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Quantification of the volatile organic compounds in the smoke from prescribed burning and comparison with the occupational exposure limits

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Abstract

Prescribed burning represents a serious threat to the personnel fighting fires because of smoke inhalation. This study aims to increase the knowledge about foresters exposure to the prescribed burning smoke by focusing on exposure to volatile organic compounds (VOCs). We initially assessed the methodology for smoke sampling. Then, we identified potentially dangerous molecules among the VOCs identified at 4 prescribed burning sites located around Corsica. The values measured were very high, exceeding the exposure limits, particularly for benzene, phenol, and furfural, whose concentrations were above short-term exposure limit (STEL) values. In conclusion, obvious but necessary recommendations were made for the protection of the personnel involved in fighting fires on a professional basis.

1 Introduction

The large quantities of smoke produced during forest fires can remain in the atmosphere for many days (Dokas et al., 2007). Smoke is composed of combustion gases, water droplets, fuel in suspension, and soots. Combustion gases include “permanent” gases (e.g., carbon monoxide [CO] and dioxide [CO_2], methane [CH_4], etc.), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and particulate matter (Barboni and Chiaramonti, 2010; Barboni et al., 2006, 2010; Dost, 1991; Miranda, 2004; Statheropoulos and Karma, 2007; Ward, 1999) produced by incomplete plants combustion during thermal degradation. VOCs include hydrocarbons (Miranda, 2004; Statheropoulos and Karma, 2007; Shauer et al., 2001; Ward, 1998) and aromatic hydrocarbons (Barboni et al., 2010; Reisen, 2006; Reisen and Brown, 2009). In addition, VOCs include oxygenated compounds such as alcohols (Barboni et al., 2010; Statheropoulos and Karma, 2007; Shauer et al., 2001), aldehydes (Barboni et al., 2010; Statheropoulos and Karma, 2007; Reinhardt and Ottmar, 2004; Shauer et al., 2001), ketones (Barboni et al., 2010; Statheropoulos and Karma, 2007), furans, carboxylic acids, and esters (Barboni et al., 2010; Muraleedharan et al., 2000; Statheropoulos and Karma, 2007). Among the VOCs identified in the smoke from forest fires, only a small part of these compounds have a known toxicity, and therefore, a known short-term exposure limit (STEL) and time-weighted average (TWA) values. The VOCs such as formaldehyde, acrolein, benzene, toluene, xylenes, phenol, etc., were identified by several authors, based on available data regarding prescribed burning (Barboni and Chiaramonti., 2010; De Vos et al., 2009; Reisen and Brown, 2009; Statheropoulos and Karma, 2007), smoke chamber (De Vos et al., 2009), and chimney combustion experiments (Ciccioli et al., 2001). Formaldehyde and acrolein has been identified as the main toxic VOCs emitted by bushfires (Reinhardt et al., 2001; Reinhardt and Ottmar, 2004); other studies have also identified these compounds, as well as acetaldehyde, benzene, toluene, xylene, and phenol (Barboni et al., 2010; De Vos et al., 2009; Reisen, 2006; Statheropoulos and Karma, 2007). These compounds were found to be in concentrations below 1 ppm, different than those identified in the forest fire incident in Greece and higher than those noted in other studies (De Vos et al., 2009; Reisen, 2006; Reisen and Brown, 2009; Statheropoulos and Karma, 2007). It is therefore, important to assess exposure levels for Mediterranean conditions on a local basis. It is possible to measure total VOCs by using sampling devices with appropriate detectors; the authors have measured the total VOC and demonstrated a maximum VOC concentration of 88 ppm for the fire experiments (Miranda et al., 2010). However, the National or International Legislation sets (Threshold limit value) TLV-TWA, TLV-STEL, or peak limits individually for specific compounds, but not collectively for the total VOCs (Miranda et al., 2010).

Compounds emitted by the smoke potentially present an important public health issue for the communities that are directly affected, and especially for the personnel involved in firefighting operations (Barboni et al., 2010; Miranda et al., 1994, 2010; Reinhardt et al., 2001, 2004; Ward et al., 1973). To assess the effects of smoke-compound combinations on the respiratory system, scientists (Reisen and Brown, 2009; Slaughter, et al., 2004) used an index that was notated “E_m,” which provides a respiratory irritant exposure index. The effects in firefighters may be acute, sub-chronic, or chronic, and are typically associated with acute decreases in respiratory function because of increasing exposure (Barboni et al., 2010; Miranda et al., 1994, 2010; Reinhardt et al., 2001; Slaughter, et al., 2004; Ward et al., 1973). Other groups concluded that exposure to the smoke from prescribed burning was associated with significant degeneration in lung function (Materna et al., 1992; Malilay, 1999; Mustajbegovic et al., 2001; Liu et al., 1992; Reinhardt et al., 2000; Rothman et al., 1991), but others (Betchley et al., 1997; Slaughter, et al., 2004) found not so significant degeneration.

The objective of this work was to identify the VOCs emitted during plant combustion, and to determine the most toxic VOCs present in the smoke in order to protect foresters during prescribed burning. This study was conducted in 3 steps. We first identified VOCs present in the smoke of burning Mediterranean plant species. We then compared the identities and amounts of these compounds with those from prescribed burning smoke. Finally, we assessed the toxicity of these compounds in relation to the limit values (LVs) of the French government and the American Conference of Governmental Industrial Hygienists (ACGIH).

2 Experimental methods

2.1 Experimental sites and sampling

Sampling was conducted on the island of Corsica at 4 different sites (Barboni et al., 2010). Sites selection was established by the “Office National des Forêts” (ONF) and regional foresters.

The first site (1) is located in southern Corsica (41°42′ N, 09°20′ E). During summer, this area is frequently subjected to wildfires, because of windy conditions, high temperature, and high incidence of drought that increase the risk of wildfires occurence. The experimental site was rectangular, 30 m long and 80 m wide, with a slope of $< 2°$. A desert-like area was established around the site to avoid the flame front spreading beyond the area of the prescribed burning site. The average height of the vegetation ranged from 80 cm to 2.5 m. The vegetation here consists of several species, i.e., *Quercus ilex* L., *Olea europaea* L., *Arbutus unedo* L., *Cistus monspeliensis* L., *Cytisus triflorus* L., and *Erica arborea* L. The site was equipped with 2 devices for preconcentration of the smoke. For the other sites (numbers 2–4), only the second device was used.

The second site (2) was located south of Corsica (Cuttoli, 41°59′ N, 08°54′ E), near the city of Ajaccio. This site is characterized by several plants, with *A unedo* L., *E. arborea* L., and *C. monspeliensis* L. being the dominant species. The site was equipped with device 1. Prescribed burning was conducted in collaboration with the ONF. The site was at 650 m above the sea level with a small slope of $< 10\,\%$.

The third site (3) was located to the north of Corsica, (Corte, 42°18′ N, 09°09′ E, 450 m, slope: 0 %, no wind). This site was rectangular, with an area of 0.4 ha. Burning was conducted by the Task Lights from the University of Corsica, in agreement with the prefect of Corsica, and firefighters. The vegetation consists of *Q. ilex* L.

The fourth site (4) was located in South Corsica, in the Quenza region (41°46′ N, 09°08′ E), at an altitude of 800 m and a slope of 10–20 %. The site was fitted with device 1. Prescribed burning was done by ONF. The site is covered with *Genista salzmanni* L.

Characteristics of the experimental plots and available fuel are presented in Table 1.

Sampling was carried out by the foresters who performed prescribed burning at the 4 sites. The first device consisted of a portable pump and bags (Tedlar). The pump was used to draw the smoke emitted from the burning vegetation through a heat-resistant Teflon tube. The smoke was then stocked in 25 L bags. Sampling was carried out for 30 min at a flow rate of 500 mL min^{-1}. The distance between the sampling area and the fire front varied depending on the natural fire spread. Sampling began at the fire ignition until the fire reached the sampling point (Fig. 1). The sampling area was located in the middle of the plot, had a height ranging from 20 cm to 2 m (Fig. 1, to right). Only 1 experiment was conducted at site 1.

The second device was composed of a portable pump connected to Tenax TA® tubes (Fig. 1). The tubes were placed in the breast pocket of a firefighter's jacket. Smoke emissions were measured in mixed samples (without distinguishing between the flaming and smoldering phases) during the prescribed burning. The distances between the sampling area and the fire front ranged from 1 m to 10 m, corresponding to the position of the operating staff. The staff consisted of 4 persons who controlled the fire by using flaming torches. Each person was equipped with a portable sampling pump. The operating staff performed the sampling with Tenax TA® tubes at 3 different times during the prescribed burning, in order to obtain 3 measurements per firefighter. Twelve samples were collected at each site and analyzed (3 measurements ×4 persons). In total, 48 samples (12 samples × 4 sampling sites) were studied using device 2. Sampling was carried out for 15 min at a flow rate of 150 mL min^{-1}. The Tenax TA® sorbent tubes used were Multibed glass tubes (11.5 cm × 6 mm o.d. ×4 mm i.d.). The sorbent tubes and Tedlar bags were transferred to the lab and analyzed with an Automatic Thermal Desorption–Gas Chromatographic/Mass Spectrometry (ATD-GC/MS) instrument.

2.2 Evaluation criteria for occupational exposure assessment

Exposure risk assessment to humans (or firefighters) is defined by the European directive (EN 481), in accordance with the ISO (International Organization for Standardization) and ACGIH, for many compounds inhaled by humans. The LV for a chemical compound represents its concentration in the air that a person may breathe for a specified time without any risk to his or her health. Exposure to elevated levels of smoke can have short-term adverse health effects on humans. In France, there are 2 LVs. The first is the value in the short-term (VLCT), which is designed to protect against the effects of peak exposures within a 15 min period. The second LV is for average exposure (VME), and relates to a period of 8 h. Different countries have different LVs for the same periods. For instance, in the United States, ACGIH gives these values according to STEL (Short-term Exposure Limit) and TWA (time-weighted average) standards, respectively, for 15 min and 8 h periods, whereas in France, the INERIS ("Institut national de l'environnement industriel et des risques") defines these values.

2.3 ATD-GC/MS analysis

The analyses were carried out one day after each experiment at the laboratory using an Automatic Thermal Desorber Perkin Elmer® ATD turbomatrix. For the thermal desorption of VOCs, helium (He) flow was set at 30 mL min^{-1} with a column head pressure at 25 psi. The sorbent tube was brought to 280 °C in 10 min and a carrier gas flushed the sample toward a cold trap at 5 °C. In a second step, the cold trap (22 cm, 0.53 mm i.d.; Supelco®) was programmed for an increase in temperature from 5 °C to 280 °C at 40 °C s^{-1} then held an isotherm at 280 °C for 3 min. The compounds were then desorbed to the chromatograph under helium as carrier via a heated transfer line maintained at 280 °C. The injector temperature was set to 280 °C. The energy ionization for mass detection was set to 70 eV and electron ionization mass spectra were acquired over the mass range 35–350 Da. The chromatograph and the mass spectrometer are Perkin Elmer® Clarus 500® apparatus. The chromatograph was equipped with a non-polar column (Rtx-1, dimethylsiloxan), length: 60 m and internal diameter: 0.22 µm. This column was coupled to the mass detector. Detection was made using a quadrupole analyzer made up of an assembly of four parallel electrodes of cylindrical section. The oven temperature of the chromatograph was programmed from 50 to 260 °C at 2 °C min^{-1} and then held isothermally at 260 °C for 10 min.

2.4 Identification and quantification

The methodology carried out for identification of individual components was based on:

- the comparison of their GC retention indices (RI) on non polar and polar columns, with those of authentic compounds or literature data (König et al., 2001; NIST, 2005). RI on non-polar and polar columns was determined relative to the retention time of a series of *n*-alkanes with linear interpolation (Van Den Dool and Kratz, 1963);

- computer matching with commercial mass spectral libraries (Adams, 2001; König et al., 2001; NIST, 1999) and comparison of spectra with those of our laboratory-made library.

The quantification was performed in equivalent benzene for the group I (benzene, toluene, ethylbenzene, xylenes, styrene, propylbenzene, *α*-methlstyrene, trimethylbenzene and biphenyl), in equivalent phenol for the group II (phenol, cresols and 4-methoxyphenol), in furfural and naphthalene. The method of external calibration was used with commercial compounds (Restek®). Triplicate injections of standards were made for each level (5 points) to obtain curves for external calibration standards. The correlation coefficient (R^2) for the linear regression of the curves of external calibration standards, varied between 0.987 and 0.999 ensuring a good correlation between the detector's response and the concentration of injected products.

3 Results and discussion

3.1 Methodologies for pre-concentration of the VOCs in smoke

Initially, it was necessary to establish a methodology for analyzing the VOCs present in the smoke. Both devices 1 and 2 could capture these compounds in the smoke. The main advantage of device 1 is that it allows a greater amount of sample to be captured and subsequently analyzed, and the device is not selective. It pumps the whole air-smoke mixture. Device 2 is selective and allows for the trapping of the VOCs only, and increases the concentration of molecules without altering their relative concentrations. It measures compounds in trace amounts that would not be measurable with device 1. The adsorption of compounds is selective, and it can adsorb certain classes of VOC families according to their nature (polarity, size, volatility, etc.). We observed that device

2 could be used to identify a larger number of compounds (Fig. 2). In fact, we identified 71 compounds using pre-concentration tubes (device 2) vs. 21 compounds using the Tedlar bag (device 1). This is because the Tedlar bags involve nonselective sampling of molecules. The VOCs are mixed with a large amount of air and permanent gases (N_2, O_2, CO_2, CO, etc.), and may be present in trace amounts only (below the detection limit for the molecules). While using device 1, the VOCs were diluted in the air and were below the limit of detection (LOD) for the analytical instrument. Therefore, the rate of identification of the VOCs was low. This contrasts with the selective sampling device (device 2), which allowed for the adsorption of the desired molecules without air. When injected into the chromatograph, these molecules were sent to the column in higher concentrations. In view of these results, we preferred to use device 2 on the other 3 sites (2–4). Moreover, this device was simpler to implement, and was more suited for the determination of the actual quantities inhaled by the personnel, because the device was placed near their breathing zone.

3.2 Discussion

In a previous study (Barboni et al., 2010), we identified 71 VOCs in the smoke arising from prescribed burning. On the basis of these results, we characterized these compounds based on the existing toxicity data from the INERIS and ACGIH agencies. We have chosen to quantify 14 VOCs with known toxicities and STEL and TWA data. Table 2 lists the VOCs that have been identified in the smoke from prescribed burning, that are likely to cause adverse health effects. For example, it is known that benzene is a carcinogen, respiratory irritant, and central nervous system depressant. The aromatic products (toluene, xylenes, styrene, etc.) are irritants, and cause respiratory, skin, and eye inflammatory reactions. Phenol is corrosive and causes severe destruction of non-specific tissue (respiratory, skin, eyes, and digestive tract), and its derivatives such as cresols cause dryness of the mucous membranes and long-term systemic poisoning. Naphthalene inhaled in high concentrations induces headache and nausea. Furfural irritates the eyes and the mucous membranes of the respiratory tract, and is considered a probable carcinogen (INRS, web site). The United States Department of Agriculture (USDA) classifies the effects of smoke into 3 categories: short-term effects, including irritation, headache, and reduced capacity to work; intermediate effects causing temporary reduction in lung function and chronic bronchitis, etc.; and long-term effects comparable to those caused by inhalation of cigarette smoke. This suggests the possibility of developing cancer (for example, from benzene) or heart failure. Unfortunately, long-term effects are not well studied, which makes it difficult to assess associated health risks due to exposure to toxic compounds in the smoke from prescribed burning.

The concentrations summarized in Table 3 are the maximum and minimum values obtained during a 15 min period from 48 samples. We observed that the concentrations of the toxic VOCs are higher compared to those obtained in previous studies. Benzene, toluene, ethyl benzene, xylenes, and phenols are the major components of the most toxic VOCs. Concentrations reported in the literature are lower than those observed in the present study (Barboni and Chiaramonti, 2009; Miranda et al., 2005; Reisen, 2006; Reisen and Brown, 2009; Statheropoulos and Karma, 2007). Possible explanations for the higher values are discussed below. The first is the sampling distance; indeed during prescribed burnings, the foresters are close to the flame (< 10 m). This short distance influences the VOC concentration. Indeed, more foresters are near the fire where the density of smoke is strong, and therefore, knowing the VOC concentration is important. Statheropoulos and Karma (2007) reported that the benzene concentration is $0.696\,\mathrm{mg\,m^{-3}}$ at 70 m, and $0.085\,\mathrm{mg\,m^{-3}}$ at 150 m. The second explanation is related to the specific conditions of prescribed burning. Indeed, it involves a fire that occurs during non-drought periods, and therefore, the vegetation is wet. In addition, the fire is controlled, and therefore, less intense than a forest fire. Furthermore, during prescribed burning, the fires are of low intensity, ranging from $27\,\mathrm{kW\,m^{-1}}$ to $57\,\mathrm{kW\,m^{-1}}$ (Byram's intensity, Cannac et al., 2009). These conditions involve low combustion efficiency, and therefore, the concentration of evolved gases is higher. Moreover, the foresters used flaming torches; this process also emits benzene and hydrocarbons. The high values of hydrocarbons in the smoke from prescribed burning may be attributed, in part, to the flaming torches used. Indeed, there is proximity between the sampling system (on the foresters) and the flaming torches. Moreover, the foresters constantly feed the fire with their flaming torches (Reisen and Brown, 2009). We found that some compounds present in diesel/gasoline such as alkane hydrocarbons (Barboni et al., 2010) are inhaled by foresters as well as accumulate in the emitted smoke at the sites of burning. Reinhardt and Ottmar (2004) explained that benzene evolved originates from the engines and torches burning petroleum-based fuel. Again, the differences in fuel characteristics, e.g., fuel type, fuel load, and fuel moisture, can influence the combustion efficiency, and thus, the concentration of compounds in the smoke. Santoni et al. (2011) showed that the combustion efficiency was characteristic of the type of fuel.

Table 3 presents the concentrations of the 14 toxic VOCs from the smoke arising from prescribed burning in comparison to the occupational exposure limits defined by INERIS (web site) and ACGIH (web site), National Institute for Occupational Safety and Health (NIOSH, 2006), and Occupational Safety and Health Administration (OSHA, web site). The values presented in Table 3 are the minimum and maximum concentrations of VOCs in 48 samples from 4 sites of prescribed burning. The sampling duration was 15 min. Benzene, phenol, and furfural exceeded the VLCT (France) and the STEL (USA) values for 15 min sampling durations. Indeed, the benzene concentration ranged from 27 to 54 mg m^{-3}, while the recommendation states that it should not to exceed 0.32–16 mg m^{-3}(STEL). Exposure to 160 mg m^{-3} benzene for 60 min can cause symptoms of nausea, whereas exposure to 16–50 mg m^{-3} benzene for 5 h results in headache, lassitude, and weakness (NIOSH, 2006). The phenol concentration was between 12 and 29 mg m^{-3}, exceeding the VLCT level (15.6 mg m^{-3}), while the value set by NIOSH (STEL, 60 mg m^{-3}) is higher than the French standard. The concentration of furfural is 3.2–19 mg m^{-3}, a value that exceeds the VLCT values (15.6 mg m^{-3}). Widespread irritation in the eye and respiratory tract has been noted in workers exposed to concentrations ranging from 10 to 32 mg m^{-3}. Headache, itching of the throat, and red and watery eyes have been observed at concentrations ranging from 3.8 to 28 $\mathrm{mg\,m^{-3}}$.

Considering exposure to a mixture of smoke pollutants, we can use a mathematical formula to sum the individual contributions made to the LV. We calculated the respiratory irritant exposure index (E_m) by using the literature formula with C_i is the concentration of component i in $\mathrm{mg\,m^{-3}}$ of air (Reisen and Brown, 2009; Slaughter et al., 2004):

$$E_\mathrm{m} = \sum_{i=1}^{n} \frac{C_i}{\mathrm{VLCT}_i \text{ or } \mathrm{STEL}_i} \leq 1$$

The associated VLCT and STEL values are not available for all the VOCs included in the list (Table 3). BTEXS pollutants (benzene, toluene, ethylbenzene, xylenes, and styrene) cause irritation in the respiratory tract and mucous membranes. We found that the E_m for the BTEXS pollutants based on STEL values (using the minimum values given by INERIS, ACGIH, NIOSH, or OSHA) for the maximum concentration of a BTEXS pollutant (Table 3) is 169, and thus, greater than 1. These 5 compounds are noted at high concentrations, and the atmosphere containing them could be very irritable to the foresters. If we calculate this coefficient excluding benzene concentration, as this value already exceeded the STEL, the value is 0.28. TEXSs are molecules with relatively low toxicity as their STEL values are high.

For phenol and phenol derivatives, we calculated the E_m coefficient by extrapolation by using the TWA values, because the STEL values are unavailable. E_m was calculated with the TWA values supplied by ACGIH. We observed that the exposure index (E_m) for phenol and phenol derivatives is 3, and thus, greater than 1. In conclusion, these molecules have a strong irritant potential, and pose a problem that warrants consideration, with respect to reducing the health risks for the foresters. The E_m for the phenol derivatives (without phenol) is equal to 1.5. We show that the amount of these compounds, all with similar toxic potential, influences the quality of air inhaled by the foresters during prescribed burning, although during prescribed burning, firefighters are not daily exposed to 8 h of smoke, and neither do they work throughout the year in such conditions. In Corsica, the firefighters work on 80 ha of land per year. It is difficult to establish a correlation between the exposure to smoke during prescribed burning and the LVs set by authorities for protection of workers. Nevertheless, we observed that the higher concentrations of benzene, phenol, and furfural exceeded the STEL (or VLCT).

4 Conclusions

The present work presented chemical analysis of the smoke released from prescribed burning in Corsica, by using ATD-GC/MS. We have shown that pre-concentration of VOC is the most appropriate method for analyzing the VOCs present in the smoke samples. As a second step, we determined the level of VOC toxicity present in the smoke based on known toxicity data. Indeed, the STEL and TWA values are missing for many compounds present in the smoke samples. We have shown that concentrations of benzene, phenol, and furfural exceeded the STEL. The potential toxicities for benzene and phenol derivatives were greater than 1, implying that the atmosphere was toxic for the foresters. Thus, we conclude with 2 recommendations. As a precaution, we suggest that the foresters should not work for > 8 h without protection, or should wear a protective respirator. In addition, we advocate using an alternative mode of fire ignition than the flaming torch, because this method possibly increases the potential exposure to high concentrations of toxic molecules.

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Table 1. Main characteristics of the experimental plots.

	Site 1	Site 2	Site 3	Site 4
Elevation (m)	0	650	400	800
Slope (%)	0–2	0–10	0	0–20
Vegetation height (cm)	80–250	80–150	1–10	10–20
Fuel load ($\mathrm{g\,m^{-2}}$)	1160	1200	1370	1450
Vegetation cover (%)	50–60	50–60	60–70	70–80
Burning area (ha)	0.06	2	0.4	2
Relative humidity RH (%) (min. and max.)	20–23	22–25	24–25	30–35
Temperature (°C)	30–32	22–24	22–25	14–16
Wind velocity ($\mathrm{km\,h^{-1}}$)	40	20	< 5	< 5

Table 2. Toxicity of 14 VOCs emitted by vegetation during the prescribed burnings (INERIS and ACGIH).

Compounds	Toxicity
benzene	irritation eyes, skin, nose, respiratory system; dizziness; headache, nausea, staggered gait; anorexia, lassitude (weakness, exhaustion); dermatitis; bone marrow depression; [potential occupational carcinogen]
toluene	irritation eyes, nose; lassitude (weakness, exhaustion), confusion, euphoria, dizziness, headache; dilated pupils, lacrimation (discharge of tears); anxiety, muscle fatigue, insomnia; paresthesia; dermatitis; liver, kidney damage
ethylbenzene	irritation eyes, skin, mucous membrane; headache; dermatitis; narcosis, coma
xylenes	irritation eyes, skin, nose, throat; dizziness, excitement, drowsiness, incoordination, staggering gait; corneal vacuolization; anorexia, nausea, vomiting, abdominal pain; dermatitis
styrene	irritation eyes, nose, respiratory system; headache, lassitude (weakness, exhaustion), dizziness, confusion, malaise (vague feeling of discomfort), drowsiness, unsteady gait; narcosis; defatting dermatitis; possible liver injury; reproductive effects
propylbenzene	irritation eyes, skin, mucous membrane; dermatitis; headache, narcosis, coma
α-methylstyrene	irritation eyes, skin, nose, throat; drowsiness; dermatitis
trimethylbenzene	irritation eyes, skin, nose, throat, respiratory system; bronchitis; hypochromic anemia; headache, drowsiness, lassitude (weakness, exhaustion), dizziness, nausea, incoordination; vomiting, confusion; chemical pneumonitis (aspiration liquid)
biphenyl	irritation eyes, throat; headache, nausea, lassitude (weakness, exhaustion), numb limbs; liver damage
phenol	irritation eyes, nose, throat; anorexia, weight loss; lassitude (weakness, exhaustion), muscle ache, pain; dark urine; cyanosis; liver, kidney damage; skin burns; dermatitis; ochronosis; tremor, convulsions, twitching
cresols	irritation eyes, skin, mucous membrane; central nervous system effects: confusion, depression, resp failure; dyspnea (breathing difficulty), irreg rapid resp, weak pulse; eye, skin burns; dermatitis; lung, liver, kidney, pancreas damage
4-methoxyphenol	irritation eyes, skin, nose, throat, upper respiratory system; eye, skin burns; central nervous system depression
furfural	irritation eyes, skin, upper respiratory system; headache; dermatitis
naphtalene	irritation eyes; headache, confusion, excitement, malaise (vague feeling of discomfort); nausea, vomiting, abdominal pain; irritation bladder; profuse sweating; jaundice; hematuria (blood in the urine), renal shutdown; dermatitis, optical neuritis, corneal damage

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Table 3. Concentration of major toxic VOCs emitted by vegetation during the prescribed burnings.

compounds	Concentration (min–max) ($mg\,m^{-3}$)	STEL (15 min)	TWA (8 h)
benzene	27–54	16^{h}, 8.1^{b}, 0.32^{g}	30^{f}, $3.2^{g,h}$
toluene	28–42	$560^{g,h}$	$188^{f,g}375^{g,h}$
ethylbenzene	22–67	$543^{f,g,h}$	$434^{f,g,h}$
(o+m+p)-xylene	19–37	$655^{gf,g,h}$	$435^{gf,g,h}$
styrene	1.0–7.6	$425^{f,g,h}$	$215^{f,g,h}$
propylbenzene	tr-4.7	–	245^{f}
α-methylstyrene	< 3.8	$483^{f,g,h}$	$242^{f,g,h}$
trimethylbenzene	< 3.8	–	123^{f}
Diphenyl	< 0.8	–	$1^{f,g,h}$
phenol	12–29	60^{g}	$19^{f,g,h}$
cresols (o+m+p)	3–14	–	$22^{f,h}$,10^{g}
4-methoxyphenol	0.2–4.4	–	5^{f}
furfural	3.2–19	–	7.9^{f}
naphtalene	1.2–4.2	$75^{f,g,h}$	$50^{f,g,h}$

[e] INERIS; [f] ACGIH; [g] NIOSH , [h] OSHA; ([a] De vos et al., [b] Stratopolous and Krama, [c] Reisen et al., in $mg\,m^{-3}$), ([d] Ciccioli et al., in $g\,kg^{-1}$ dry weight).

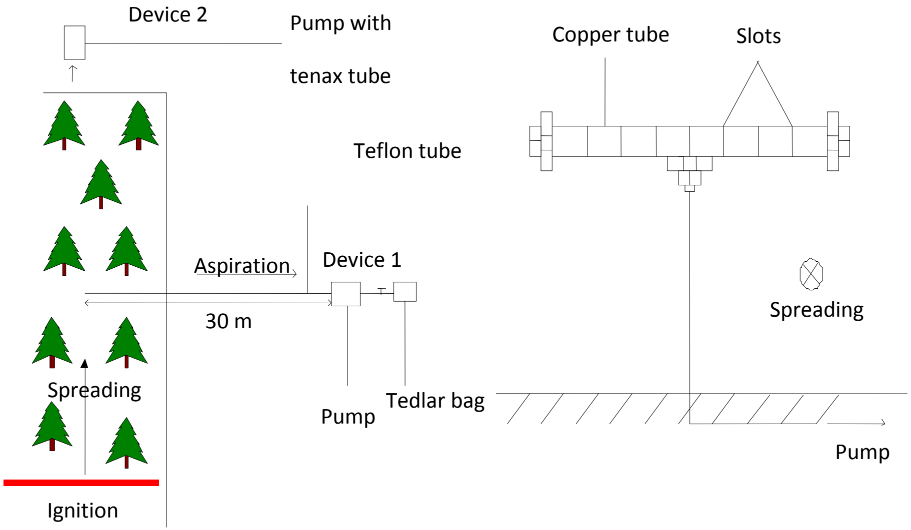

Fig. 1. Experimental devices for the smoke capture.

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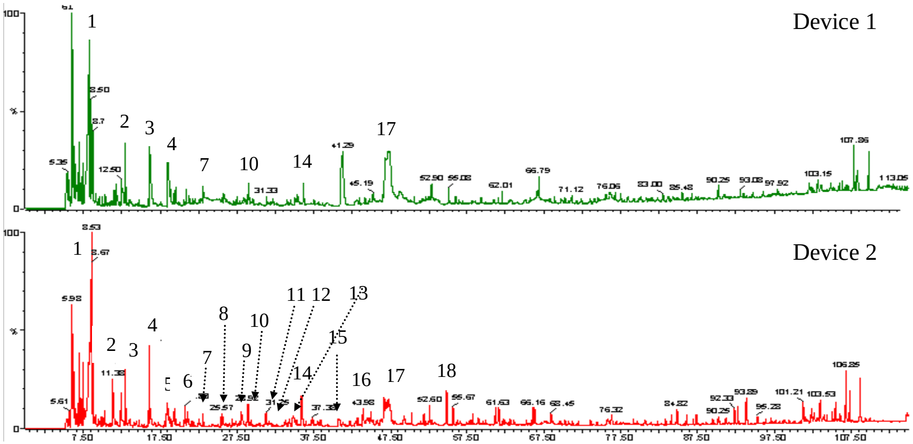

Fig. 2. Chromatogram profile of principal VOC in smoke from prescribed burnings (1: benzene; 2: toluene, 3: furfural, 4: ethylbenzene, 5: ($m+p$)-xylene, 6: styrene, 7: *o*-xylene, 8: propylbenzene, 9: *α*-methlstyrene, 10: phenol, 11 and 12: trimethylbenzene, 13: *o*-cresol, 14: *p*-cresol, 15: *m*-cresol, 16: 4-methoxyphenol, 17: naphthalene, 18: biphenyl).