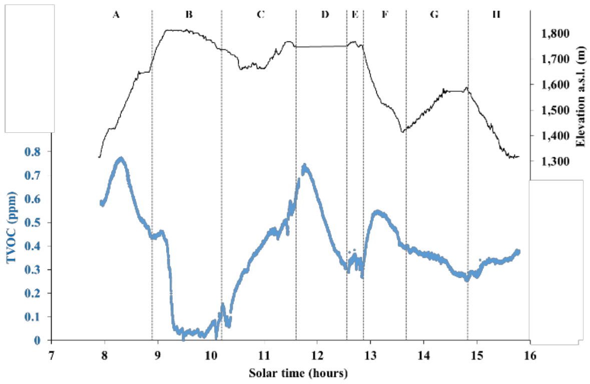
TVOC concentrations, along most of the downhill route, were much lower than along the uphill route, which is apparent after comparing the maps in Figure 6(a) and 7(a). This comes to little surprise, because air temperatures were generally lower and global radiation even more, due to increased cloudiness and the progression of time in the afternoon. The lower part of the downhill route (parts E, D+C, and H in Figure 7(b)) could have been deeply affected by the changed conditions, with TVOC concentration levels lower by 0.25 to 0.45 ppm in comparison with the uphill route.

The absolute minimum in TVOC concentration levels in part F of the downhill route, shown in Figure 7(b), and corresponding to the red colored tags in Figure 7(a), could be especially suggestive. Such levels were as much as nearly 0.9 ppm lower than the levels observed along the same part of the route just 3 hours earlier. Indeed, this part crossed mainly mountain grasslands, and most of observed VOCs were likely to be the result of the advection from the nearby forest. With lower radiation and somewhat lower wind intensity, likely both BVOC emissions from forest trees, and the respective advection, decreased, resulting in remarkably lower TVOC concentration.

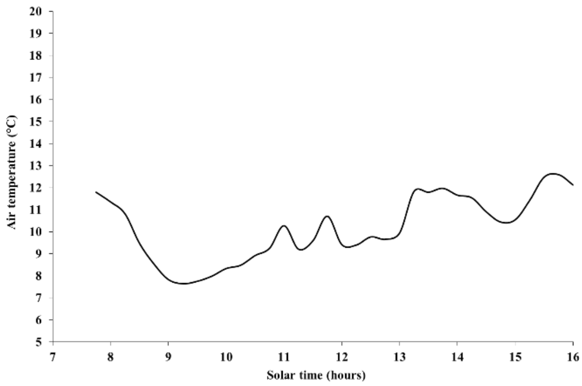
Figure 8(a)-(e) show TVOC concentration, both superimposed on a topographic map and represented as a chart along with the local elevation, and weather data series for the ring-shaped hiking trail labeled as H2 in Table 1, measured on September 29, 2019.



(a)



(b)



(c)

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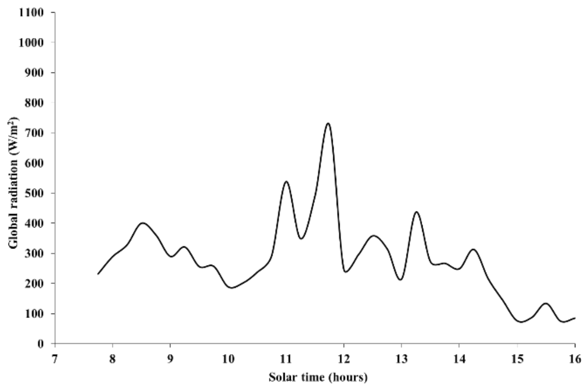
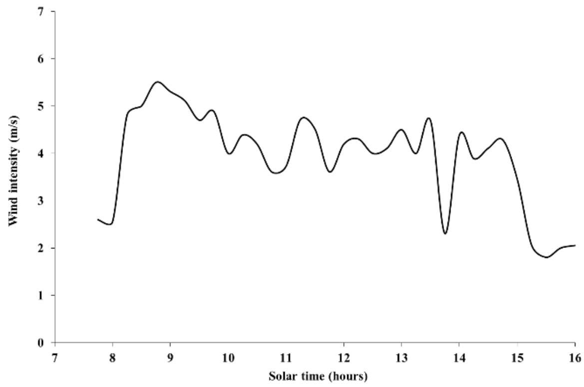


(**d**)



(**e**)

Figure 8. Data along the hiking trail H2, on September 29, 2019: (**a**) TVOC concentration classes on a topographical map (red, 0-0.194 ppm; yellow, 0.194-0.388 ppm; blue, 0.388-0.582 ppm; green, 0.582-0.776 ppm), with the square symbol with white background representing the "Segheria" refuge, managed by the Tuscan-Emilian Apennine National Park, and the symbol with blue shield surmounted by an eagle representing the "C. Battisti" refuge, managed by the Italian Alpine Club; (**b**) Elevation and TVOC concentration; (**c**) Air temperature; (**d**) Global radiation; (**e**) Wind intensity.

TVOC concentration levels oscillated with a maximum amplitude greater than 0.75 ppm along the ring-shaped route. The highest peak occurred along the part of the route labeled as A in Figure 8(b), in early morning (8 to 8:40 am), at elevations of 1400 to 1550 m a.s.l., in a mixed beech – fir trees forest, with both silver firs and Douglas firs. Weather conditions were characterized by moderate global radiation (300-400 Wm^{-2}), relatively low temperature (9-11°C) and wind intensity (3 to 4.5 ms^{-1}), likely leading to a shallow neutral to unstable vertical atmospheric profile.

Subsequently, part B of the route (8:45 to 10:15 am) developed across mountain grasslands, at higher elevations (from more than 1800 to about 1750 m a.s.l.), with lower temperatures (about 8°C), lower radiation levels (200-300 Wm^{-2}), and stronger wind (up to 5.5 ms^{-1}). TVOC concentration levels dropped to a prolonged absolute minimum, starting from the ridge and further along the leeward side (wind was blowing from the south-west). Likely, no effective advection of VOCs occurred, from forests located at least 200 m below the ridge, and constituted – on the windward side – by pure beech stands.

Along part C (10:15 to 11:30 am), at elevations between 1650 and 1750 m a.s.l., alternately crossing grasslands and forest stands with both beech and fir trees, TVOC concentration gradually increased, eventually by nearly as much as 0.6 ppm, possibly in response to both the presence of tree vegetation and increased radiation, the latter reaching about 500 Wm^{-2}. During about 11:30 to 12:30 am (part D), the TVOC concentration measurements were taken at a fixed point ("C. Battisti" refuge, managed by the Italian Alpine Club), at the elevation of 1765 m a.s.l., immersed in a mixed beech – fir tree forest. TVOC concentrations initially increased by further 0.1 ppm, later dropping steeply by as much as 0.45 ppm, possibly because of radiation, first increasing up to more than 700 Wm^{-2} and later dropping to an average of 350 Wm^{-2}.

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During part E of the route (12:30 to 12:50 am), developing on the ridge covered by a grassland, at elevations around 1780 m a.s.l., TVOC concentrations remained stationary around a local minimum. Later, they increased remarkably, by about 0.25 ppm at the local peak, during the descent across an historic forest ("Abetina Reale"), dominated by silver fir trees, along with beeches and Norway spruce (Part F, 12:50 am to 1:40 pm), down to about 1400 m a.s.l. (location of the "Segheria" refuge, managed by the Tuscan-Emilian Apennine National Park). While slightly stronger radiation (up to about 440 Wm^{-2}) and relatively higher temperature (up to about 12°C) could not be ruled out, the forest vegetation was likely the main driver for local BVOC emissions and, consequently, increased concentration near the ground.

Finally, a forest path crossed a pure beech forest in parts G and H of the route (ascent to the ridge at the elevation of 1570 m a.s.l., and descent to the starting point of the trail, respectively). Either decreasing radiation levels, or the forest composition, or both, could have contributed to the relatively lower TVOC concentrations (about 0.2 ppm below the local peak observed in the "Abetina Reale" forest).

4. Discussion

The first and basic findings of this study concerned the remarkable variability of TVOC concentrations in space and time, both on fixed sites and along paths, as well as in different environments, *i.e.*, low hill, mid-mountain sites, and mountain sites up to over the upper limit of tree vegetation. Indeed, within the same day, relative changes of TVOC concentration commonly exceeded 0.5 ppm, often even reaching levels as high as 0.9 ppm, on the order of magnitude of the highest BVOC concentration levels observed in the forest air, *i.e.*, 1 ppm [31].

Such changes occurred within times as short as a few tens of minutes, and within distances of the order of several hundred meters along paths and hiking trails. The takeaway message from these findings is that, as far as BVOCs are considered an essential resource contributing to the forest healing effects, not all times are equally effective, even on clear and calm days, as well as trail sections should be carefully selected in order to optimize forest therapy sessions. Milder, unassisted forest bathing practices could as well take advantage of these finding, allowing to choose proper times and sites, as well as hikers could incorporate these information into their walking plans, in order to add the benefits of BVOC inhalation to the advantages deriving from the physical exercise.

However, at least preliminary guidelines could add to the usefulness of these findings. Within the level of significance allowed by the measurement campaigns carried out, covering a limited sample of natural areas in central Italy, during about less than three months between August and October in a single year, and referring to the only daylight hours, preliminary guidelines can be summarized as follows:

- Early in the morning, the soil heats up due to the emerging solar radiation, and a strong mixed layer develops and grows in the atmosphere just above the ground. Although BVOC emissions from trees are still limited by low radiation and temperature, BOVCs diffuse within a limited vertical layer and can accumulate near the ground, up to relatively high concentration levels. Early morning could to be a relatively good time for the contribution of BVOCs to forest healing effects.
- Mid-morning, the atmospheric mixed layer grows rapidly in depth, driven by the increasing radiation, while BVOC emissions are still moderate. As a result, BOVCs diffuse within a relatively deep vertical layer and their accumulation near the ground can temporarily decrease, in comparison to early morning. Mid-morning could be a relatively disadvantaged time.
- In the hours just after noon, with solar radiation and air temperature around their peaks, BOVC emissions peak too, leading to the highest concentrations near the ground, despite the high dilution rate of BVOCs within the deep atmospheric mixed layer. The middle of the day, and early afternoon, could be the best time for the contribution of BVOCs to forest healing effects, provided that other factors, such as those defining the bioclimatic comfort, are on acceptable levels.

- Late in the afternoon, with vanishing solar radiation, a stable atmospheric layer develops just above the ground, with very limited vertical mixing, in turn surmounted by a residual mixing layer. The combination of declining BVOC emissions, due to low radiation levels and falling temperature, and the inhibition of their mixing from elevated sources (tree foliage) down to the ground, can lead to the lowest concentration levels. Late afternoon could be the most disadvantaged time for the contribution of BVOCs to forest healing effects.
- Based on the results of this study, and under the specific meteorological conditions, conifer trees seemed to be more efficient as regard to BVOC concentrations in the forest air, at least in comparison with beech trees (the most widespread tree in Italy, concentrated in mountainous areas and especially in the Apennines, particularly at elevations above 1200 m). Thus, when different alternatives are available, pure fir or mixed beech-fir forests could be preferred over pure beech forests. However, the evidence was quite limited, and the above statement might not apply to different deciduous tree species, which are widespread at lower elevations. In any case, further research is recommended in order to score different tree types with regard to their effect on the variability of BVOC concentrations in the forest air, including the dependence on season and weather conditions, as well as accounting for emissions from both plants and soil.

The above-listed points referred only to clear and calm days, which are generally preferable for forest bathing activities, due to the higher level of comfort. More quantitative relationships could not be derived, also due to uncertainties in the meteorological data: in future research, the use of gridded data over a geographical domain is recommended, for example from reanalyses or very short-term forecasts generated by high-resolution mesoscale atmospheric models.

Cloudiness prevents most of the solar radiation from reaching the ground and the tree foliage, primarily leading to reduced BVOC emissions, as well as to the limitation of atmospheric vertical mixing, the latter hindering the ground accumulation of BVOCs early in the morning, while attenuating the vertical dilution around noon, in comparison with clear conditions. Overall, based on the results presented in Section 3, cloudiness seems to lead to lower BVOC concentrations near the ground. Strong winds drive remarkable horizontal advection of substances in the atmosphere, which can unpredictably lead to higher or lower BVOC local concentrations near the ground, depending on the presence, composition and emission rates of forest stands on the windward side, as well as on other uncontrollable factors such as turbulence, leeward wakes, and other disturbances to the atmospheric vertical mixing. Finally, the effects of further disturbances, such as drought and rain, and the BVOC concentration daily cycles in different seasons, such as spring, early summer, late autumn and winter, were not investigated and are recommended for further research.

Figure 9 shows a simple conceptual model representing such findings.

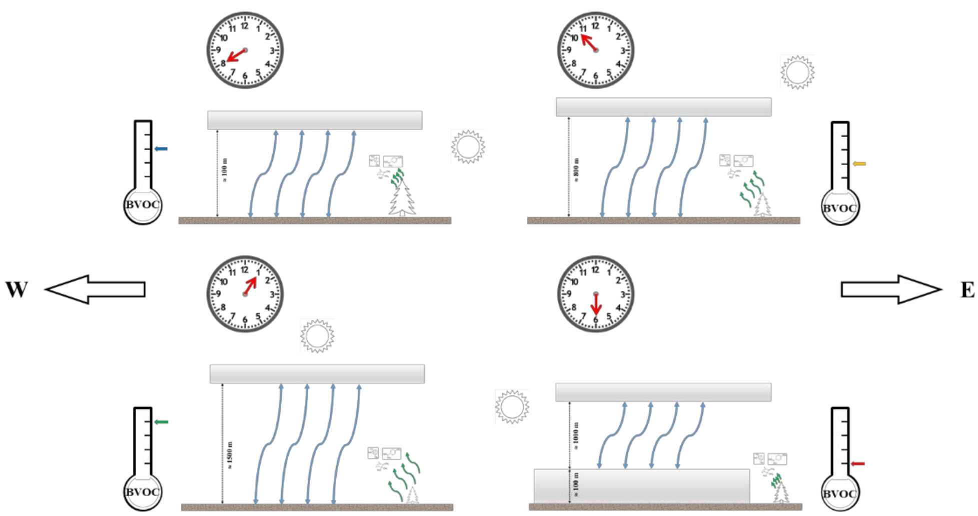

Figure 9. Conceptual model of BVOC relative concentration at different times during daylight hours, in clear and calm days. The horizontal bars in shades of gray represent stable atmospheric layers. The curved lines in blue represent strong mixed layers. Curved lines in green represent BVOC emissions

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from trees, with lengths indicatives of the respective emission rates. Elements of the picture are not to scale.

The presented findings are partially contrasting with results recently obtained in Korea, where peak BVOC concentrations were found around 5 pm, and lowest in early morning [51]. However, different sampling frequencies, forest environments and latitudes seriously limit the meaningfulness of a comparison between the two studies. To the authors' best knowledge, no other studies to date match the requirements for a meaningful comparison.

The advantages of using a PID for the measurement of VOC concentrations in forest air consist of the very high measurement and logging frequency (2 s), allowing to detect changes in real time on fixed sites, and about every 2 m along paths, of the portability of the instrument, as well as of the low cost of measurements. The results of this study demonstrate that high frequency measurements are needed in order to capture the substantial variability of TVOC concentrations in forest air, occurring within a few tents of minutes and several hundred meters. The main and substantial disadvantage consist of the unselective measurements, which leave unknown the composition of the detected VOCs.

The meaningfulness of this study and the related findings relies upon the representativeness of TVOC concentrations measured by means of a PID with respect to BVOC. Since the components of the detected TVOCs were not analyzed in any study sites and paths, in principle their origin was unknown, *i.e.*, they could be either biogenic, or anthropogenic, or both. However, the remoteness of the areas into consideration from anthropogenic sources, as well as the adoption of a variable offset concentration level, equal to the absolute minimum during any measurement day, with respect to which all the other data were referred, should have minimized the chance of substantial contributions of anthropogenic sources to the reported TVOC concentration data.

The detection of the specific composition of VOCs, enabling their attribution to biogenic or anthropogenic sources, thus both a more accurate representation of BVOC concentration, and the analysis of possible changes in time and space of the composition of BVOCs in the forest air, would require completely different devices. For example, absorbent tubes that must be deployed at least in triplicate at any point of measurement, require at least 60 min for any absorption session, and must be thermally desorbed offline [51].

While the characterization of single sites in terms of BVOC concentration levels could be afforded by means of absorbent tubes or similar techniques, as indeed was successfully performed [51], the same would be practically unfeasible in the case of paths and hiking trails. However, a recommended direction for future research about the characterization of forest sites and paths in terms of BVOC concentrations, concerns the coupling of a high frequency PID with analytical devices, such as absorbent tubes, in order to calibrate the PID-based TVOC measurements at selected sites.

This direction aims at defining the relative contribution of BVOC to TVOC concentration and, likely even more important, the detailed composition of BVOCs, which could change with season, time of day, weather conditions, composition of the forest, and soil conditions [51]. Due to the remarkable specialization of different components of BVOCs with regard to the biological activities [32], the functionality, or healing effectivity, of a forest site or path would require the knowledge of the concentration not only of total BVOCs, but also of the relative abundance of their most active constituents, and the respective variability in time and space.

5. Conclusions

The knowledge of the variability of BVOC concentration in forest air can contribute to optimize the forest healing effects. In particular, it could assist in planning forest therapy sessions and practices, as well as allow hikers to gain most advantage from their walking along forest and mountain trails. For the first time, this study demonstrated that the variability scale of TVOC concentration could be comparable to the absolute concentration levels, within time scales of less than one hour, and spatial scales of several hundred meters.

These result were achieved by using a photoionization detector that, while not allowing the detection of individual components, allowed high frequency measurements both on fixed sites and along paths. The remoteness of the study areas from anthropogenic VOC sources, along with suitable data processing, ensured a reasonable representativeness of the results with regard to BVOCs.

A conceptual model was developed, and provisional guidelines were formulated, about the evolution of BVOC concentrations during daylight hours, suggesting the likelihood of peak BVOC concentration during very few hours after noon, a secondary peak in early morning, and lowest concentration in late afternoon. As well, the very preliminary conclusion was drafted, that conifer trees are more efficient than beeches with regard to BVOC concentration in forest air.

This study should be considered as a starting point and possibly as a methodological reference for further investigation and research, aimed at detecting individual TVOC components, expanding the seasonal coverage of measurements and the study areas, and using high resolution gridded meteorological data. However, the basic finding and its consequences appear indisputable: as long as BVOCs are considered as an essential resource contributing to forest healing effects, a detailed knowledge of the respective concentration patterns in forest air, and a careful planning of practices, are needed in order to substantially optimize the benefits for human mental and physiological health.

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