

Complexity and origin of the smoke components as measured near the flame-front of a real forest fire incident: A case study

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Abstract

A case study of a real forest fire incident is presented, where field measurements held out near the flame-front in smoky, hostile conditions. Permanent gases, such as CO, CO₂, NH₃, volatile organic compounds (VOCs) and particulate matter (PM_{2.5}, PM₁₀) were monitored. Complexity and possible origin of some of the forest fire smoke components are examined and discussed; styrene identified seems that was originated mostly from the combustion of plastics, due to the forest fire expansion to a plastics storehouse. A new approach, regarding the chemical composition of forest fire smoke and possible origin of smoke components depending on the flame-front expansion (e.g. to rural fields, rural and urban constructions or landfills), is presented in the format of a road-map. The case study tests part of the validity of the road-map, which could be used for air-quality indications and risk assessment in a forest fire. Criteria for monitoring air-quality in a forest fire, for health and safety issues, are also discussed.

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1. Introduction

Forest fire smoke is a complicated mixture of gases, liquids and solids. Forest fuel combustion has been studied so far in lab scale [1–4], as well as, in prescribed burning [5]. Measurements in a distance from the flame-front have been carried out during large-scale forest fires, such as the ones that took place in SE Asia in 1998 [6], in USA. Montana in 2000 [7] and in Russia during May 2003 [8], in order to assess the impact of the resultant haze.

However, composition of forest fire smoke can become much more complicated if the forest fire expands, i.e. to rural fields, rural/urban constructions, or landfills. As a result, wood, plastics, fertilizers, pesticides, fungicides, wastes can also be burned and hence, some of the components of the forest fire smoke can have a different origin than that of the forest fuel. In addition, forest fire smoke can mix or even react with urban or industrial pollutants, if it passes over urban or industrial areas

and hence, secondary products can be produced [9]. As a result, forest fire smoke can have serious short- and long-term health impacts on the fire-fighters and the exposed population [10–12].

It is in the purpose of this work to present a case study of a real forest fire incident, where field measurements were carried out in a smoky, hostile environment close to the flame-front; in addition, to show that some of the forest fire smoke components determined had different origin than that of the forest fuel, due to the forest fire expansion to a plastics storehouse. Classification of forest fire smoke components takes place in the format of a road-map. Possible health effects, due to the exposure to forest fire smoke, are also discussed.

2. Experimental part

The case study is based on a forest fire that took place in Attica, Greece. It was initiated in a forest at an altitude of 400 m, which was situated in the interface of an urban area. The forest was covered with pine trees and bushes with high vegetation density. The fire was initiated during the midday (12.45 p.m.), where the temperature was 32 °C and the relative humidity (RH%) was 22%. Due to the North strong wind (35–40 km h⁻¹),

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the fire was extended with a burning rate of about 5 km h^{-1} and co-burned 10 houses, as well as, a storehouse of plastics that were nearby the forest. As a result, wood and other building materials (due to the houses), as well as, significant quantities of plastics, such as polystyrene (due to the plastics storehouse), were co-burned with the pine trees. The total area burned was 24.2 ha and the fire lasted for about 35 h. It should be noted that while the storehouse was burning, large quantities of black smoke were produced.

Measurements were carried out near the flame-front under smoky conditions, at the side of the plastics storehouse, by using a portable unit and taking all necessary personal protection measures.

2.1. Instrumentation

2.1.1. Portable unit

The portable unit consisted of various portable devices, such as a small meteorological station, a particle analyser (Dustrack TSI, linearity area: $0\text{--}100 \text{ mg m}^{-3}$), a CO electrochemical detector (Anagas CD 98 plus, linearity area: $0\text{--}500 \text{ ppm}$), a CO₂ infrared detector (Anagas CD 98 Plus, linearity area: $0\text{--}60\%$) and a NH₃ electrochemical detector (TX 2000 Oldham S.A., linearity area: $0\text{--}100 \text{ ppm}$). Filters were used to protect the sensors from possible contamination, due to the heavy environment of sampling (soots, tars, ash). A VOCs sampling system was also used to collect samples of smoke in multibed sorbent tubes, by using a portable pump. An open filter holder (Aluminum Gelman), with a glass microfibre filter (GF/A Whatman, $\varnothing 47 \text{ mm}$), was put on the top of the tube to protect sorbent materials from contamination. The portable unit also included personal protective tools (masks), communication devices and a GPS.

2.1.2. TDU/GC/MS instrument

Sorbent tubes were thermally desorbed to an HP 5890/5972 gas chromatography/mass spectrometry (GC/MS) system, by using an in-house-made thermal desorption unit (TDU/GC/MS). Details of TDU are explained elsewhere [13,14]. A standard mixture of hydrocarbons was used in four replicates of $1 \mu\text{L}$, in order to define the relative standard deviation (R.S.D.) of the system. More specifically for hexane, with concentration 3.508 mg mL^{-1} in the above mixture, the R.S.D. was estimated 5%. Linearity (r^2) and sensitivity were identified for hexane, by using a volume range between 0.5 and $1 \mu\text{L}$ of this mixture to make the respective calibration curve; they were found 0.899 and $6 \times 10^7 \text{ au } \mu\text{g}^{-1}$ respectively, where au is attributed to the arbitrary units given by the mass spectrometer, which were detected as signal intensities of the specific quantities of the standard used.

2.2. Field sampling

On-line measurements and smoke samples were taken during the fire at four different sites (A–D), in a distance of 70–150 m from the flame-front. The GPS was used to record the coordinates of the sites. It should be noted that replicates of

smoke samples for each site were very difficult to be taken, because of the heavy environment and for safety reasons.

The sorbent tubes used were glass multibed tubes with dimensions of $11.5 \text{ cm} \times 6 \text{ mm o.d.} \times 4 \text{ mm i.d.}$, Supelco (60:80 Carbo-pack C/60:80 Carbo-pack B/60:80 Carbosieve SIII), so as to capture organic compounds of low, medium and high volatility. A methanolic solution of chlorobenzene-*d*₅ ($1 \mu\text{L}$) was used as an internal standard (i.s), spiked into the sorbent tubes, before taking them to the field for sampling. More details about preparation of sorbent tubes before sampling are described elsewhere [13]. The sampling was done at a flow-rate of 200 mL min^{-1} .

The sorbent tubes were transferred in a freezing box to the lab and analyzed 1 day after, by the TDU-GC-MS instrument.

2.3. TDU-GC-MS analysis of VOCs

For the thermal desorption of VOCs, He flow was set at 30 mL min^{-1} (column head pressure 25 psia). Thermal desorption of the sorbent tube lasted for 20 min at $200 \text{ }^\circ\text{C}$, to maximize recovery. The cryotrap capillary was 22 cm, 0.53 mm i.d. , AT-Q, Q-Plot column (Alltech Associates). The dimensions were chosen to trap ultra-VOCs and contribute to the increase of chromatographic resolution. In order to achieve flash “injection” to GC column of the trapped analytes, a heating pulse of 20 s was set. Cryotrapping was done by using liquid nitrogen.

An intermediate SPB-624 capillary column with $1.4 \mu\text{m}$ film and dimensions $60 \text{ m} \times 0.25 \text{ mm}$ (Supelco) was used for the high-resolution chromatographic separation. Heating of the GC column started at $60 \text{ }^\circ\text{C}$ for 4 min and increased with a temperature rate of $4 \text{ }^\circ\text{C min}^{-1}$ to $225 \text{ }^\circ\text{C}$, where held for 30 min. The MSD was in full scan operation mode, with mass range $35\text{--}200 \text{ amu}$ and the benefit of 1.8 scans s^{-1} . Transfer line temperature was at $280 \text{ }^\circ\text{C}$.

2.4. Data processing

The qualitative identification of chromatographic peaks was done by using the Wiley 138 library and the data base “Easy Id” HP Chemstation. The semi-quantitative determination of VOCs was carried out by using the respective relative response factors (RRF). More details regarding the semi-quantitative determination procedure are described elsewhere [13]. Prior to quantitation, subtraction of the background took place. Background measurements were carried out in long distance from the flame-front.

3. Results and discussion

3.1. Classification of forest fire smoke components

In Table 1, classification of forest fire smoke components takes place in the format of a road-map, where possible physical and chemical processes, as well as, chemical components of forest fire smoke and their physical and chemical properties, are correlated to the forest fire flame-front and smoke pathway.

Table 1
Road-map of forest fire flame-front and smoke pathway

| | Forest fire flame-front pathway | Rural fields | Rural or urban constructions | Landfills | Illegal waste disposal | Forest fire retardants | Smoke pathway: liquids and solids | Urban or industrial areas |
|------------------------------|--|--|--|--|--|--|--------------------------------------|--|
| Physical/chemical processes | Pyrolysis and combustion of forest fuel | Pyrolysis and combustion of agricultural fields, fungicides, fertilizers, pesticides, e.g. 4-chloro-2-methyl phenoxy acetic acid (MCPA) | Pyrolysis and combustion of paint, glue, wood, plastics, glass, cement, plaster, asbestos can be contained in the smoke produced | Pyrolysis and combustion of household waste, plastic, rubber, paper, glass and metals can be contained in the smoke produced | Pyrolysis and combustion of organic residues, lead-acid vehicle batteries, electric appliances, radioactive contaminants | Pyrolysis and combustion of diammonium phosphate (DAP), ammonium sulfate and other commercial retardants | Mixture of gases, liquids and solids | Mixing of forest fire smoke with urban and industrial pollutants, possible photochemical reactions |
| Chemical components | | | | | | | | |
| (a) Organic | (a) VOCs (hydrocarbons, aldehydes, furans, carboxylic acids, BTEX), SVOCs (PAHs) | (a) VOCs, SVOCs (PAHs), PCDDs, PCDFs | (a) Non polar VOCs (e.g BTEX, styrene), SVOCs (PAHs), PCDDs, PCDFs, PCBs | (a) VOCs, chloro-benzenes, chloro-phenols, SVOCs (PAHs), Carbonyls, PCDDs, PCDFs, PCBs | (a) PCDDs, PCDFs, Co-PCBs | | | (a) Aliphatic H/C, VOCs, BTEX, styrene, PAHs, saturated hydrocarbons (PAR), mercaptans |
| (b) Inorganic | (b) CO, CO ₂ , NO _x , SO _x , trace elements (e.g. S, Cl, K, Na, Mg, Cu, Ni, Cu, Zn) | (b) CO, CO ₂ , CH ₄ , HCl, SO ₂ , NO _x , PO _x , NH ₃ , CS ₂ , H ₂ S, HCN | (b) CO, CO ₂ , metals (e.g. Ca, Mg, Ti, Al) | (b) CO, CO ₂ , heavy metals (e.g. Pb, Cd, Cr, Cu, Zn) | (b) CO, CO ₂ , radionuclides (I-29, Cs-137, Cl-36) | (b) NH ₃ , SO ₂ | | (b) CO, CO ₂ , NO _x , SO ₂ , H ₂ S, O ₃ |
| Physical properties | | | | | | | | |
| (a) Particle size | (a) Coarse (PM10) and fine (PM2.5) | (a) Coarse (PM10) and fine (PM2.5) | (a) Coarse (PM10) and fine (PM2.5) | (a) Mainly fine particles (PM2.5<) | | (a) Mainly fine particles (PM2.5<) | | (a) Coarse (PM10) and fine (PM2.5) |
| (b) Particle shape | (b) Spherical, fibrous | | | | | | | (b) Irregular |
| Chemical properties: | | | | | | | | |
| (a) Alkalinity/acidity | | | (a) Alkaline pH | | | | | |
| (b) Photo-chemical reactions | | | | | | | | (b) PAH photo-degradation, photo-chemical O ₃ |

Physical properties of forest fire smoke components include the size of particles that is known to be related with health impacts on the exposed population and firemen; particle sizes less than 2.5 μm are more hazardous, because they penetrate more easily the respiratory system and cause asthma or other chronic obstructive pulmonary diseases [15–18]. Moreover, small particles are characterized by a large surface area, which facilitates absorption of chemical compounds [19]. In addition, particle size is considered very important physical parameter, as long as it significantly affects visibility in the area. Reduction of visibility in highways or airports during a big forest fire may affect public safety.

Particle shape (spherical, irregular, fibrous) depends on the combustion temperature and also affects penetration capabilities of particles. Particles observed in urban areas are highly irregular in shape [19]. Microscopic analysis of particles produced by a pine forest fire, shown that their morphological feature was fibrous and nearly spherical [20].

Chemical properties of smoke components can be correlated to health impacts. Alkalinity/acidity of particles, measured by pH, is significant information for first response measures (personal protective equipment, such as masks, respiratory equipment), as soon as, alkaline pH is known to cause nose and chest irritation. In addition, vapor pressure of forest fire smoke components is correlated with their ability to persist in the environment (degradation in water, air). Another parameter is Henry's low constant, which provides additional information regarding how compounds are distributed between gas and liquid phase and hence, how easily are inhaled. Moreover, chemical's octanol–water partition coefficient gives information regarding compound absorption efficiency from human body. In addition, organic carbon sorption coefficient of compounds characterizes the ability of special filters to absorb a compound and hence, to indicate indirectly filters for personal protective equipment (PPE) [21].

The road-map presented in Table 1 can also be seen as possible scenarios of forest fire expansion (pathway); the most common areas that forest fire can expand are rural fields, constructions and landfills.

Rural fields (agricultural fields/crops) are known to be treated with chemicals, such as fertilizers, fungicides and pesticides, e.g. the 4-chloro-2-methylphenoxy acetic acid (MCPA). Pyrolysis and/or combustion of those materials can give a broad range of compounds [22–28].

When the flame-front passes through rural or urban constructions, e.g. buildings, storehouses, etc. paint, glue, wood and plastic can be burned. Moreover, pulverized glass, cement dust, asbestos or plaster can be contained in the smoke produced, as airborne particles. A study of experimental fires of common materials has shown that the most abundant VOCs produced were non-polar VOCs (benzene, toluene, 1,3-butadiene, naphthalene, styrene) and a parallel increase of CO level was also observed [29]. Moreover, polychlorinated dibenzo-*p*-dioxines/polychlorinated dibenzo-furans (PCDDs/PCDFs), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and other semi-volatile organic compounds (SVOCs) were also identified in ash, soil and dust

samples taken from fires in collapsed buildings due to earthquake or other reasons [30,31]. Particulate matter produced during a fire in a building contained pulverized building material, rendering it alkaline (pH.9), and also significant amounts of inorganic matter and metals (Ca, Mg, Ti, Al) [32].

Landfills usually contain plastics, rubber, paper, glass, metals that can be disposed, as well as, household waste. In case of a fire in a landfill, a number of toxic compounds can be produced [28,33–35]. It has been found that during experimental landfill fires and a real landfill fire, PCDD/PCDFs daily intake for workers exceeded the acceptable daily intake of 5 pg kg^{-1} [33]. Heavy metals have also been detected in soil and sand samples, taken after an uncontrolled combustion of municipal soil wastes in an open landfill [36]. It is known that during a forest fire soil can become airborne, when it is disturbed due to strong winds and/or fire attack methods [37].

It should be noted that waste disposals can, occasionally, be “illegal”. In this case, organic residues, lead-acid vehicle batteries, electric appliances and even radioactive contaminants can be burned, so that the situation can become really hazardous [18]. According to the literature [31], burning of electric appliances produced PCDDs /PCDFs and PCBs; toxic equivalent quantity (TEQ) level in such case was found significant (22.800 pg TEQ g^{-1}).

In order to reduce or inhibit combustion and decrease the rate flame spread, fire chemicals (forest fire retardants) can be used. The effect of forest fire retardants on the pyrolysis products of forest fuels, such as cellulose and pine needles, has been studied in lab scale [38–41]. Retardants can be used for prevention (ground means) and for aerial suppression of fires, and are usually mixtures of ammonium phosphate and ammonium sulfate. During a forest fire in Oregon mountain, where a commercial forest fire retardant was used, ammonia was released due to thermal decomposition of the retardant; it was found that in the vicinity of the fire, ammonia exceeded 25 ppm, which is the threshold limit value–time weighted average (TLV–TWA), assuming 8 h/day, according to the American Conference of Governmental Industrial Hygienists (ACGIH) [42].

Urban and industrial pollution, which have been extensively studied [43–46], can interact with forest fire smoke when the smoke plume passes over an urban or industrial area. Forest fire smoke components, when mixed with urban and industrial pollutants, may have additive or even synergistic results. Under sun radiation, this mixture of pollutants (i.e. hydrocarbons, VOCs, CO), photochemically react with OH radicals in the presence of NO_x and produce ground level ozone [47], known to cause possible health impacts.

3.2. Case study results

Meteorological conditions during sampling for each site are presented in Table 2. It appears that a combination of high temperatures ($>30^\circ\text{C}$), low relative humidity ($<25\%$) and strong wind ($>30\text{--}35\text{ km h}^{-1}$) existed. Those conditions facilitated the ignition and also the expansion of the forest fire.

Table 2
 Meteorological data, as well as, median and maximum (in parenthesis) values of the permanent gases and particulate matter, measured at the monitoring sites in the forest fire incident

| | Site A | Site B | Site C | Site D |
|--|-------------|-----------------|----------------|-------------|
| Distance from the flame-front (m) | 100 | 100 | 70 | 150 |
| Total elapsed time (min) | 30 | 60 ^a | 30 | 30 |
| Relative humidity RH% (min and max) | 23–28 | 21–28 | 20–22 | 23–25 |
| Temperature (°C) ^b | 31 | 32 | 32 | 29 |
| Wind velocity (km h ⁻¹) ^b | 37 | 38 | 15 | 26 |
| CO ^c | 2 (15) | 1 (3) | 8 (44) | 0 |
| CO ₂ ^c | 400 (800) | 350 (500) | 350 (500) | 350 (350) |
| NH ₃ ^c | N.D. | N.D. | N.D. | N.D. |
| PM _{2.5} ^d | 335 (9.708) | 2.485 (6.400) | 6.865 (49.484) | 148 (2.000) |
| PM ₁₀ ^d | N.M. | 1.300 (5.500) | N.M. | N.M. |

N.D.: not detected; N.M.: not measured.

^a 30 min sampling for permanent gases, 30 min sampling for PM_{2.5} and 30 min sampling for PM₁₀.

^b Average value.

^c ppm.

^d μg m⁻³.

Permanent gases concentrations (maximum and median values), measured near the flame-front are also presented in Table 2. Comparing the CO concentrations, measured in this fire incident, with the 25 ppm TLV–TWA limit of ACGIH it seems that this limit is not exceeded at any of the sites; an exception is at site C, where CO reached a maximum value of 44 ppm. It should be noted that ACGIH levels are referred to 8 h occupational indoor daily exposure and not to field outdoor exposure or to specific heavy conditions. There have been some efforts [37,48] to calculate CO exposure limits for extended work-shifts of the fire-fighters, taking into consideration factors, such as the altitude of the forest, the duration of fire-fighters exposure to smoke and the distance of camping sites from smoke front. It has been reported in literature [49] that during fire-fighters' exposure to smoky conditions, the CO level exceeded the 200 ppm ceiling limit of the National Institute for Occupational Safety and Health (NIOSH). According to the same source, exposure to CO peak concentrations can cause a number of short-term effects, such as, eye, nose and respiratory irritation, fatigue, inability to concentrate on complex tasks, headache, dizziness, as well as nausea. That is because CO inhalation produces concentration level of carboxyhaemoglobin (COHb) in blood that exceeds 5%. It has been reported that generally a level of 5% COHb results from 3 to 4 h of exposure to CO concentrations of 35 ppm and it may cause disorientation or fatigue [50]. Immediately dangerous to life or health concentration (IDLH) of CO, based on acute inhalation toxicity data in humans, is 1.200 ppm according to NIOSH. It has been stated that a 1 h exposure to 1.000–1.200 ppm would cause unpleasant but no dangerous symptoms, whereas 1.500–2.000 ppm might be a dangerous concentration after 1 h of exposure [51]. The lethal concentration of 50% kill (LC50) for CO in rats by inhalation is 6.822 ppm (30 min time adjusted), whereas the lowest published lethal concentration in humans (LCLo) is 4.000 ppm [52].

Generally, CO₂ is considered a major product of forest fires, due to complete combustion. However, it seems that in this fire

incident complete combustion at the specific sampling sites was not favored, as the maximum CO₂ concentrations measured ranged between 350 and 800 ppm; a typical concentration of CO₂ in ambient air is 350 ppm. Ammonia was not detected at any of the sites.

In Table 2, concentrations of particulate matter (PM) (maximum and median values) are also presented. Exposure limits to PM are usually given for 24 h exposure by various Health Organizations. During a forest fire, very high concentrations of particles at short time duration may be observed; that short-term peaks may cause some of the most significant health implications. According to the above, exposure limits to particles during a forest fire should be reconsidered for the operational people of the front-line and the sensitive groups. It should be emphasized that official exposure limits of particles in the front-line are not exist. However, there are efforts to provide with some criteria, in order to assess the severity of the situation in a forest fire [53]. According to these short-term criteria, emergency airborne concentrations of particles are given as average concentrations of PM_{2.5} or PM₁₀ (in μg m⁻³), during 1 h or 3 h of exposure; the respective characterization of the situation is also provided. More specifically, concentrations of 0–40, 41–80, 81–175, 176–300, 301–500 and over 500 μg m⁻³ result to situations characterized as

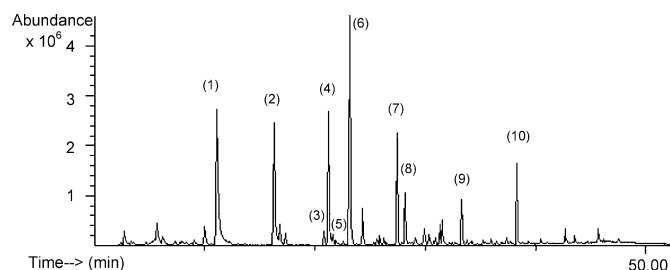


Fig. 1. A typical chromatogram of VOCs evolved in the forest fire incident (site C). The numbered peaks indicate the most prominent VOCs: (1) benzene, (2) toluene, (3) chlorobenzene-d₅ (i.s.), (4) ethyl benzene, (5) xylene (6) styrene, (7) benzene (1-methylethenyl), (8) benzaldehyde, (9) ethanone, 1-phenyl, (10) naphthalene.

good, moderate, unhealthy for sensitive groups, unhealthy, very unhealthy and hazardous, respectively. Following those short-term criteria, situation in site D of the fire incident is characterized unhealthy for sensitive groups, in site A unhealthy and in sites C and D hazardous.

In Fig. 1, a typical chromatogram of the VOCs identified at site C is presented. The numbered peaks indicate the most prominent VOCs. Totally, 76 different VOCs were identified in the smoke samples taken from the four sites, presented in Table 3 according to their retention time. Aromatic compounds, such as benzene, toluene, ethyl benzene, xylene (BTEX) and many benzene derivatives, naphthalene and its derivatives, phenol, styrene, 1-H-indene, furan and derivatives, alkanes, such as hexane and heptane, alkenes, such as 1-undecene and 1-dodecene, aldehydes, such as furfural and benzaldehyde, were some of the identified VOCs. The number of common VOCs identified at all four sites was 10.

Table 3
VOCs measured in the forest fire incident, presented according to their retention time

| | |
|--------------------------------------|---|
| (1) 1-Propene | (39) Decane |
| (2) Methane-chloro | (40) Benzene, 1-ethyl-2-methyl |
| (3) 1-Propene, 2-methyl | (41) Benzene, 1-methylethenyl |
| (4) 1-Pentene | (42) Benzene 1,3,5- trimethyl |
| (5) Furan | (43) Benzaldehyde |
| (6) 2-Propanone | (44) Octanal |
| (7) Acetonitrile | (45) 1-Hexanol, 2-ethyl |
| (8) 1-Hexene | (46) DL-Limonene |
| (9) Hexane | (47) Undecane, 5,7-dimethyl |
| (10) 2-Butenal | (48) Benzofuran |
| (11) 2-Propen-1-ol | (49) Benzene, 1-propenyl |
| (12) Furan, 2-methyl | (50) Benzonitrile |
| (13) Butanone-2 | (51) Benzene, 3-butenyl |
| (14) 1,3-Dioxolane, 2-methyl | (52) Benzene, butyl |
| (15) Benzene | (53) 1-Undecene |
| (16) Heptane | (54) Undecane |
| (17) 1,4-Dioxane | (55) 1-H-Indene |
| (18) 1-H-Pyrrole, 1-methyl | (56) Phenol |
| (19) Benzene, methyl | (57) Benzene, 1-ethenyl-3,5-dimethyl |
| (20) Hexane, 2,3,4-trimethyl | (58) Nonanal |
| (21) Octane | (59) 1-H-Indene, 2,3-dihydro-2-methyl |
| (22) 1,3-Dioxolane, 2-ethyl-4-methyl | (60) Benzene, 1,2,4,5-trimethyl |
| (23) Cyclopentanone | (61) Benzene, diethenyl |
| (24) Benzene, ethyl | (62) Ethanone, 1-phenyl |
| (25) Cyclopropane, 1-methyl-2-pentyl | (63) Benzoic acid, methyl ester |
| (26) 1-Nonanol | (64) Benzenemethanol |
| (27) Nonane | (65) 1-Dodecene |
| (28) Xylene | (66) 1-H-Indene, 1-methyl |
| (29) Furfural | (67) 1-Propanone, 1-phenyl |
| (30) Benzene, ethynyl | (68) Decanal |
| (31) Styrene | (69) Naphthalene |
| (32) A-Pinene | (70) Decane, 2,3,5-trimethyl |
| (33) Cyclohexanone | (71) Benzoic acid, 2-propenyl ester |
| (34) Benzene, 1-methylethyl | (72) Meso-2,3-diethyl-2,3-dimethylsuccinic acid dinitrile |
| (35) Camphene | (73) Naphthalene, 1-methyl |
| (36) Benzene, propyl | (74) Naphthalene, 2-methyl |
| (37) Benzene, 2-propenyl | (75) Naphthalene, 2-ethenyl |
| (38) 1-Decene | (76) 1,1'-Biphenyl-2-methyl |

Table 4

Concentrations of six prominent VOCs (in $\mu\text{g m}^{-3}$), identified at all four sites in the forest fire incident (30 min TWA values)

| | Benzene | Toluene | Ethyl benzene | Xylene | Styrene | Naphthalene |
|--------|---------|---------|---------------|--------|---------|-------------|
| Site A | 84 | 56 | 29 | 13 | 34 | 15 |
| Site B | 112 | 47 | 6 | 21 | 106 | 10 |
| Site C | 696 | 436 | 17 | 347 | 657 | 182 |
| Site D | 85 | 34 | 23 | 34 | 102 | 8 |

In Table 4, the concentrations in $\mu\text{g m}^{-3}$ of six of the most prominent VOCs (benzene, toluene, ethyl benzene, xylene, styrene, naphthalene), identified at all four sites in the forest fire incident, are presented. These results should be interpreted as semi-quantitative and express the time weighted average values for 30 min sampling process of VOCs in each site. The above analytes were chosen because they have also been identified in other forest fires [6,48] and their concentrations are given for comparison, as shown in Table 5. Although these pollutants are considered as background of an urban area (traffic emissions), concentrations determined in four sites were at higher levels than those found in blank samples representative of an urban area. Maximum concentration of benzene, which is considered a potential carcinogen, was determined at site C ($696 \mu\text{g m}^{-3}$). However, it was found to be 2×10^3 times sub-multiple compared to the IDLH of NIOSH, 4.6×10^4 sub-multiple, compared to the LC50 for mouse inhalation and 9×10^3 sub-multiple, compared to the respective LCLo (NIOSH). According to the literature [54], exposure at 160 mg m^{-3} of benzene for 60 min leads to symptoms of illness, exposure of $16\text{--}50 \text{ mg m}^{-3}$ for 5 h results to headache, lassitude and weakness; exposure at 8 mg m^{-3} for 8 h has no effect.

In Table 5, the concentration ranges of the permanent gases, VOCs and particulate matter measured in different forest fires are presented for comparison. However, it is important to take into consideration the different conditions that took place in each forest fire. More generally, measurements near the flame-front are considered as measurements in dynamic situations; rapid changes of concentration gradients in space and time usually take place. Consequently, measurements presented in this work are indicative of the concentration profiles.

It should be emphasized that styrene concentration appeared to be unusually high in this fire incident, especially at site C. Styrene/benzene concentrations ratio was used to monitor styrene evolution in this fire that burned a forest mainly covered by pine trees and also a storehouse of plastics. In order to define styrene/benzene concentrations ratio in case of pure forest fuel combustion, data were used from pure pine needles lab-scale combustion experiments (hood and wind tunnel). The mean value of this ratio was found 0.67 for the forest fire incident and 0.23 for the pure pine needles, while the standard deviations were found 0.25 and 0.09, respectively. The difference between the two mean values was found statistically significant (99% probability). It appears that styrene identified in the forest fire smoke mostly originated from the combustion of the plastics storehouse.

Table 5
Concentration ranges of the permanent gases, VOCs and particulate matter measured in different forest fires

| Location | Permanent gases ^a | | Volatile organic compounds ^b | | | | | | Particulate matter ^b | |
|------------------------------------|------------------------------|-----------------|---|----------|-------------|---------|---------------|----------|---------------------------------|-----------|
| | CO | CO ₂ | Benzene | Toluene | Naphthalene | Styrene | Ethyl benzene | Xylene | PM 10 | PM 2.5 |
| Greece ^c (in this work) | 1–8 | 350–400 | 84–696 | 34–436 | 8–182 | 34–657 | 6–29 | 13–347 | 1.300 ^d | 148–6.865 |
| South east Asia ^c | N.M. | N.M. | 0.4–24.8 | 2.1–15.5 | 2.1–15.2 | N.M. | 0.14–2.01 | 3.7–28.7 | 49–372 | N.M. |
| Shoshone ^f (USA) | 22.2–23.3 | N.M. | 64–96 | 38 | N.D. | N.M. | N.M. | N.M. | 900–1.000 | N.M. |
| Clover Mist ^f (USA) | 3.9–4.6 | 700–750 | 64 | N.D. | 2.74 | N.M. | N.M. | N.M. | 200–15.900 | N.M. |
| North Fork ^f (USA) | 7.9–11.5 | N.M. | N.D. | N.D. | 2.99–3.27 | N.M. | N.M. | N.M. | 1.200–47.600 | N.M. |

^a ppm.

^b $\mu\text{g m}^{-3}$.

^c 30 min median values (for permanent gases and particulate matter) and 30 min TWA values (for VOCs), measured in a distance of 70–150 m from the flame-front.

^d PM₁₀ were measured only in a distance of 100 m from the flame-front.

^e 24 h average values measured over a 5-day period, in a distance of 3.5 km from the flame-front.

^f Area air sampling near the firemen crew.

4. Conclusions

Forest fire smoke components can have different physical and chemical properties, depending on their origin, which can be correlated to health impacts on the exposed population and firemen. In the present case study, styrene identified in the forest fire smoke mostly originated from the combustion of plastics (polystyrene), due to the expansion of the forest fire to the plastics storehouse.

The road-map presented in this work is a first approach to integrate data regarding forest fire smoke that can be useful for providing an initial indication of the air-quality in a forest fire. However, it needs to be interpreted carefully; further lab-scale and field experiments are needed for making its conclusions solid.

Finally, it appears from this work that criteria for air-quality monitoring in a forest fire have to be established.

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