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Emissions of volatile organic compounds (VOCs) from biomass burning

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.**Abstract**

Vegetation fires, such as savanna and forest fires, domestic fuels and agricultural wastes burnings, are a significant source of gases as carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nitrous oxide (NO) and volatile organic compounds (VOC) that are annually released into the atmosphere and could affect the atmospheric chemistry through the "greenhouse" effect and the photochemical ozone formation . Biomass burning also exacerbates atmospheric particulate matter loadings, releasing primary fine carbonaceous particle. This in turn leads to significant health implications, particularly for the respirable fraction (fine particles less than 2.5 μm in diameter) and impact on the Earth's radiative budget. Furthermore, the fine particles increase the cloud albedo partly and, by acting as cloud condensation nuclei, they could modify the rainfall regimes. It is presented so a general overview about volatile organic compounds, their interactions with the atmosphere and the general aspects about biomass burning. Then we demonstrate the performance of a recently developed combustion chamber, showing its capability in estimating the emission from wildland fire through a case study with dried leaf litter of *Quercus robur*. The combustion chamber was equipped with a thermocouple, a high resolution balance, an epiradiometer, two different sampling lines to collect volatile organic compounds (VOCs) and particles, a portable analyzer to measure carbon monoxide (CO) and carbon dioxide (CO_2) emission and a methane (CH_4) analyzer. VOCs were determined by gas chromatography–mass spectrometry (GC-MS) after enrichment on adsorption traps, but also monitored on-line with a proton-transfer-reaction mass spectrometer (PTR-MS). Preliminary qualitative analyses of emissions from burning dried leaf litter of *Q. robur* found CO_2 and CO as the main gaseous species emitted during the flaming and smoldering stages, respectively. Aromatic VOCs, such as benzene and toluene, were detected together with several oxygenated VOCs, like acetaldehyde and methanol.

Biomass burning is an important ecological factor in the Mediterranean ecosystem where wildfires are very frequent and the predicted future of possible increase of fires could modify drastically the vegetation scenarios. The gaseous and particulate emissions from the combustion of three different plant tissues (leaves, woody branches and litter) of two tree species (*Pinus halepensis* and *Quercus pubescens*) are reported. These species are very common across the Mediterranean area and often subject to wildfires. Experiments were carried out in the combustion chamber previously described. The percentages and the trends of gaseous emissions during the different stages of burning (pre-ignition, flaming and smoldering) were reported. We identified and quantified 83 volatile organic compounds (VOC_S) including important carcinogenic species that can affect the human health. The CO and CO_2 confirmed again as the main gaseous species emitted, benzene and toluene were the dominant aromatic hydrocarbons, methyl vinyl ketone and methyl ethyl ketone were the most abundant measured OVOCs. CO_2 and CH_4 emissions showed the peak of emissions during the flaming phase, while the peak of CO emission occurred during smoldering phase. In general the combustion of leaves released in the atmosphere a greater quantity of VOCs than the combustion of woody branches and litter. There are little differences between the emissions from the combustion of the two tree species, except for some compounds. The combustion of *P. halepensis* released a great amount of monoterpenes as α-pinene, β-pinene, β-cymene, sabinene, Δ^3-carene, terpinolene, camphene that are not emitted from the combustion of *Q. pubescens*. The combustion of woody branches showed the highest duration of flaming and peak of heat. Moreover, the carbon budget emitted during the biomass combustion was obtained. Data presented in this thesis reveal the favorability of using a combustion chamber to better understand how different typologies of biomass can affect wildfires and the speciation profile of their emission. Furthermore, these data describe in detail the phases occurring during biomass combustion that could be crucial for modeling assessments.

Riassunto

Ogni anno una grande quantità di composti gassosi come anidride carbonica (CO_2), monossido di carbonio (CO), metano (CH_4), monossido di azoto (NO), ed altri composti organici volatili (VOCs) sono immessi in atmosfera durante la combustione di biomassa vegetale e possono influenzarne la chimica attraverso l'effetto "serra" e la formazione fotochimica dell'ozono. La combustione di biomassa, rilasciando in aria grandi quantità di piccole particelle carboniose, contribuisce ad aumentare la quantità totale di particolato in atmosfera. Ciò può avere importanti conseguenze sulla salute umana, soprattutto per quanto riguarda la frazione di particolato respirabile (particelle di diametro inferiori a 2.5 μm), e può avere un impatto molto significativo sul budget radiativo della Terra. Inoltre, le piccole particelle carboniose aumentano l'effetto albedo ed agendo come nuclei di condensazione possono modificare il regime delle precipitazioni.

Gli incendi boschivi sono un fattore ecologico molto importante nell'ecosistema del Mediterraneo e gli scenari futuri di un possibile aumento del rischio di incendi potrebbero modificare drasticamente lo scenario vegetazionale.

Questa tesi si propone di integrare le conoscenze sui composti gassosi ed il particolato immesso in atmosfera durante un incendio forestale tramite esperimenti di combustione svolti in laboratorio.

È stata quindi ideata e costruita una camera di combustione al fine di studiare le emissioni da combustione di biomassa. La camera di combustione è dotata di una termocoppia, una bilancia ad alta risoluzione, un epiradiometro, due differenti linee di campionamento per campionare i composti organici volatili (VOCs) ed il particolato, un analizzatore portatile per misurare le emissioni di monossido di carbonio e anidride carbonica ed un analizzatore di metano. I composti organici volatili, collezionati all'interno di trappole assorbenti durante le prove di combustione, sono stati determinati tramite analisi al gas-cromatografo accoppiato con uno spettrometro di

massa (GC-MS). I composti organici volatili sono inoltre monitorati in tempo reale utilizzando uno spettrometro di massa (PTR-MS).

I primi risultati per testare la validità della camera di combustione sono presentati attraverso il caso studio su foglie disidratate di farnia (*Quercus robur)*. Le prime analisi qualitative sulle emissioni da combustione di foglie di farnia indicano che la CO_2 ed il CO sono le specie gassose principalmente emesse durante, rispettivamente, la fase di *flaming* e la fase di *smoldering*. Sono stati identificati molti composti organici volatili aromatici, come il benzene ed il toluene, ed altri composti organici volatili ossigenati come l'acetaldeide ed il metanolo.

Successivamente, le emissioni di specie gassose e di particolato derivanti dalla combustione di tre differenti materiali vegetali (foglie, rametti e lettiera) di due diverse specie arboree, il pino d'Aleppo (*Pinus halepensis*) e la roverella (*Quercus pubescens*) sono riportate come caso studio di incendi che ogni anno si verificano nel Mediterraneo, in particolar modo nell'ecosistema murgiano del Parco Nazionale dell'Alta Murgia dove sono stati campionati e di cui ne caratterizzano la vegetazione arborea principale. Sono stati identificati e quantificati 83 composti organici volatili, incluse importanti specie cancerogene che possono arrecare danni alla salute umana. La CO_2 ed il CO si confermano le principali specie gassose emesse, il benzene ed il toluene sono tra i composti organici aromatici dominanti, mentre il metiletilchetone ed il metilvinilchetone sono tra i composti organici ossigenati maggiormente emessi. L'anidride carbonica ed il metano mostrano picchi di emissione durante la fase di *flaming*, mentre il picco del monossido di carbonio si verifica durante la fase di *smoldering*. In generale, la combustione di foglie rilascia in atmosfera la maggiore quantità di VOCs rispetto la combustione di rametti e lettiera. Per quanto riguarda le emissioni di composti organici volatili, le maggiori differenze riscontrate tra le due specie arboree riguardano l'emissione di terpenoidi. La combustione di pino d'Aleppo rilascia una grande quantità di monoterpeni come α-pinene, β-pinene, β-cymene, sabinene, Δ^3-carene, terpinolene e canfene, i

quali sono invece assenti nella combustione di roverella. Differenze significative si rilevano anche nelle caratteristiche della combustione, in particolare i rametti di entrambe le specie mostrano durata della fase di *flaming* e picco di calore sviluppato durante la combustione significativamente più alti rispetto foglie e lettiera.

Sono stati infine stimati la quantità di carbonio totale ed il particolato emessi durante la combustione di biomassa.

I dati presentati in questa tesi mettono in luce i numerosi vantaggi offerti dall'uso di una camera di combustione per valutare in modo approfondito come le differenti tipologie di biomassa possono influire sugli incendi e sul profilo delle specie emesse durante essi. Questi risultati descrivono in dettaglio le differenti fasi del processo di combustione e forniscono i fattori di emissione di molte specie gassose emesse che potranno essere utilizzati per lo sviluppo di modelli previsionali.

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1 An overview on biosphere-atmosphere gas exchange

The terrestrial biosphere covers approximately 30% of the Earth's surface, and vegetation plays an important role in the interaction between the land surface and the physical and chemical atmosphere, influencing them through many processes. Energy, water, carbon, and other trace gases are constantly exchanged between the biosphere and the atmosphere behaving as a coupled system. The biosphere and atmosphere are dynamic and reflect constantly these interactions and feedbacks. These exchanges modify mass transport and the thermodynamic structure of the atmosphere, which in turn affect atmospheric circulation, cloud formation, and rainfall, as well as land processes involving the carbon cycle, the hydrologic cycle, and the radiative budget of Earth's surface. In particular the exchange of gases and aerosols between the Earth's surface and the atmosphere plays a fundamental role in determining air quality, and it is an important driver of climate at both regional and global scales. Molecules of the gases and aerosol can be exchanged between the atmosphere and Earth's surface by physical processes (e.g. evaporation, volcanic eruption, continental weathering, wind blowing) or biological processes (e.g. evapotranspiration, photosynthesis, bushfires) or anthropogenic processes (e.g. burning fossil fuels, industrial activities).

Regarding the biological processes and thus the biogenic emission, there are physical, biological and chemical processes that affect in turn the emissions. Important physical processes include atmospheric turbulence, molecular diffusion and energy exchange, while important biological and biogeochemical processes include the regulation of biological barriers (stomata and cuticle) that control the diffusion of trace gases but also biological factors as respiration, transpiration, decomposition of plant material by microbes, mineralization, nitrification, denitrification at plant community scale release trace gases in atmosphere.

2 Biogenic Volatile Organic Compounds (BVOCs)

Biogenic volatile organic compounds (BVOCs) are emitted by almost all plants. They are involved in a range of ecological functions, including indirect plant defense against insects, pollinator attractor, plant-plant communications, plant-pathogen interactions, reactive oxygen species removal, thermo-tolerance and environmental stress adaptation. Their evolution is complex and it is driven by interaction of plants with biotic and abiotic factors in constantly changing environment, at local and global level (Spinelli et al., 2011). They includes volatile isoprenoids (isoprene, monoterpenes, sesquiterpenes) which are the major fraction of biogenic VOC emissions, followed by oxygenated volatile compounds (alcohols, aldehydes, ketones, ester), alkenes and in a minor part also alkanes and aromatics (e.g. ethane and toluene). Global emission have been estimated at around 800 Tg C y^{-1} although this estimation is continuously updated based on the latest laboratory results and large-scale monitoring (Fowler et al., 2009)

2.1 Volatile isoprenoids

Volatile isoprenoids have a relevant role in the atmosphere and important functions in plant vs. environment interaction (Fowler et al., 2009). Isoprene and monoterpenes are produced from the precursor dimethylallyl diphosphate (DMAPP) and its isomer isopentenyl diphosphate (IPP), which are synthesized by the deoxyxylulose-5-phosphate (DXP) pathway in the chloroplast and by the mevalonate pathway in the cytoplasm (Lichtenthaler, 1999). Isoprenoids carbon skeletons are composed of five-carbon building blocks that may be assembled in a variety of formations and contain many different modifications.

2.1.1 Monoterpenes and sesquterpenes

Monoterpenes and sesquiterpens are active compounds in plant interactions with other organisms (Fowler et al., 2009) as attractors or deterrents for herbivores or carnivores and attractors for pollinators (Gershenzon and Duradeva, 2007). For instance menthol plays a role as mild antimicrobial, citral and geraniol are aroma components, citronellal is an insect repellent, linalool acts as parasitoid wasp attractant, and camphor has an allelopathic function (Paiva, 2000).

Monoterpenes are lipid-soluble molecules and may protect plant membranes from thermal and oxidative stress (Sharkey and Yeh, 2001). Their production is strongly specie-specific (Fowler et al., 2009). Monoterpenes and sesquiterpenes are emitted from specialized storage structures such as resin ducts present in conifers, glandular trichomes in species from Lamiaceae (peppermint) and oil glands in Rutaceae (lemon, orange) and Myrtaceae (eucalypts). Monoterpenes, such as eucalyptol, linalool, camphor, α-pinene, β-pinene, α-terpineol, borneol and many others are the principal components of aromatic plant volatile oil (Dorman and Deans, 2000; Candan et al., 2003).

Many sesquiterpenes are typical fragrances emitted from flowers (Chen et al., 2003) but also from the herbivore-damaged foliage (Vourinen et al., 2004). High levels of sesquiterpenes are produced also after O_3 exposure in O_3-resistant tobacco (Holopainen, 2004).

2.1.2 Isoprene

Isoprene (C_5H_8, 2-methyl 1,3-butadiene) is the dominant hydrocarbon that moves from plants to the air and its global emission is estimated to be about 500 Tg C yr^{-1} (Guenther et al., 1995; Wang

and Shallcross, 2000). The biosynthesis of isoprene requires an high cost in term of energy and carbon but its benefits are numerous as it is a leaf thermoprotector, a flowering hormone (Terry et al., 1995), an antioxidant (Zeidler et al., 1997), and a metabolite overflow to get rid of excess carbon (Logan et al., 2000). Isoprene is not stored within the leaf but it is immediately emitted through the stomata upon its production. For this reason its synthesis is dependent on photosynthesis. Therefore, the factors affecting photosynthesis such as water stress, light and temperature excesses usually influence also isoprene emission. Isoprene emission is very sensitive to temperature, whereas seem to be only marginally effected by moderate water-stress even if drought directly affects stomatal conductance and produce diffusive and biochemical limitations of photosynthesis (Tingey et al., 1981). Isoprene has also an important role thermotolerance during short high-temperature episodes (Singsaas and Sharkey, 1998) probably thanks to the stabilization of membrane lipid bilayer by enhancing the hydrophobic interactions (Gounaris et al., 1984). Isoprene may play also an important role as antioxidant in leaves. It react with ozone and hydroxyl radicals reducing rapidly the damage caused by acute and short (3h, 300nL L^{-1}) or relatively low and long (8h, 100nl L^{-1}) ozone treatments in leaves (Loreto et al., 2001).

2.2 Oxygenated volatile compounds

The denomination oxygenated organic compounds includes a wide range of organic molecules as alcohols (R-OH), ketones (R_1-CO-R_2), aldehydes (R-CHO), ethers (R_1-O-R_2), esters (R_1-COO-R_2) and acids (R-COOH). They are emitted by all plants (Fowler et al., 2009) or are produced in the atmosphere in the course of the oxidation of hydrocarbons (Monk et al., 2009). The emission of these compounds may be induced by developmental and stress factors and they may be large at certain periods of the year and by certain vegetation types.

Methanol, acetaldehyde and other C-6 compounds are often emitted in large quantities, especially in the presence of mechanical wounding or other stress (Loreto et al., 2006). Formaldehyde (HCHO) plays a key role in atmospheric chemistry as it readily photolyses, being a source of the hydroperoxyl radical (HO_2) and of ozone (in the presence of NO_x). It is formed either as an intermediate during the oxidation of many VOC or is emitted directly by fossil fuel combustion or biomass burning (Monks et al., 2009). The release of methanol (CH_3OH) is associated with cell wall damage occurring because of wounding (Karl et al., 2001), growing plant tissues (Harley et al., 2007), senescing tissues (Fall, 2003). It is the most abundant non-methane VOC in the atmosphere. Large fluxes of acetaldehyde (CH_3CHO) have been observed in conditions of root anoxia such as under waterlogging stress and under natural condition (Lathiere et al., 2006). Short-lived emissions of acetaldehyde are also observed from darkened leaves (Karl et al., 2002), but also following wounding and ozone stress episodes. Acetone (CH_3COCH_3) is primarily emitted by biomass burning and anthropogenic activities. It has been suggested that in the dry conditions of the higher troposphere acetone can act as an important source for OH and peroxy radicals (HO_x) (Jaegle et al., 2001).

2.3 The BVOCs emissions and their role in the atmosphere

Emissions essentially result from diffusion of BOVCs along a vapore-pressure gradient from cellular compartments of relatively high concentrations to the air surrounding the leaf, where there are relatively low concentrations because of the transport, extreme reactivity and brief lifetime of most BOVCs (Penuelas and Llusia, 2003).

Emission of storing species seems to depend more on temperature, whereas emission of non-storing species seems to depend more on PFD and photosynthetic rate (Penuelas and Llusia, 1999) that alter the production of monoterpenes and so affect their vapor pressure according to a concentration-dependent relationship (Llusia and Penuelas, 2000).

BVOC could protect plants against high temperature, but, in their turn, BVOC emissions increase with warming, and might produce both negative and positive feedback on climate warming through aerosol formation and direct and indirect greenhouse effects.

BVOCs emissions regulate crucial features of atmospheric chemistry and their impact depend on two main factors: its atmospheric lifetime, which is controlled by its rate of reaction with the common atmospheric oxidants, O_3, OH and NO_3, and the mechanism of its oxidation (Monks et al., 2009). BVOCs are, in general, extremely reactive and their emission constitute a significant input of precursors for photochemical oxidant being the major reaction partner for OH (Trainer et al., 1993; Simpson et al., 1995). They actually influence the oxidizing potential of the troposphere by affecting the concentration of the main atmospheric oxidant, the hydroxyl radical (Penuelas and Llusia, 2003; Monks et al., 2009). Many studies have also demonstrated that BVOC contribute to the formation of tropospheric ozone (Chameides et al., 1988; Tao et al., 2003; Bell and Ellis, 2004; Hogrefe et al., 2011) in the presence of NO_x. The oxidation of isoprene and monoterpenes has been postulated to be a large potential source of CO in the troposphere (Fehsenfeld et al.,

1992). In turn, the concentration of carbon monoxide in the atmosphere is a major factor in the control of the OH radicals levels in the atmosphere.

The oxidation of the biogenic hydrocarbons is initiated by the highly reactive O_3 and the ubiquitous, transient HO and NO_3 radicals.

The atmospheric oxidation of isoprene for instance, is dominated by its reaction with OH during the day and its reaction with NO_3 during the night, while ozone plays a minor role day and night. Methyl vinyl ketone (MVK) and methacrolein have long to been known to account for about 60% of the isoprene reacted (Tuazon and Atkinson, 1990), with formaldehyde as a co-product in each case.

BOVCs, particularly sesquiterpenes and monoterpenes (Monks et al., 2009), also generate large quantities of secondary organic aereosol particles (SOA) by either direct condensation of the BVOC, or the products from the atmospheric oxidation. The organic aereosol particles scatter and absorb radiation, and could affect cloud formation and precipitation by acting as cloud condensation nuclei (Hoffmann et al., 1997; Hartz et al., 2005; Dusek et al., 2006).

Also the oxygenated VOCs can have a significant role in tropospheric chemistry. For example, acetone is believed to play an active role in the formation of peroxyacetyl nitrate and in the formation of OHx radicals (Singh et al., 1995).

2.4 Abiotic factor that influence the BVOC emission

Stored VOCs may be volatilized into the atmosphere by healthy unwounded plants depending on their concentration and physiochemical properties (Niinemets et al., 2004). In addition to the constitutive emission by constitutively emitting species, the emission of volatile compounds are induced in response to stress in practically all plant species, also in those not emitting volatile

isoprenoids under optimal growth conditions (Heiden et al., 1999). The induced VOCs are produced only after biotic and abiotic inductions and they have the advantages that they are *de novo* synthesized only when needed and therefore they optimize carbon usage and do not reduce plant fitness (Dicke, 2000).

Many environmental factors can influence the biogenic volatile organic emission. They include drought, light, soil/litter moisture, humidity, salinity, ozone exposure, wind and turbulence, static pressure fluctuations, nutrient deficiency, chemical, hydraulic, and thermal properties of the soil.

Many oxygenated volatile compounds for instance are emitted from leaves subject to various stresses such as wounding (e.g. as a consequence of cutting hay), insect feeding, ozone stress and heat stress. Also the synthesis of volatile isoprenoids is induced in many species in response to biotic (e.g. attack of herbivores and pathogen), and abiotic (e.g. ozone stress, heat stress) stresses (Beachamp et al., 2005; Blande et al., 2005; Loreto et al., 2006).

In constitutively emitting species, the volatile isoprenoids blend differs between induced and constitutive emissions. For instance in non- stressed conditions, the emissions of the monoterpene-emitting species *Pinus pinea* are dominated by limonene, but the emissions in conditions of high temperature and low water availability are dominated by linalool and ocimene (Staudt et al., 2000). The BVOCs emission represent a large carbon loss and can be up to ~ 10% of that fixed by photosynthesis under stressfull condition.

Land use change, with consequent shifts in species dominance, also have the potential to change BVOC emissions dramatically because these emissions are specie-specific (Lerdau and Slobodkin, 2002).

2.4.1 Effect of temperature

As other physiological processes (e.g. photosynthesis) also biogenic VOC emissions are very sensitive to changes in temperature.

Temperature increases the emission rates of most BVOC exponentially by enhancing the enzymatic activities of synthesis (Loreto and Schnitzler, 2010), by raising the BVOC vapor pressure, and by decreasing the resistance of the diffusion pathway (Tingey et al., 1991). For VOC compounds with low air-liquid phase partition coefficient (Henry's law constant), stomatal closure may constrain emission rates, and, specifically changes in temperature can alter the gas/liquid phase partitioning (as well as the biosynthesis rate of the compound) (Filella et al., 2007). This may affect emission flux rates (Niinemets and Reichstein, 2003) and alter the expected exponential response to temperature. Also, the stress produced by high temperature may generate additional emissions of stress-related volatiles, such as hexenal and hexenols among others (Heiden et al., 2003).

2.4.2 Effect of CO_2

The effect of the progressive rise of atmospheric CO_2 concentration on the emission rate of BVOCs has been investigated in a number of studies, and different responses have often been observed. The responses of plant emissions to rising [CO_2] can differ among species and among plants of different ages. The responses can also vary with different experimental lay-outs, times of exposure, and with water and nutrient supply.

For instance, there is a high degree of species-specific variability in the response of isoprene emission to elevated [CO_2], although generally a decreased emission is observed both in the short-

term and in the long-term experiments. But the responses of isoprene emissions to changes in [CO_2] is the effect of drought, which can offset the negative effect of elevated [CO_2]. Emissions from poplar trees grown under elevated [CO_2] showed a significant stimulation under drought as compared to those grown under ambient [CO_2]. Only when drought stress became severe, the emission decreased under elevated [CO_2] (Pegoraro et al., 2007).

2.4.3 Effect of drought

It is well know that drought will impact some plant physiological processes. The physiological response to moderate drought include significant reductions in stomatal conductance and photosynthetic rates. Extreme drought reduces these rate to zero and results in senescence (the plant drops its leaves) in some plants. Specific response vary considerably among different species (Guenther, 2001). For example *Quercus virginiana* is fairly drought resistant and showed no change in isoprene emission despite of the large decrease in photosynthesis after a treatment of drought (Tingey et al., 1981). Sharkey and Loreto (1993) showed even an increment of isoprene emission during the drought stress in *Pueraria lobata* even if the photosynthesis rates drop to zero. The response to the drought stress could be very differ depending on species considered, however, there is a general consensus (Fuentes et al., 2000; Guenther et al., 2000) that extreme and extended drought will lower the isoprene emission capacity of plant.

The variability of responses to drought depending also on what VOC species are considered because probably emissions of some VOC compounds will be less responsive while other are more responsive. Bertin and Staudt (1996) studied the effect of drought on *Quercus ilex* and showed that monoterpene emissions were reduced only after severe drought. Monoterpenes are not stored in *Q. ilex* and their light dependent production and emission pattern are similar to isoprene.

The emissions of monoterpenes that have been stored in plant tissue (e.g from the pine trees) are likely to be very unsensitive to drought (Guenther et al., 2001).

The oxygenated VOC emissions showed a strong correlation with stomatal conductance. The lower stomatal conductance observed with drought conditions might lead to large decrease in these emission. Nonetheless it was observed in some cases that some oxygenated VOC emissions appear to be greatly increased by stress and so drought might increase their emissions (Guenther et al., 2001).

3 Emissions from vegetation fire

Biomass burning is widespread in the Earth, it could result from wildfire that naturally trigger in the ecosystem, but more often there are human-induced fires. The use of fire as a tool to manipulate the environment has been instrumental in the human conquest of Earth, the first evidence of the use of fire by early hominids dating back to 1 million to 1.5 million years ago (Schule, 1990). Nowadays biomass burning serves a variety of purpose, such as clearing of forest and brushland for agricultural use, control of pests, insect and weeds, nutrient mobilization, agricultural waste burning and removal of dry savanna vegetation and firewood, prescribed burning for forest management (Crutzen and Andreae, 1990). Vegetation fires release a great amount of trace gases as carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nitrous oxide (NO), volatile organic compounds (VOC) as aldehydes, ketones, alcohols and acid organic annually that could affect the atmospheric chemistry and biogeochemical cycles (Crutzen and Andreae, 1990; Lobert et al., 1990; Miranda et al., 1994; Holzinger et al., 2004; Yokelson et al., 2007) at regional scale but also, due to the transportation of gaseous species over large distances, at global scale (Duck et al., 2007; Petzold et al., 2007; Liu et al., 2010; Alves et al., 2011;

Warneke et al., 2011). Results of chemical measurement from satellite, space shuttle, aircraft, and research vessels indicate that pyrogenic emissions are transported around the globe (Crutzen and Andrea, 1990). For instance, soot C and other pyrogenic aerosol constituents have been measured during research cruiser over the remote Atlantic and Pacific (Andrea, 1983), high levels of O_3 and CO have also been observed from satellites over the tropical region of Africa and South America, and large areas of surrounding oceans (Fishma and Larsen, 1987; Crutzen and Andrea, 1990).

The emissions of CO, CO_2, CH_4, hydrocarbons and NO_x play an important role through the "greenhouse" effect and the photochemical ozone formation (Hegg et al., 1987; Schultz et al., 1999; Koppmann et al., 2005). In the presence of high concentration of hydrocarbon, CO but also NO_x, as will be the case in the smoke plumes, the oxidation of CO and hydrocarbons, that is favored by the exposition to sunlight, is accompanied by the formation of O_3 (Kirchhoff and Marinho, 1989). Increased concentration of O_3 promote high concentrations of OH radicals and thus increase the overall photochemical activity of air masses affected by biomass burning (Crutzen and Andrea, 1990). Studies in temperate forest regions have linked such levels of O_3 pollution to damage to trees and vegetation, which has become widespread in Europe and North America (Prinz, 1988).

Biomass burning acts also as a perturbation factor of oxidant cycles in the troposphere. Many gases, particularly hydrocarbons, are emitted in large quantities from fire but their increase in the atmosphere is prevented by a self-cleaning mechanism through their oxidation promoted by OH. The global decreases in OH, the primary sink for CH_4 and CO, could led through a feedback mechanism to a further increase in CO and CH_4. The large amount of NO_x emitted from biomass burning could, at regionally level, counteract this effect because hydrocarbon oxidation in the presence of elevated amounts of NO_x creates additional O_3 and OH. Moreover, the vegetation fire remove the tree and consequently eliminates the large emissions of isoprene which normally react

with and strongly deplete OH. This contribute to enhancement the boundary layer of O_3 and OH concentrations in atmosphere. However, the increase of CO and CH_4 emissions due to biomass burning will lead to decreasing average of OH concentration and thereby to the increase of the many gases that are removed from the atmosphere by reaction with OH.

Biomass burning also exacerbates atmospheric particulate matter loadings (Ward and Hardy, 1991). This in turn leads to significant health implications, particularly for the respirable fraction (fine particles less than 2.5 μm in diameter) and impact on the Earth's radiative budged because they reflect sunlight back into space. Smoke particles also contain black (elemental) C, which may strongly absorb sunlight and thus cause a heating of the atmosphere and less penetration of solar energy to Earth's surface. Such an effect has an influence on the heat balance of the lower troposphere resulting in less solar heating of the surface, warming of the atmosphere and more stable meteorological conditions (Crutzen and Andrea, 1990). The submicrometer-sized pyrogenic particles have a great influence on the microphysical properties of clouds and climate. By acting as cloud condensation nuclei (CCN), that are the aerosol particles on which cloud droplets form, fine particles increase the cloud albedo partly counteracting the greenhouse effect (Delmas et al., 1995; Scholes et al., 1996; Reid et al., 2005). The properties of the cloud depend on the number of available CCN: the more CCN, the more droplets that can form and the smaller the droplet size for a given amount of water. Clouds made up of smaller droplets reflect more sunlight back into the space, and, because these clouds are also less likely to produce rain, cloud coverage also may increase. Because clouds are one of the most important controls on the heat balance of Earth, any large-scale modification of cloud properties is likely to have a strong impact on climate (Crutzen and Andrea, 1990). Particularly, low intensity fires produce high particulate matter emissions due to the agglomeration of condensed hydrocarbon and tar material, as well as the contemporary incorporation of ash and fragment of vegetation (Ward and Hardy, 1991). Smoke particles, in

addition to affecting the radiative properties of clouds and Earth's radiation balance, may also disturb the hydrological cycle, with potential repercussion for regional and possibly global climate.

Black carbon (BC) is the most strongly light-absorbing component of particulate matter (PM) and is emitted directly into the atmosphere in the form of fine particles ($PM_{2.5}$). BC is a major component of "soot", a complex light-absorbing mixture that also contains some organic carbon. It is found in smoke as well as in the residues on the ground and it comprises a range of materials from high aromatic to largely elemental or graphitic carbon and can be found in soils, ice and sediments (Kuhlbush and Crutzen, 1995). Since black carbon will not, or only slowly decompose, this carbon will be sequestered from the short- to the long- term carbon pool and will thus represent a sink of biospheric carbon and of atmospheric CO_2 (Seiler and Crutzen, 1980). Lignin, a major constituent of wood, promotes the formation of black carbon much more than other constituents as cellulose (Cadle and Groblicki, 1982).

Biomass burning is also responsible for the direct production of formic and acetic acid that are chemically produced in the plumes (Crutzen and Andrea, 1990). Nitric acid is formed photochemically from the NO_x emitted in the fires (Keller et al., 1991). Acid substances in the atmosphere can be deposited onto plants and soil either by rain and fog (wet deposition) or by the direct removal of aerosol and gases onto surfaces (dry deposition). Acid deposition has been linked to forest damage in Europe and the eastern United States (Bormann, 1985). Acid deposition can act on an ecosystem trough two major pathways: directly through the deposition of acidic aereosol and gases on leaves, or soil acidification.

3.1 The combustion processes

In smoke plumes from fire, volatile organic compounds could be derived from stress of vegetation, distillation phenomena and pyrolysis processes (Greenberg et al., 2006; Niinemets et al., 2010, Evtyugina et al., 2013) of cellulose, hemicelluloses and lignin of which the dry biomass is substantial composed (Van Loo and Koppejan, 2007) but also of lipids, fatty acids, resin acids, sterol, aminoacids, protein and waxes (Rowell et al., 2012; Ciccioli et al., 2014). In particular, the several phases of the combustion process are characterized by distinct emission and emission rate, thus, to describe the emissions of biomass burning, it is necessary to understand the processes involved in the combustion of vegetation.

The ignition of biomass is dependent on both fuel and environmental factors (fuel moisture and type, temperature, relative humidity and wind) (Lobert and Warnatz, 1993). The pre-ignition stage is considered the period of time before the development of flame, when moisture together with some fuel pyrolysis products are released (Patterson and McMahon, 1984). It include different processes as distillation (up to a temperature of 200 °C), endothermic pyrolysis (thermal degradation of compounds between 200° and 280°C), exotermic pyrolysis (between 280° and 500°) that ignite the flaming phase (Greenberg et al., 2006). During the distillation phenomena the biomass become dry by losing free water and the majority of BVOCs stored in liquid pool as formic and acetic acids, methanol are emitted (Greenberg et al., 2006; De Lillis et al., 2009). During the endothermic pyrolysis the most of oxygenated VOCs are released.

Above the temperature of 500 °C, the mixture of gases accumulated in the hot zone over the biomass becomes a flammable fuel trigging the flaming processes. The flaming stage therefore, is the phase of combustion associated with visible flame during which oxidized compounds, such as CO_2, CO, NO_x together with the substantial amount of pyrogenic VOCs (aromatic, olefinic and aliphatic organic compounds) are emitted (Lobert et al., 1990; Greenberg et al., 2006). The influence of turbulence (generated by wither wind or shearing effects due to velocity differences

of outgassing material within the fuel bed) basically enhances the mixing process of fuel and air (Lobert and Warnatz, 1993).

The following smoldering phase begins after the flame extinction and a considerable amount of smoke is produced. It is characterized by high emission of CO (Ward and Hardy, 1991) and other less oxidized compunds (Lobert and Warnatz, 1993; Andreae and Merlet, 2001).

3.2 The impact of vegetation fire on carbon cycle

Fires represent a loss of stored terrestrial carbon and are responsible for the release of 3800 to 4300 Tg C yr^{-1} to the atmosphere on a global basis (Andrea, 1991; Andreae and Merlet, 2001; Giglio et al., 2006). According to some authors, global forest fire contributed to about 16% of the global estimate. Other C emissions came from fire in grasslands and savannas (44%), from tropical deforestation and degradation fires (20%), woodland fires (15%), agricultural waste burning (3%) and tropical peat fires (2%) (van der Werf et al. 2010; Bertolin et al., 2015). The sum of CO_2 and CO represents more than 90% of the carbon released during the biomass burning (Ward and Hardy, 1991; Andreae et al., 1998; Reid et al., 2005). Biomass burning causes a prompt release of CO_2 but does not necessarily imply a net release of CO_2 to the atmosphere, as the C that is lost to the atmosphere may be returned by subsequent regrowth of vegetation (Crutzen and Andreae, 1990). So, as far as the carbon balance at ecosystem level is concerned, long-term effects of wildfires on atmospheric CO_2 are considered small because part of the emitted CO_2 is taken up by the biomass during the vegetation regrowth (Wiedinmyer and Neff, 2007), even though the burning of long rotation biomass (e.g. forest wood) can have some impact on climate because of the slow growth rate of this type of vegetation (Cherubini et al., 2011). Furthermore, during the canopy reconstruction phase, the new foliage that emerges in the months following a fire, is not

immediately photosynthetically competent with leaf respiration rates exceeding leaf photosynthesis rate resulting still a source of carbon (Cernusak et al., 2006; Beringer et al., 2015). Short-term effects of vegetation fires can be, instead, important as CO_2 emission can match or even exceed industrial emission at a regional scale (Amiro et al., 2001; Wiedinmyer and Neff, 2007). Before being captured by biomass regrowth, CO_2 molecules spend time in the atmosphere and contribute to global warming (Cherubini et al., 2011).

Estimates of fire emission of CO_2 depend on a wide range of factors, including the severity and type of burns, as well as the spatial heterogeneity of vegetation and fire intensity (van der Werf et al., 2006). A shortening of fire return intervals increases in area burned, and/or increase of fire severity can lead to net emissions of CO_2, even on a multi-decadal times scale despite the equilibrium effect of forest regrowth. Dore et al. (2008) studied the effect of a high-intensity stand-replacing fire in a Ponderosa pine forest which killed all trees reducing the total carbon storage and shifted ecosystem carbon allocation from the forest floor and living biomass to necromass. They showed that ten years after the fire, the burned site was still a source of CO_2 to the atmosphere in all months, due to slow recovery of the gross primary production.

So, due to the high variability of fire emission in both space and time as well as the uncertainty of emission and removal estimates (Chiriacò et al., 2013), the impact of forest fires on the carbon budget is difficult to be assessed at ecosystem level. Van der Werf et al. (2003), using the Tropical Rainfall Measuring Mission (TRMM) satellite which observe the earth between 38°N and 38°S (tropics area) estimated that for the region observed, 2.6 Pg C yr^{-1} (or 6% of NPP) was lost as direct emissions (vegetation fire and fuelwood combustion) and an extra 1.2 Pg C yr^{-1} (or 3% of NPP) was lost as respiration from fire-induced mortality. Also these results are highly uncertain because of uncertainties in estimates of burned area and fuel loads.

It also important to take into consideration also the effects of post fire, for instance Kim and Tanaka (2003) showed elevated CO_2 emission in burned black spruce after at least three years which was ascribed to the higher soil temperature than that before the burning. This suggest that solar irradiation transfers more easily to the burned stand surface than to the unburned floor due to the lower soil-water content (Richter et al., 2000). The black carbon aerosols that, blackening the soil surface, have strong positive radiative forcing (Ramanathan andand Carmichael, 2008) may also change the surface albedo of burned area thereby increasing solar energy absorption (Govaerts, 2002). Furthermore forest fire significantly decreased soil CO_2 fluxes, but the post-fire condition may stimulate microbial respiration because of higher nutrients and substrates remnant soil after the burning, leading to an increase of CO_2 flux (Schlentner and Van Cleve, 1985) changing the ecosystem from a sink to a source of CO_2 (Van Cleve et al., 1983*;* Kim and Tanaka, 2003; Dore et al., 2008). On the other hand, the formation of black carbon by vegetation fire might significantly reduce the net carbon flux (Kuhlbusch and Crutzen, 1995) for its role of carbon sequestration in a long-term pool.

4 Novel application of a combustion chamber for experimental assessment of biomass burning emission

4.1 Introduction

Laboratory experiments have a great importance on the study of emissions from vegetation fire, providing a deeply insight into the burning process, and are a useful tool to understand the contribution of the various type of vegetation communities to the available fuels for wildland fire. In many studies, the emission has been determined in combustion chambers where vegetation fires are carried out under controlled conditions (Lobert et al., 1990; Kannan et al., 2004; Zhang et al., 2008; Soares Neto et al., 2011; Warneke et al., 2011). Only with this approach it is, in fact, possible to follow in detail the combustion of the different vegetation compartments, such as leaves, bark, trunk, and the accumulated biomass in the soil, involved in forest fires. In addition to this, only experiments performed under controlled conditions allow to follow the progressive release of both reduced and various oxidized forms of carbon, such as CO_2, CO, CH_4, VOCs and particulate matter during the different phases of vegetation combustion, separating the contribution coming from pre-ignition, flaming and smoldering. This allows to get detailed information on the gas and particle emission originated from the combustion of plant species and vegetation compartments present in different forest ecosystems that can be useful for landscape management (Moreira et al., 2011). Emissions from fire of biomass produced by human activities as agricultural crop residues (Zhang et al., 2008), cereal waste (Ortiz de Zàrate et al., 2000) and garden (Kannan et al., 2004) were deeply investigated using experimental systems. Several laboratory studies focused on the emission from tropical forest (Yokelson et al., 2008; Neto et al., 2011) and savanna fires (Lobert et al., 1991; Christian et al., 2003). The main disadvantage of

laboratory studies is the fact that the simulation of fire is an artificial condition that could not reproduce the complexity of reality.

Experimental data could be integrated with field data conducted in airborne campaign, during open fire, using aircraft and platforms equipped with various type of sampling instruments. This has the advantage to be applied to a real situation but could over- or under-estimate flaming emission due to the type of platforms that are used (Yokelson et al., 2008). Basing on data from laboratory and field experiments, numerous studies have attempted to estimate emissions from fires in regional, national or even higher scale (Crutzen et al., 1990; Miranda et al., 1994; Scholes et al., 1996; Cofer et al., 1998; Andreae and Marlet, 2001; de Gouw et al., 2006; Yokelson et al., 2007) but there is still uncertainty and understanding how the emission from biomass burning could impact the atmospheric chemistry is still developing.

In this section, a combustion chamber designed for the determination of gases and particles emitted from vegetation fire is described. Data collected during the combustion of *Quercus robur* dried leaves are presented to show the potential of this approach.

4.2 Materials and Method

4.2.1 Description of the combustion chamber

A 3D image and a schematic diagram of combustion chamber designed at CNR-IBAF are shown in Fig. 1 and 2. The chamber was built by NOSELAB ATS s.r.l., Italy.

The stainless steel chamber has a size of 106x80x50 cm with a diameter of the exhaust chimney of 10 cm. The internal walls of the chambers are coated by Teflon@ to limit the reactivity of the emitted compounds at the chamber surface. The chamber is equipped with a stainless steel burning basket of 16x16 cm, covered by a grid where the biomass to burn is located, and is internally coated by ceramic panels for thermal insulation. A thermocouple located in the basket allows the continuous determination of the temperature during the whole combustion experiment. The basket is placed in a scaffold supported by four cylinders. These cylinders transfer the pressure generated by the biomass weight to a high-resolution balance. This allows the continuous recording of weight losses occurring during vegetation combustion experiments. The scaffold is equipped with a ceramic platform for thermal insulation and for the protection of the loading cell. An epiradiometer, equipped with ceramic coated wires, is used as a source to heat the biomass and ignite the emitted gases. It is placed on an adjustable support to heat in a reproducible way the biomass in the basket. The chamber is continuously flushed with an air flow in order to ensure the constancy in combustion and in the removal of gases and particles from the chamber. Air is delivered to the chamber with an electrical fan placed at the bottom of the chamber. The fan is equipped with a power controller to regulate the air flow.

Data of the internal temperature and sample weight during the combustion experiments are stored in an acquisition system connected to a personal computer through an USB 2.0 connection. The

chamber is equipped with the data logger HD 2103.2 (Delta Hom srl, Italy) to store the air flow rate values measured by a hot-wire anemometric probe AP471S1 working in a range of 0.1-40 m/s and -25°C +80°C, with a detection limit of 0.01 m/s and 0.1°C. The probe is equipped with a SICRAM module to provide calibrated data. The data logger can store up to 38,000 samples that can be transferred to a PC via the serial port multi-standard RS232C and USB 2.0. The anemometer is used also to get the temperature of the smoke. This value provides an index of heat dispersion from the fire, when associated with that of the inner temperature.

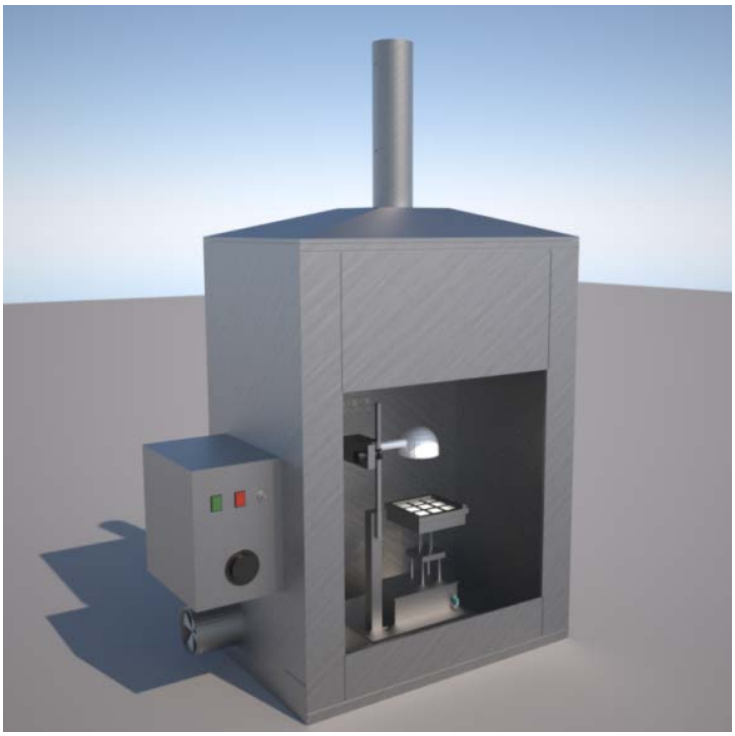

Fig 1 A tridimensional image of the combustion chamber installed at the Institute of Agro-environmental and Forest Biology of CNR.

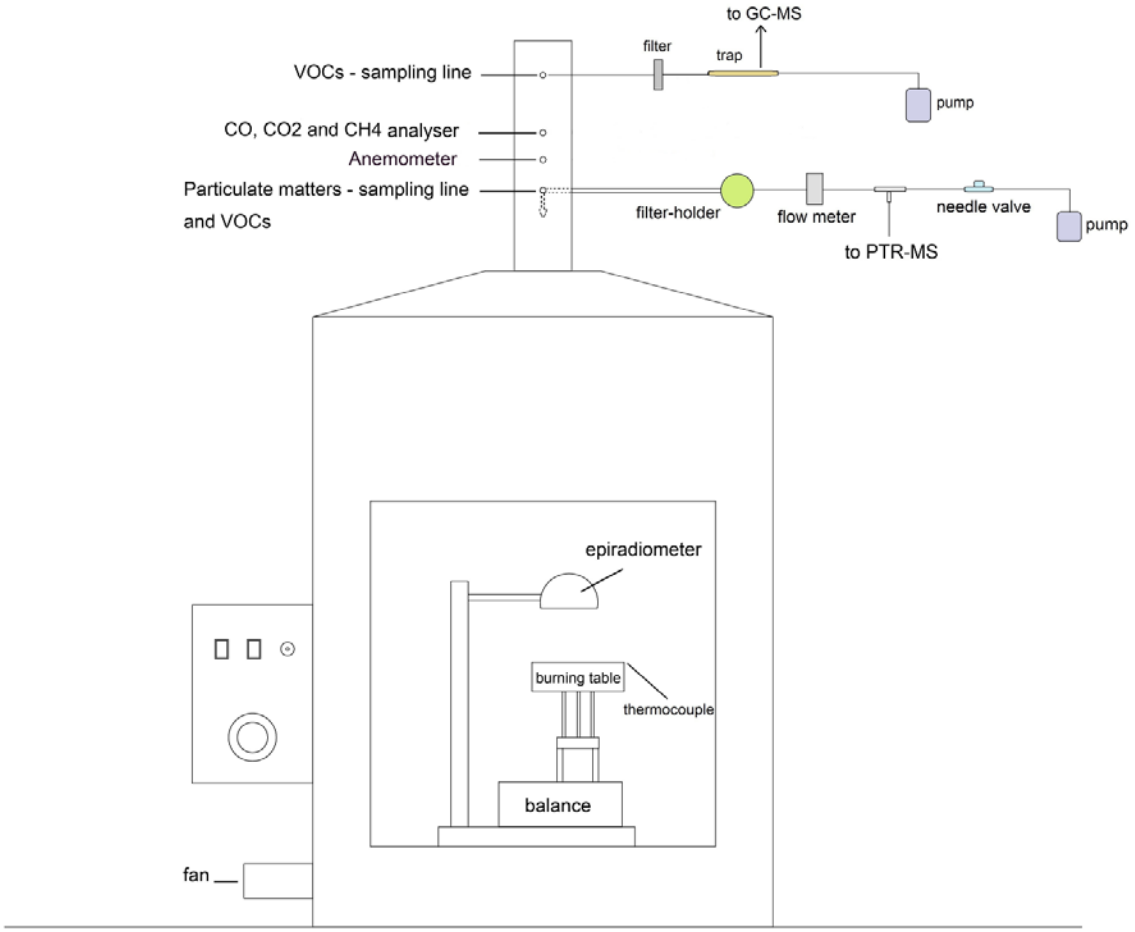

Fig 2 The combustion chamber for laboratory biomass burning. The main components of the combustion chamber and the sampling lines of particulate matter and gases are indicated.

4.2.2 CO and CO_2 measurements

A portable analyzer MRU NOVA PLUS (MRU ITALIA srl, Italy) was used for the continuous measure of CO and CO_2. It uses a CO sensor (compensated H2) in the range of 0 – 4.000 parts per million (ppm) (maximum limit 10.000 ppm), whereas it uses an infrared cell for the measurement of higher concentration of CO (range of 0-10 %) and CO_2 (range of 0-30%). The analyzer was equipped with a software for the automatic storage of settable times and a gas cooler (Peltier). It contains a pump for the automatic discharge of condensed water. Once calibrated, this unit is

inserted inside the exhaust chimney through a hole, and data transferred to a remote display with a wireless connection.

4.2.3 Particulate sampling

An isokinetic sampling line was used for the collection of particulate matter in the exhaust chimney located at the top of the combustion chamber. It consisted of a threaded stainless steel line equipped with a nozzle (6 mm internal diameter) connected to a stainless steel filter holder able to host circular filters with a diameter of 47 mm to retain particles. The nozzle for collecting the fumes was placed at the center of the chimney in order to limit the disturbance of the walls on the fluid moving through. The filter holder was connected to an aspirating pump provided by KNF (Neuberger GmbH, Germany) through a Teflon tube (6 mm inner diameter). To achieve isokinetic sampling of particles, a needle valve was inserted between pump and the filter holder in order to set the flow rate through the sampling system at the same value of the fluid moving inside the exhaust chimney. Both flow rates were measured with a flow meter. The needle valve allowed also to maintain an isokinetic regime through the line when the filter pores got partly clogged by particles. The filter holder can host filters made by different materials, such as cellulose, glass or quartz fibers. Cellulose filters, able to retain particles with an aerodynamic diameters <0.45 µm (Tecnochimica Moderna Srl., Italy) were preferred in our experiments as we wanted to use them for a subsequent morphological and elemental analysis of particles by scanning electron microscope (SEM). Glass and quartz fiber filters were expected to be used when wet analysis of particles or the extraction of organic material was needed. In all cases, filters were dried in a stove at 60 °C for 30 min to remove the atmospheric humidity.

4.2.4 VOC sampling

The VOC sampling line consisted of a glass tube inserted perpendicularly to the exhaust chimney. It was connected through to a Sylcosteel adsorption trap 3 1/2" long with an inner diameter of 1/4", filled with Tenax TA particles 35-60 mesh in size (Markes International Limited, Llantrisant, UK). The trap outlet was connected to an aspirating pump ensuring a flow rate of 200 ml min^{-1} through the enriching system.

VOCs retained on the adsorption traps were thermally desorbed at 275°C for 10 min in a Markes Unity 1 thermal desorption unit (Markes International Limited, Llantrisant, UK) under a flow rate of helium, cryofocused in a cold trap containing a 2 mm diameter x 60 mm long bed of Tenax TA backed up by Carbograph 1TDTM separated and supported at each end by quarz wool and kept at −10°C by a Peltier cell. By rapid heating the cryogenic trap at 300°C, VOCs were injected into a 30 m MS-5HP capillary column with an inner diameter of 0.25mm (J&W Scientific USA, Agilent Technologies, Palo Alto, CA, USA), connected to a gas chromatographic-mass spectrometric unit (GC-MS-MSD 5975C) supplied by the same company. The column temperature was maintained at 40°C for 1 min, and then increased up to 210°C at a rate of 5°C/min. A final temperature of 250°C was reached using a rate of 20°C/min. Helium was used as a carrier gas. One trap for each combustion experiment was collected. The background levels of VOCs in the exhaust chimney were determined by collecting a trap before each combustion experiment.

Online VOC determinations were carried out by using proton-transfer-reaction mass spectrometer (PTR-MS, IONICON, Innsbruck, Austria) equipped with a quadrupole mass filter. The system, which provides high sensitivity, is able to record spectra from m/z 18 to m/z 220 at a rate of 100ms for each m/z seconds. VOCs were sampled by aspirating the air sample from the same line

used for the collection of particulate matter. This was carried out by placing a T connection after the filter holder.

4.2.5 The experiment set up and combustion test

The suitability of the chamber to investigate the combustion process of vegetation samples is tested by using about 50 g of leaf litter of *Q. robur* that was previously desiccated in a stove. The sample was placed on the grid of the burning system and the epiradiometer was placed just above the litter at a distance of 1 cm. Leaf litter was oven dried to standardize measurements during different experiments. The fan speed was regulated to maintain a constant air flow of 0.7 m s^{-1} inside the chimney. This air flow provided a good circulation of air within the chamber ensuring a good supply of oxygen for the combustion and avoiding an excessive turbulence which could move the ash from the burning basket.

Once the biomass was placed in the basket and flows adjusted, the gas analyzer and the epiradiometer were both turned on. For safety reasons, the power of the epiradiometer was maintained at 50% in the first two minutes of the experiment, and then increased to 100%. The concentration values of CO_2 and CO were automatically stored every ten seconds, whereas those of the sensors of the combustion chamber (weight and temperature) were collected every second. As soon as the release of smoke were detected, the sampling of VOCs and particulate matter started. In the sets of experiments reported here VOC sampling was performed for 15 minutes. Particulate matter was sampled for the entire duration of the experiment to quantify the total amount released from the pre ignition phase to the end of the smoldering phase. At the end of the experiment the filter was dried at 60 °C for 30 min in an oven to remove water and to get correct amounts of particulate matter. The analysis of VOCs by PTR-MS was performed in selected ion

mode, by selecting the ions of the most important volatile and toxic components known to be emitted by biomass burning. The first five acquisition cycles were used to determine the background levels of VOCs in the air circulating inside the chamber (blank). As soon as the epiradiometer was switched on, 20 acquisition cycles were performed from m/z 19 to m/z 200 to select the specific ions to be monitored. After setting the proper ions, a continuous acquisition was performed until the end of the fire. During the experiment the level of the primary H3O+ ions used for the ionization was maintained in the range of 6 x 10^6 counts per seconds. A representative image of the experiment was provided in Fig. 3.

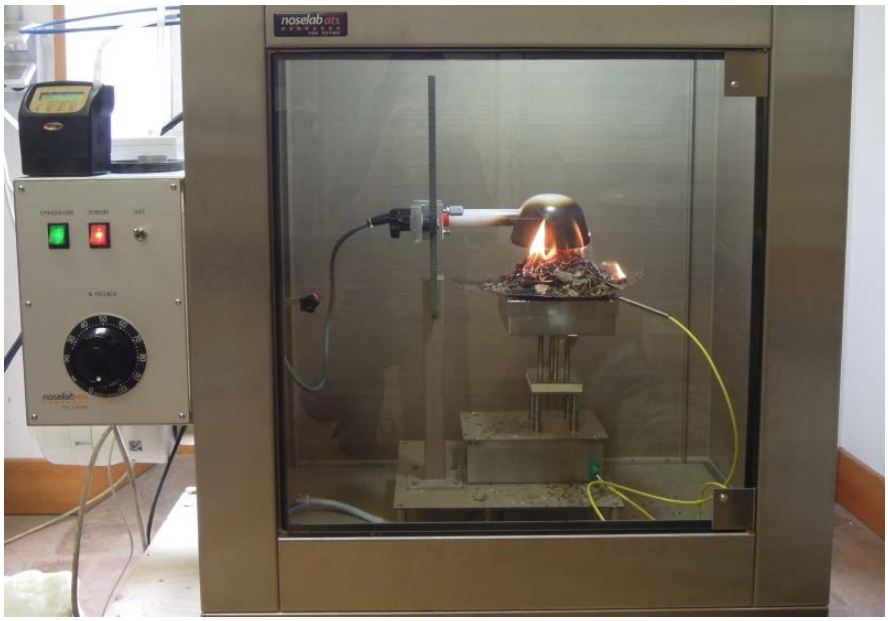

Fig 3 A picture of a representative experiments during the flaming phase.

4.2.6 Preliminary Calculations

The chamber was designed in order to get the most relevant combustion parameters. The first one is the combustion efficiency (CE), which is the ratio between the amount of CO_2 and that of the total carbon mass emitted during combustion (Ward et al., 1992):

$$\mathrm{CE} = \frac{\mathrm{C}_{[\mathrm{CO}_2]}}{\mathrm{C}_{[\mathrm{total}]}}$$

where $\mathrm{C}_{[\mathrm{CO}_2]}$ is the fraction of emitted carbon which is completely oxidized to CO_2; $\mathrm{C}_{[\mathrm{total}]}$ represent the total amounts of emitted carbon products (CO_2, CO, CH_4, non-methane hydrocarbons NMHCs and particulate carbon PC). This parameter is useful to assess the extent to which carbon is oxidized to CO_2 during vegetation combustion.

The second parameter is the modified combustion efficiency (MCE) defined as:

$$\mathrm{MCE} = \frac{[\mathrm{CO}_2]}{[\mathrm{CO}_2] + [\mathrm{CO}]}$$

The MCE requires only the measure of CO_2 and CO. It allows to assess the transition between the flaming and smoldering phases, because the highest efficiency is observed in the flaming phase in which MCE=0.9-1 (Reid et al., 2005).

4.3 Preliminary results

4.3.1 CO_2 and CO emission

The aim of the first experiments was mainly to characterize qualitatively the potentiality of the chamber in terms of data collected rather than quantifying the proportion of the different compounds emitted during the combustion. Fifty experiments were carried out with the chamber. For sake of simplicity we report here the data of one of these experiment, that was representative of all the ones performed. Data in Fig. 4 show that with the type of sample used CO and CO_2 reached their maximum values with a time difference of about 70 seconds. The pre-ignition phase started 380 seconds after the beginning of the experiment, and was followed by the flaming phase that started after 630 seconds and lasted for 120 seconds. Maximum values of 16,100 and 1,250 ppm were measured for CO_2 and CO, respectively. Formation of smoke started in the pre-ignition phase, and it was followed by an important increase of CO emission. In the type of investigated samples, the smoldering phase was particularly short, and characterized by a limited emission of smoke. Values of MCE in the range of 0.92 were typically measured during the flaming phase (Alves et al., 2010a). Values higher than 0.9 are indicative of the fact that more than 50% of the emission is produced during the flaming phase (Ward and Hardy, 1991).

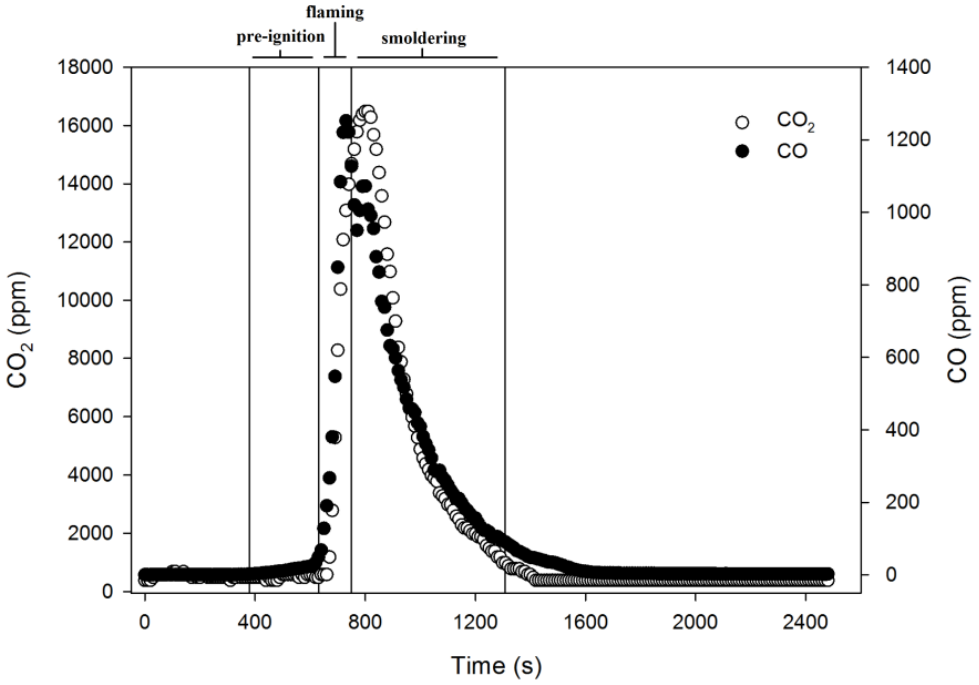

Fig 4 Emitted CO and CO_2 concentrations over time from a burning experiment with leaf litter of *Quercus robur*. The vertical lines indicate the beginning of each combustion phase: pre-ignition (380 s), flaming (630 s), smoldering (750 s). The CO emission is indicated by black circles, CO_2 emission is indicated by white circles.

4.3.2 VOC emission

Due to short duration of the combustion and the sampling protocol used, the GC-MS analysis provided an integrated value of the VOCs emitted during the flaming as well as the smoldering phase. The typical GC-MS profile of pyrogenic VOCs emitted during the biomass burning of dry litter is shown in Fig. 5. Identification of the various emitted components was carried out by combining selective ion detection information with retention indices (RI) according to the method proposed by Ciccioli et al. (2002). Several aromatic compounds were detected in the emission. The most abundant were benzene, toluene and naphthalene. Other VOCs present at lower amounts were furfural, ethylbenzene, m-,p-, and o-xylene, styrene, benzaldehyde, phenol and benzofuran.

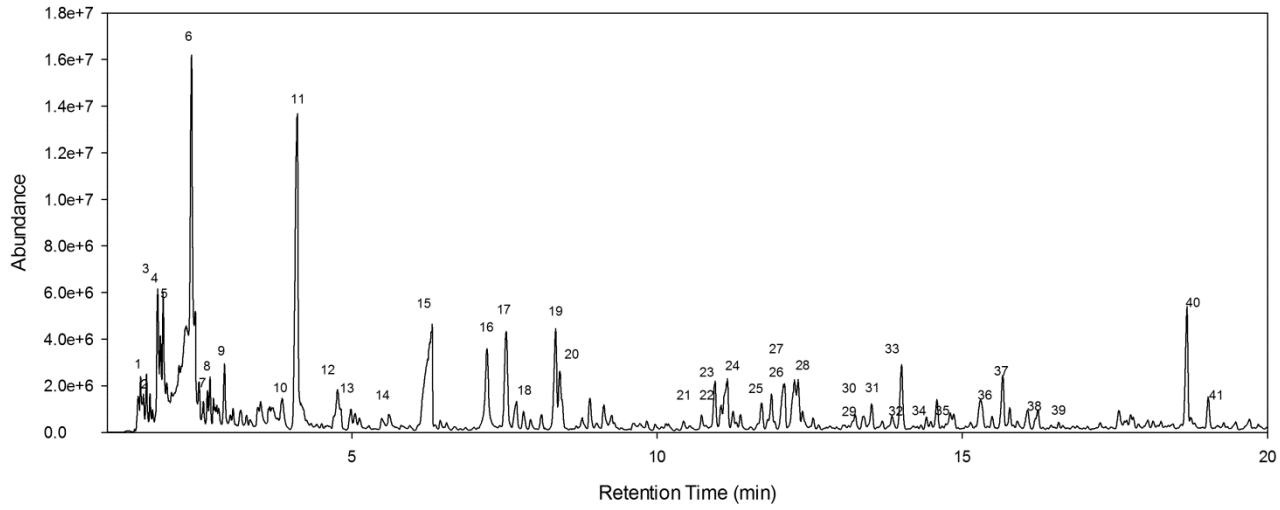

Fig 5 The chromatogram obtained by submitting to GC-MS analysis a trap sampled during a burning experiment with leaf litter of *Quercus robur*. The identified gaseous compounds are listed: 1) 1,3 Cyclopentene; 2) Cyclopentene; 3) 3-Buten 2-one; 4) Pentene 2-methyl; 5) Furan 2-methyl; 6) Benzene; 7) Bibromomethane; 8) 2-Methylhexane; 9) 1,3 Dimethyl cyclopentane; 10) 2,3,3-Trimethyl pentane; 11) Toluene; 12) 5-Hexene 2-one; 13) Octane; 14) 2,4-Hexenedial; 15) Furfural; 16) Ethylbenzene; 17) m+p Xylene; 18) Ethynilbenzene; 19) Styrene; 20) o-Xylene; 21) Benzene, isopropenyl; 22) Benzene, propyl; 23) Benzaldehyde; 24) Benzene 1-ethyl-3-methyl; 25) Benzene 1-ethyl-4-methyl; 26) Benzonitrile; 27) Phenol; 28) Benzene isopropenyl 2-propanol, 1-(2-methoxy-1-methylethoxy); 29) Benzene 1,2,3-trimethyl; 30) Benzene 1-methyl-3-isopropyl; 31) Limonene; 32) Indane; 33) Indene; 34) Benzene, butyl; 35) Benzene, dimethyl-ehtyl; 36) Phenol 4 methyl; 37) Phenol 2-methyl; 38) Benzofuran, 2-methyl; 39)2,6.Dimethyl-2,4,6-Octatriene; 40) Naphtalene; 41) Phenol, 2-methoxy-4-methyl.

The on-line determinations by PTR-MS allowed to get a more detailed view of the type and number of VOCs emitted during dry litter matter combustion, and to follow their variations during the different combustion phases. Since the most intense signal generated by PTR-MS corresponds to the protonated molecular mass of a VOC (m/z=M+1), it is impossible to distinguish with this technique isobaric compounds. However, for the VOC already identified by GC-MS there was little or no ambiguity in the mass assignment, and PTR-MS profiles were safely used to follow the emission profile generated in the various combustion phases. The emission profiles reported in Fig. 6 show the trends followed by the protonated molecular ions of some aromatic components.

Data show that most abundant were benzene (m/z 79), toluene (m/z 93), phenol (m/z 95) and styrene (m/z 105). The profile recorded at m/z=107 corresponds to the signals generated by the sum of xylenes, ethylbenzene and benzaldehyde, already identified by GC-MS.

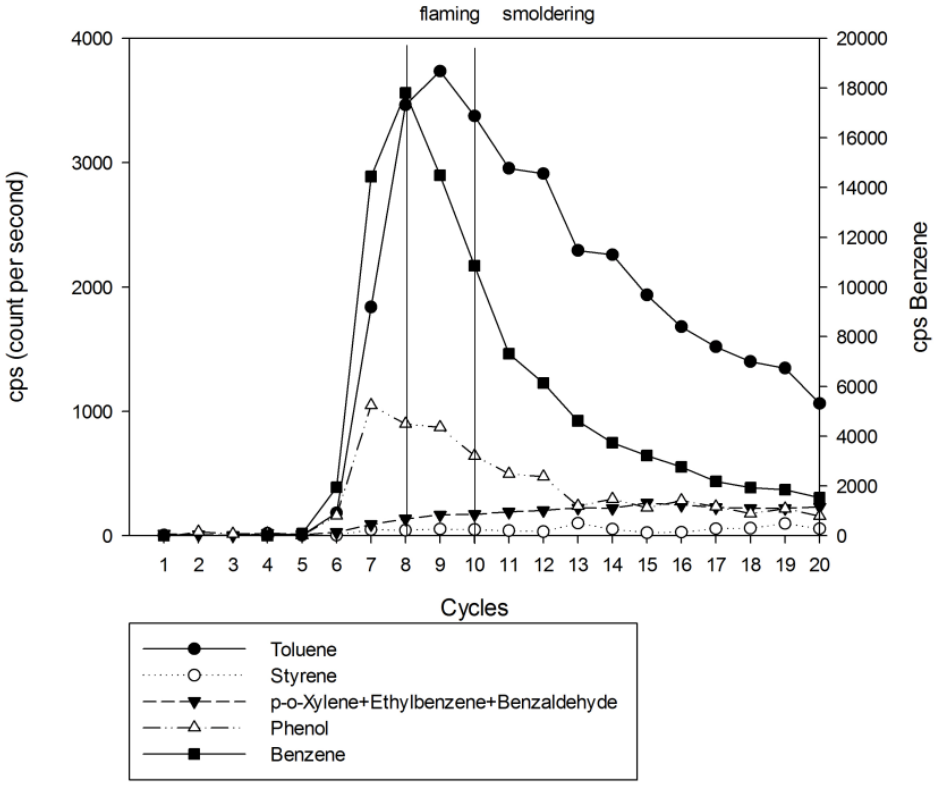

Fig 6 The on-line monitoring of aromatic VOCs released during a burning experiment with leaf litter of *Quercus robur* using PTR-MS tecnique. The vertical lines indicate the starting time of combustion phase in correspondence with the measurement cycle on the PTR-MS: flaming (cycle 8), smoldering (cycle 10).

As reported in the literature, a great amount of saturated, unsaturated and oxygenated VOCs are also released from fire (Koppman et al., 1997; Christian et al., 2003). Figs. 7b and 7c report the emission profile of compounds able to generate protonated ions corresponding to oxygenated VOCs known to be emitted by biomass burning. For some of them, such as acetaldehyde (m/z 45) and methanol (m/z 33), the assignment was certain. Their large emission was consistent with the

data reported by Simpson et al. (2011). Based on the data reported in the literature protonated ions with m/z of 31, 47, 55, 57, 59, 61, 69, 71 and 73 were believed to come most from formaldehyde, formic acid, 1-3 butadiene, acrolein, acetone, acetic acid, furan, methyl vinyl ketone (MVK) and methyl ethyl ketone (MEK), respectively. However, it is likely that butane, glycolaldehyde, methacrolein+crotonaldehyde and butanal, also contributed to generate the signal recorded at m/z 57, 61, 71 and 73, respectively.

As indicated in the literature (Andreae and Merlet, 2001; De Gouw et al., 2006) the emission of these VOCs, is accompanied by that of some nitrogen containing compounds, such as hydrocyanic acid (m/z 28) and acetonitrile (m/z 42), that are considered specific markers of biomass burning. Their profile is shown in Fig 7a. Data displayed in Fig. 6 and Fig. 7 show that in the combustion of dry leaf litter, only acetonitrile reached the maximum emission at the beginning of the smoldering phase. All other compounds were emitted at the beginning of flaming phase or just before.

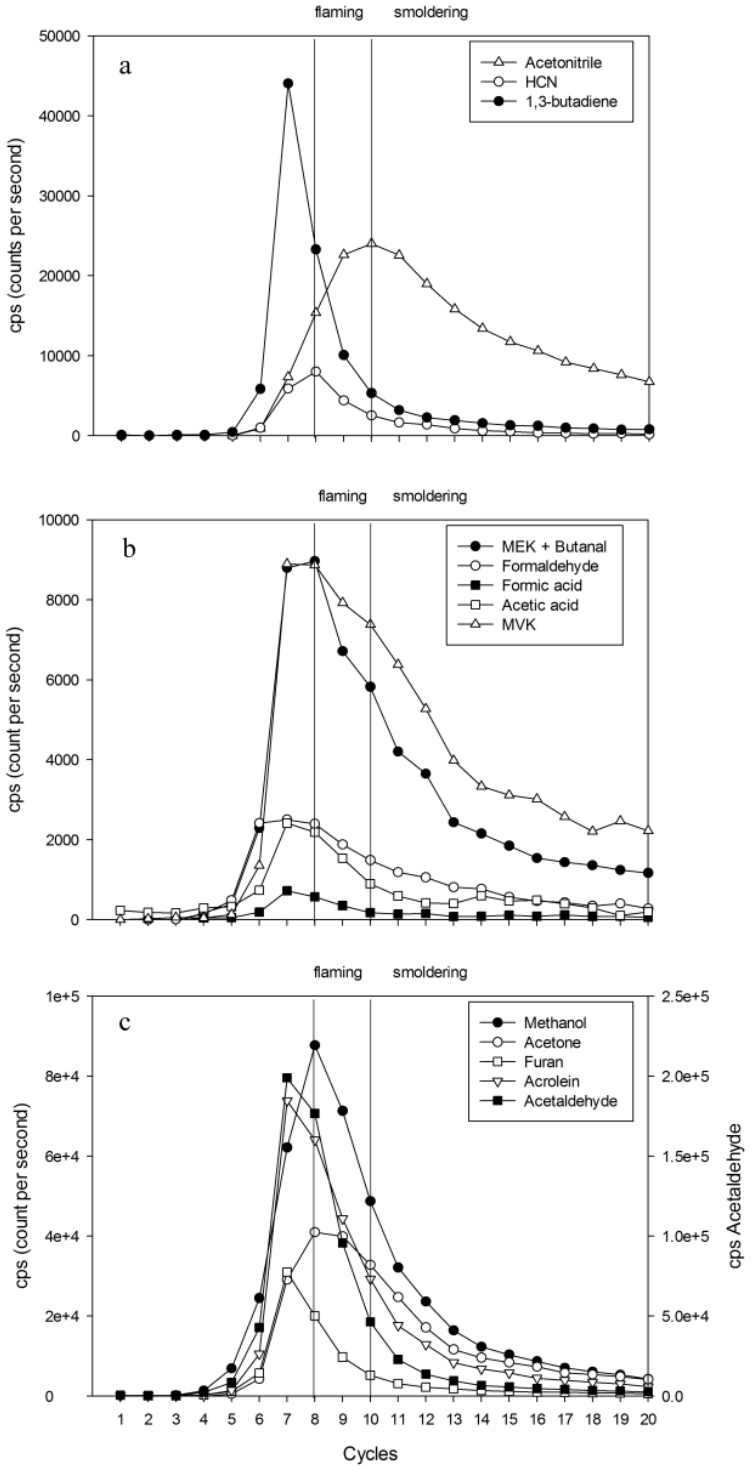

Fig 7 The on-line monitoring of VOCs released during a burning experiment with leaf litter of *Quercus robur* using PTR-MS tecnique. The vertical lines indicate the starting time of combustion phase in correspondence with the measurement cycle on the PTR-MS: flaming (cycle 8), smoldering (cycle 10).

4.3.3 Temperature and weight loss

Fig. 8 reports the profiles of the temperatures that were reached in the core of the fire (inner temperature) and in the smoke (smoke temperature) during dry leaf litter combustion experiments. They show that the smoke rising through the chimney reached a peak temperature of about 200 °C when the inner temperature was about 550 °C. These were the conditions in which the maximum emission of CO_2 occurred. The efficient combustion of dry leaf litter in the flaming phase was confirmed by the data displayed in Fig. 9, where the weight losses during combustion are reported.

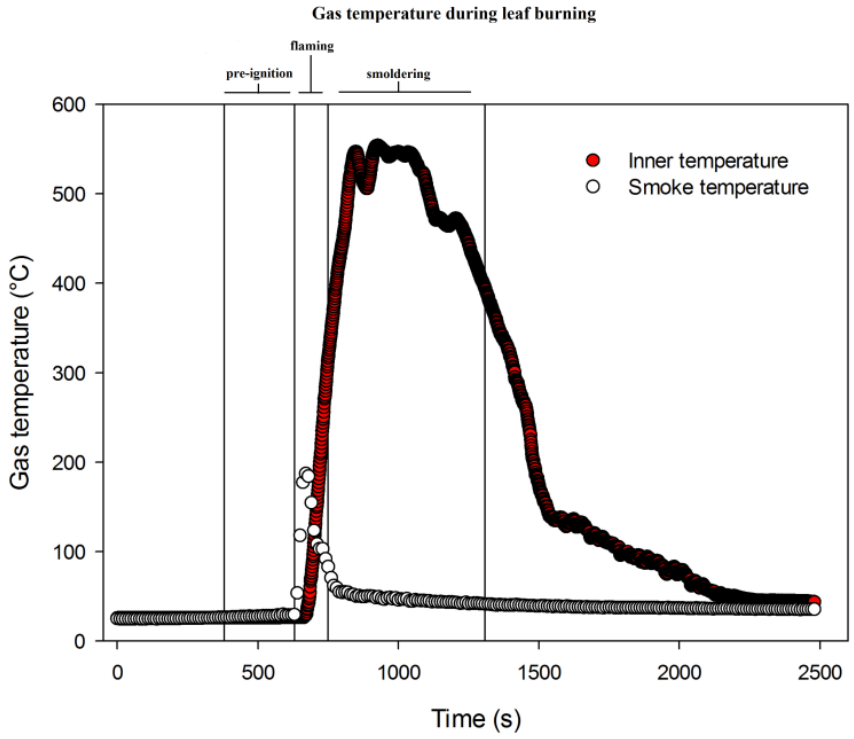

Fig 8 Inner and smoke temperature over time during a burning experiment with leaf litter of *Quercus robur*. The vertical lines indicate the starting time of combustion phase: pre-ignition (380 s), flaming (630 s), smoldering (750 s). The red circle indicated the inner temperature, the white circle indicate the temperature measured in the smoke.

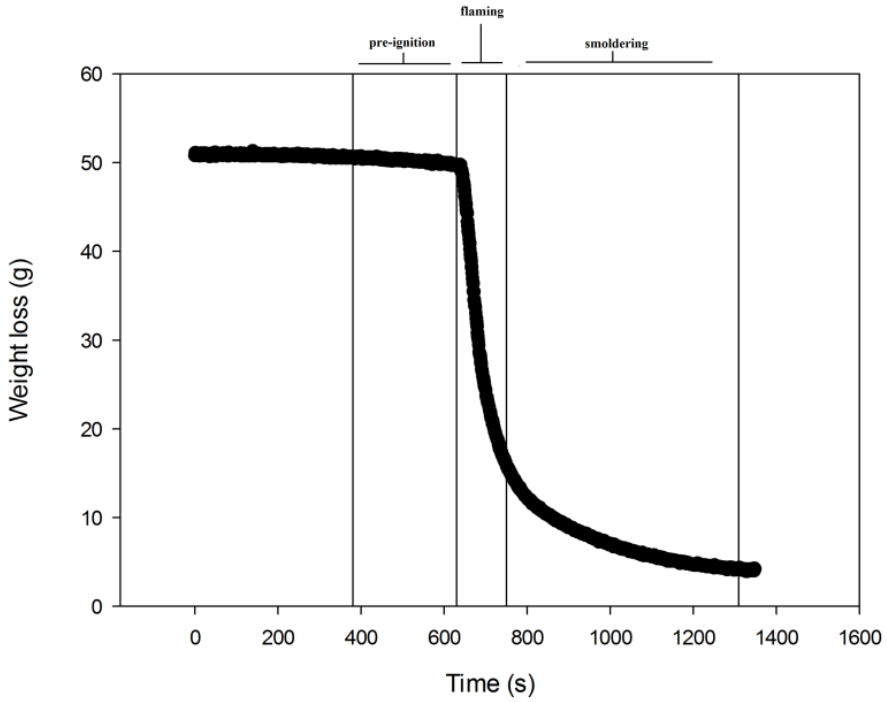

Fig 9 Weight loss over time during a burning experiment with leaf litter of *Quercus robur*. The vertical lines indicate the starting time of combustion phase: pre-ignition (380 s), flaming (630 s), smoldering (750 s).

Data show that at the end of the combustion only 4.2 g of ash remained out of 50 g of dry leaf litter burned.

4.3.4 Particulate emission

Together with the amount of ash remaining in the basket, solid matter in the form of particulate matter was also produced during combustion, the total amount of particulate retained on the filter was on average of 2.1 mg. Multiplying this weight by the section of the chimney (78.5 cm^2) and dividing by the section of the pipe of the sampling line (0.2826 cm^2), the amount of particulates emitted during the experiment was around 583 mg.

4.4 Discussion

Our study demonstrates the performance of a recently established combustion chamber and proves that it can provide useful information to thoroughly characterize the emissions during the combustion of plant tissues. The smoke formation, was abundant only during the pre-ignition, and not during the smoldering stage, as reported elsewhere (Lobert et al., 1990). The combustion of dried leaf litter of *Q. robur* was mostly characterized by the flaming phase where a strong increase of both CO and CO_2 concentrations were observed. This is confirmed by the value of MCE higher than 90% that suggest a high combustion efficiency reached in the combustion of leaf litter characterized by a low water content. This type of fuel produces a negligible amount of coal, while generates large amounts of suspended ash and particulate matter.

It is worth noting that this experiment was carried out with dry leaf litter to simulate the litter conditions existing in many Mediterranean forest areas during hot summer when accidental and natural wildfires often develop from litter. This type of biomass can also be used as a reference material to assess how the increase in the water content prevents or delays the starting of fires. Data show that heating dry leaf litter can rapidly ignite, producing a flame that can initiate wildfires under hot summer conditions.

VOCs produced by its combustion are those typically emitted by the pyrolysis and carbonization of wooden matter. It is thus dominated by the presence of aromatic hydrocarbons, such as benzene, toluene, naphatalene, benzaldehyde, furans and phenols. The pyrolysis of biopolymers (cellulose, hemicellulose and lignin) combined with the organic material contained in the cell compartments of leaves produces acetaldehyde, methanol and acetic acid as dominant components (Yokelson et al., 2008). They were detected by PTR-MS, but not seen by GC-MS. Several reasons

can be invoked to explain the lack of detection of the most volatile oxygenated VOCs by GC-MS. As far as methanol and acetaldehyde are concerned, the sampled volume passed through the trap was definitely too long to retain them on the adsorbent. Recent experiments indicate that a better recovery of the more volatile compounds can be achieved by reducing the sampling volume to less than 100 mL (Yokelson et al., 2013). As far as carboxylic acids are concerned, their lack of detection in the combustion emission is probably related to the system used to transfer the VOCs from the cryofocusing unit to the column. It has been shown that many mono-carboxylic acids are indeed eluted by low- medium-polar capillary columns, such as the one used here (Ciccioli et al., 2002), although they generate very tailed peaks hard to quantify at low levels. An important point to stress is the lack of isoprene in the combustion emission, as this compound is the most abundant emitted by *Q. robur* leaves (Karl et al., 2009). Although a signal at m/z= 69 was detected by GC-MS (Karl et al., 2007), no presence of this compound was found in all the GC-MS profiles recorded. Thus the mass seen in the PTR-MS was generated solely by furan, known to be a common pyrolysis product formed by biomass combustion (Warneke et al., 2011). The absence of isoprene is due to the fact that the broad-leaved tree species do not generally have any apparatus for the storage of biogenic hydrocarbons, particularly in the case of isoprene. On the contrary, a great amount of isoprenoid were emitted during the combustion of fresh wood and needles of coniferous trees and wheat straw (Ciccioli et al., 2001). The peculiar combustion features of the sample investigated highlights the importance of the use of a chamber for investigating the emissions of gases and particles of different plant tissues of vegetation species and to separately assess their carbon balance. The concurrent determination of the emission with the continuous monitoring of the temperature in the core of the burning biomass and fumes allows to correlate how gases are released with the heat developed during the fire. This is particularly relevant for VOCs as some of them are deeply involved in the chemistry of the atmosphere, whereas other are

highly toxic to men. Particularly important is to know how the burning of different portions of plants present in a mixed forest ecosystem contribute to the whole emission of CO, CO_2 and VOCs.

A huge number of polar and non-polar VOCs have been identified and quantified in biomass burning by GC-MS (Ciccioli et al., 2001) and PTR-MS (Yokelson et al., 2013). However, only few of them refer to plant species growing in temperate regions of the Mediterranean basin, where summer episodes of fires frequently occur. Although data collected in combustion chambers are unable to fully reproduce the complex conditions existing in forest fires, the possibility to select the plant material to be burned and to study its combustion behavior provides information that are impossible to determine in the field. This approach makes it, in fact, possible to study the dependence of emission and combustion efficiency of vegetation matter experiencing different environmental and physiological conditions, and to assess how surface fires differ from crown fires. While the former type primarily involves litter and understory vegetation moving at moderate speed, the crown fire propagates from plant to plant very fast burning mainly branches and leaves. Generally, the tall trees hardly burn during the surface fire, leading to the majority of the carbon in the canopy intact. Obviously, data collected with combustion chambers must be verified with field data conducted through ground and airborne determinations. It should be noted, however, that in order to get reliable values of vegetation combustion emission with airborne measurements it is required that the reactivity of the dispersion plume remains sufficiently low to limit the oxidation of emitted VOCs by photochemical reactions and their transfer from the gaseous to the particle phase. This is impossible whenever fire plumes are dispersed into photochemically polluted airsheds where high levels of ozone are present. This is often the case of the Mediterranean Basin where high levels of ozone are present during summer, when forest fires mainly develop.

Although outstanding progresses have been recently made in defining the potential impact of biomass burning on the chemistry of the atmosphere (Crutzen and Andreae, 1990; Miranda et al., 1994; Scholes et al., 1996; Cofer et al., 1998; Andreae and Marlet, 2001; de Gouw et al., 2006; Yokelson et al., 2007), large uncertainties still remain due to the limited number of Earth forest ecosystems investigated by the airborne approach. This is also true for the data collected with different experimental facilities. Even though emissions from biomass burning produced by agricultural crop residues (Zhang et al., 2008; Goncalves et al., 2011), cereal waste (Ortiz de Zàrate et al., 2000) and garden (Kannan et al., 2004) were deeply investigated in various combustion facilities, and similar studies have been performed on tropical forest vegetation (Yokelson et al., 2008; Soares Neto et al., 2011) and savanna (Lobert et al., 1991; Christian et al., 2003), studies on Mediterranean ecosystems are still limited. A recent investigation on mediterranean shrubland biomass burning (Alves et al., 2010a; Alves et al., 2010b; Alves et al., 2011a; Alves et al., 2011b; Vicente et al., 2011; Vicente et al., 2012; Evtyugina et al., 2013; Garcia-Hurtado et al., 2013; Vicente et al., 2013) provided information about the main gaseous compounds (CO, CO_2 and CH_4) and $PM_{2.5}$ emission factors. Since forest fires have increased in the European Mediterranean countries (Miranda, 2004; Pausas et al., 2008), their potential impact on the human health and the atmospheric chemistry needs to be better assessed, by focusing on the ecosystems where they can more easily develop. In addition to VOCs, the chemical and physical properties of particulate matter need to be better assessed, because vegetation fires represent one of the most important source of carbonaceous particles in the atmosphere.

4.5 Conclusion

The possibility afforded by a new combustion chamber in the study of the emissions from biomass burning were presented using dry leaf litter as test material. Results obtained showed that the set up used for the detection of the emission and the resolution afforded by the weighting system has the potential for making a good carbon balance of burned material. The system allowed to follow the emission of gases and vapors in each step of the combustion, from the pre-ignition to the smoldering phase. With this facility it is possible to study the combustion behavior of different compartments of the wooden matter present in mixed forest ecosystems (leaves, burk, trunk and litter) and see how this behavior is affected by environmental and physiological parameters. This would allow us to see the differences between crown fires, that mainly involve the leaf and branches of the tree canopy, and surface fires where grass and dead leaves are involved. This approach is particularly important to assess the impact of forest fires on the atmospheric quality and carbon cycle of Mediterranean ecosystems, where emission determinations by airborne measurements performed in fire plumes can be severely impaired by the high levels of ozone present in the area when vegetation fires develop. Investigations about the particulate fraction of the smoke will be also further implemented by a scanning electron microscope (SEM) analysis that will give information about the chemical composition, size and structural properties of particles emitted during smoldering and flaming stages. This component is very important because particles are a serious hazard for human health and reduce air quality and visibility with economic and environmental effects. Furthermore, it will give information on the C content of particles for the assessment of C budget.

We plan also to replace the PTR-MS equipped with a quadrupole filter with the one equipped with a time-of-flight filter, allowing to distinguish compounds with protonated molecular ions

differing by fractions of m/z. The suite will be completed by FastGC for a rapid GC-analysis of VOCs. In future, dedicated laboratory experiments with this combustion chamber will make an important contribution to the study on the impact of emissions from fires in the Mediterranean ecosystem and on the effects on the carbon cycle in the atmosphere.

In the next section, we implement the data suite by adding a continuous analyzer for CH_4.

5 Laboratory measurements of gaseous and particulate emission from biomass burning: the contribution of different tree components in a conifer and broadleaf species

5.1 Introduction

The predicted climate changes, as a result of global warning, will be characterized by up to 50% decrease in rainfall and increase of 4-5°C throughout Southern Europe in summer period that drastically rise flammability of the plant material and could bring an increase of risk of wildfire in the future (Lindner et al., 2010; Moreira et al., 2010; Vilèn et al., 2011). This could lead to a consequent increase of CO_2 and other volatile organic compound emissions. Mouillot et al. (2002) combining the scenarios of climate change from a model and a multispecies functional model for vegetation dynamics, estimated that climate change tend to decrease the time interval between two successive fire, leading to shrub-dominated landscapes. As a matter of fact, an increase in the length of fire season and an increase of extreme event were observed (Moriondo et al., 2006). The effect of warming will be particularly experienced at higher latitude and in mountains regions (Ruosteenoja et al., 2007) and the yearly averaged fire danger has already increased during the past six decades in some part of the European Alps (Wastl et al., 2012).

Many studied were conducted about biomass burning in different region of the Earth and from different type of vegetation: prescribed burning in Montana (Yokelson et al., 2012), agriculture crop residues burning in Chinese farmlands (Zangh et al., 2008), fire plumes from Alaska and Canada (de Gouw et al., 2006; Simpson et al., 2011), wildfire in Amazonia basin (Guyon et al., 2005; Soareas Neto et al., 2011), biomass burning in African savannahs (Ward et al., 1996; Wooster et al., 2011) and other more. Akagi et al. (2011) summarize the main literature on

biomass burning emission factor from different types of vegetation burning. Our activities set within the context of emission from biomass burning in Mediterranean basin where wildfire are very frequent particularly during the summer period. Every year, on average 45,000 forest-fires break out in the Mediterranean basing, causing the destruction of about 2.6 million hectares (FAO 2001) (Telesca et al., 2005). Fire is intrinsic to Mediterranean ecosystem, paleoecological studies show that fires were common during the late Quaternary and many species are adapted to frequent fire events (Carrion et al., 200) thanks to the ability to recover by means of resistant structures, namely the bud bank and germination of fire-protected seeds stored in the soil or in the canopy bank (Di Iorio, 2011). The predicted future of possible increase of fires could however modify drastically the vegetation scenarios (Pausas, 2004) notwithstanding the high resilience of Mediterranean plant community. For example, changes in the vegetation can result from changes in the composition of vegetation community, from a redistribution between over- and under-storey layers, from an abundant aboveground dead or partly dead biomass at soil (Mouillot et al., 2002). As a result of increase of fire, Mediterranean ecosystems can experience finally loss of biodiversity, soil degradation, alteration of landscape patterns and ecosystem functioning thus speeding desertification processes (Telesca et al., 2005; Pausas et al., 2008). Recent study showed that fires promote alien plant invasion, patch homogenization, and create positive feedbacks in future fire susceptibility, fuel loading, fire spreading and intensity (Cochrane et al., 1999). The use of prescribed burning can avoid the latter events by decreasing fuel loads and by disrupting the horizontal and vertical continuity of the fuel complex (Fernandes and Botelho, 2003; Vilèn et al., 2011).

Regarding the atmospheric consequence of fire, the highly reactive OVOCs and isoprenoids in wildfire emission are especially important for Mediterranean areas because, due to its morphological feature, the photochemical formation of ozone and SOA is very significant. There

are already some studies that reported the emission from biomass burning in Portugal, (Miranda et al., 1994; Vicente et al., 2009; Alves et al., 2010b; Carvalho et al., 2011; Vicente et al., 2011; Evtyugina et al., 2013; Vicente et al., 2013), Spain (Ortiz de Zarate et al., 2000; Pausas, 2004; Garcia-Hurtado et al., 2013), France (Strada et al., 2010). Many of these works were conducted in field. Aircrafts measurement in general, represent better the condition during which develop the wildfire but they incorporate emission from various fires of different biomass type. It was demonstrated that the biomass type and the biomass properties (structure, moisture content and size) can affect the speciation profile of emission (Evtyugina et al., 2013), for this it is very important characterized the emission factors of a specific ecosystem. The laboratory experiment, even if it is less representative of real condition, allowed to investigate the contribution to gases and particulate emission not only from different species burned but also from the burning of different vegetable tissue. In this chapter we reported the gaseous and particulate emissions from three different vegetable material burning (leaves, little branches and litter), the percentages and the trend of gases emissions during the different stage of burning (pre-ignition, flaming and smoldering). The vegetal material used for the experiments belongs to two tree species (*Pinus halepensis* and *Quercus pubescens*) which are predominant along the Italian peninsula, especially in central-southern regions where the risk of fire is elevated as it is shown in Fig.10 , a map that represent the fire danger level in EU using weather forecast data.

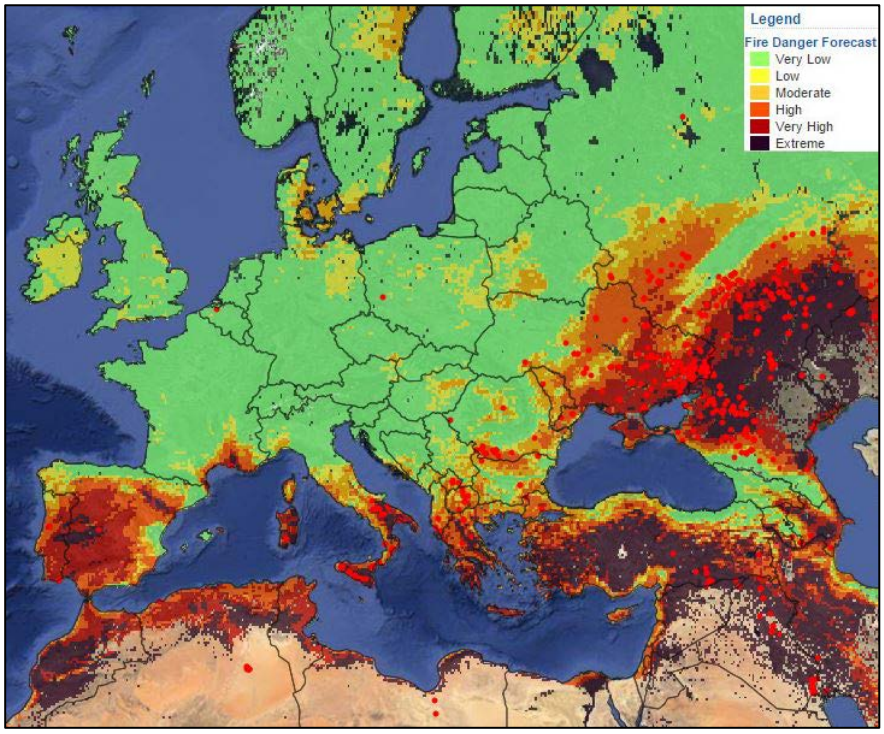

Fig 10 The map of forecasted fire danger level in Europe. Fire danger is mapped in 6 classes (very low, low, medium, high, very high and extreme). The map is the property of The European Forest Fire Information System (EFFIS) http://forest.jrc.ec.europa.eu/

5.2 Materials and method

5.2.1 Sources of forest biomass

Litter and the main part of many plants, namely leaves and little branches, were separately collected from oak (*Quercus pubescens)* and Aleppo pine (*Pinus halepensis)* in some forest of Apulia (Italy), and air-dried (leaf water content of 10%±2). For all categories, four replications of experiment were carried out.

The Apulia region

Forest fire in Italy are mainly caused by humans, and directly depend on social behavior, whether voluntary or involuntary (Leone et al., 2002). The FAO Fire Managemente and Gloabal Assessment 2007 Report estimated that the Mediterranean region accounts the larger proportion of human caused fire in the world (95%), followed by South Asia (90%), South America (85%) and Northeast Asia (80%) (Lovreglio et al., 2010).

The terrain in Apulia is mainly flat, with its highest elevation being the inner Murge Plateau, a wide, calcareous high plateau, poorly developed and scarcely inhabited, originally devote to pasture, now include in the National Park of Alta Murgia (Lovreglio et al., 2010) where the sampling were conducted. The Apulia region has the minimum percentage of forested land (forestry ratio) at the national level (only 7.7% vs. a national value of 28.8%), but a percentage of voluntary fires much above the national average (MIPAAF-CFS 2002) and relatively to forestry ratio the highest percentage of burned forested land among the Italian regions (Leone, 1997). The State Forestry Corps recorded 1135 fire events in the last three years (2012-2014) in Apulia region, for a total of 12769 ha of area burned (wooded and not).

The species

There may be different responses to fire stress depending on type of plant species. There are those that survive and persist vegetatively (resprouters) and species that are killed and regenerate from seeds (seeders or non-sprouters) (Midgley, 1996). Recent study have probed the effect of fire events in these two Mediterranean species. Both species were classified as “flammable species” by Dimitrakopoulos et al. (2001).

P. halepensis species, namely Aleppo pine, is a native pine widely distributed throughout the Mediterranean region (Mirov, 1967*).* It is called storing species because it stored the terpenes in the resin duts, a specialized storage organs,. The most abundant terpenes found *in P. halepensis* are α-pinene, Δ^3-carene, β-pinene and myrcene (Blanch et al., 2009). The plants showed an increase of terpene concentrations if they experimented high temperature and drought in a manipulative experiments (Blanch et al., 2009) that simulate the predicted conditions of next decades in the Mediterranean region. During the drought stress the plants used an important part of photosynthetic C fixation for terpene production and emission probably as a means to reduce the damage caused by oxidative stress induced by drought conditions (Blanch et al., 2009).

P. halepensis was very exploited in the past for reforestation practice in the Apulia region, especially in the 1930's and 50's, so nowadays its presence is very relevant (Fig. 11). The plantations are functional to soil protection against erosion, mainly water and wind erosion (Lovreglio et al., 2010). This pine species is a setorinous tree (Barbero et al., 1998) that remain enclosed in the cones forming an abundant canopy seed bank (Costas et al., 1996) and require an environmental cue, as Sharav wind and fire, for seed release (Nathan et al., 1999). Adult trees are usually killed by wildfire and, as it is a post-fire obligate seeder, regeneration relies exclusively on seeds (Nathan et al., 1999). Fires favored the establishment of new *P. halepensis* seedlings also by reducing interspecific competition and creating the suitable microclimatic conditions thanks to the branches and trunks covering the soil surface that are from collapsed burned tree (Ne'eman et al., 1992; Pausas et al., 2004). These branches facilitated the getting out of the cone and reaching the soil of seeds (Pausas et al., 2004).

Fig 11 A representative forests of *Pinus halepensis* and the maps of distribution of this species in the Mediterranean basin. The map is the property of Department of Environmental Science, Aarhus University (Skjøth et al. 2008).

Q. pubescens is the most widespread species of oak in Italy, naturally present in high density in hills and low mountains. This species is present mainly in degraded coppices in Apulia, the majority of them are small surfaces intermingled with cropland (Lovreglio et al., 2010) (Fig.12). It is a non-storing species and it is a strong isoprene emitters (Kesselmeier and Staudt, 1999). Isoprene is the mainly isoprenoid contained by the leaves of *Q. pubescens*, it is immediately emitted after its synthesis, it is light- and leaf temperature-dependent (Loreto et al., 1998) and it could be the consequence of the production for a regeneration of NADP+ ad phosphate within chloroplast (Sharkey, 1991) but also for defence against ozone attack (Sharkey and Loreto, 1993), heat stress and membrane disorganization (Sharkey and Singsaas, 1995; Kesselmeier et al. 1998). Other terpens emitted by *Q. pubescens*, even if in traces, are α-pinene, β-pinene, sabinene, Δ^3-carene, myrcene, limonene and 1.8-cineole (Simon et al., 2005).

The removal by fire of the aboveground biomass of *Quercus pubescens* induces a reduction in the size of the overall root system without affecting the final root architecture (Lynch, 1999; Chiatante

2006) but reduce and postponed the peak of root growth in terms of the thinnest fine root fraction and number of apices (Di Iorio et al., 2011).

Fig 12 A representative sparse woodland of *Quercus pubescens* and the map of distribution of this species in the Mediterranean basin. The map is the property of Department of Environmental Science, Aarhus University (Skjøth et al. 2008).

5.2.2 The chamber combustion

The experiments were conducted using a combustion facility that has been described in detail in the previous section (Lusini et al., 2014). The experiment set up has been slightly modified to provide a better performance. 100 gr of sample (leaves, or little branches, or litter) were located on a grid of a basket and the fire was ignited by the heat irradiated from an epiradiometer. The basket is provided with a thermocouple and it is placed on a high precision balance that allowed the continuous measurement, every second, of temperature and weight losses during the whole combustion process. The chamber is continuously flushed with an air flow by an electrical fan in order to ensure the constancy in combustion and in the removal of gases and particles from the chamber. The air flow is maintained constant at 0.5 m s^{-1}.

5.2.3 CO, CO_2 and CH_4 measurements

The concentration values of CO and CO_2 were automatically measured every ten seconds by a portable analyzer MRU NOVA PLUS (MRU ITALIA srl, Italy) whose pickup unit was insert directly inside the exhaust chimney thorough a hole. Unlike the previous version, this analytical system was improved to determine the CH_4 emission, adding a new sampling line to carry the fumes trough a Teflon tube from the exhaust chimney to the LI-7700 Open Path CH_4 Analyzer (LI-COR Inc., Lincoln, Nebraska USA) that measured every second the methane emissions (Fig 13).

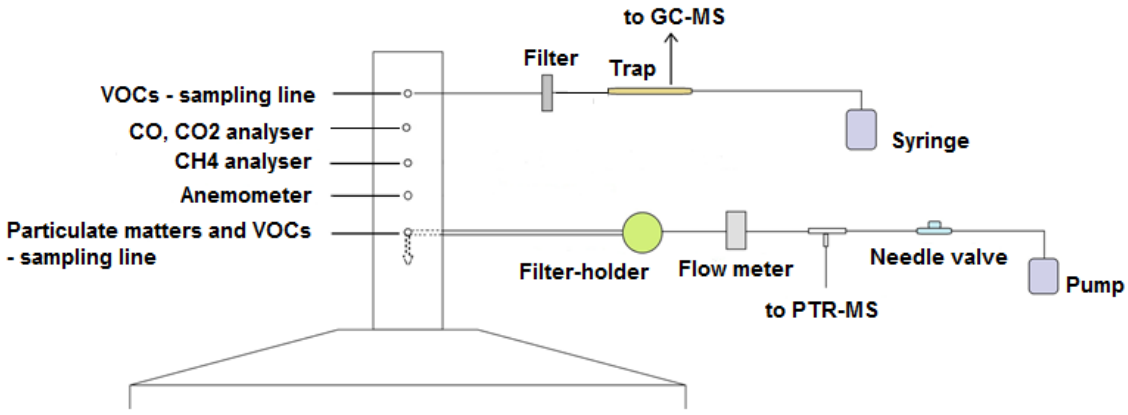

Fig 13 A detailed scheme of the new arrangement of the combustion chamber. The sampling lines of particulate matter and gases are indicated.

5.2.4 Particulate sampling

An isokinetic sampling line was used for the collection of particulate matter. It consisted of a threaded stainless steel line equipped with a nozzle connected to a stainless steel filter holder able

to host circular cellulose filters with a diameter of 47 mm to retain particles with an aerodynamic diameter < 0.45µm. Particulate matter was sampled for the entire duration of the experiment to quantify the total amount released. At the end of the experiment the filter was dried at 60° for 30 min in an oven to remove water and to get correct amounts of particulate matter.

5.2.5 VOC sampling

The VOCs emitted were sampling in two different method to combine the GC-MS and PTR-MS analysis and sampled by aspirating the air sample from two different line. The sampling line to collected sample for the GC-MS consisted of a glass tube inserted perpendicularly to the exhaust chimney, connected through a Teflon tube to a Tenax trap which retained VOCs that pass through it. The trap outlet was no longer connected to a pump, as in the previous experiment, but it was connected to a syringe for aspirate exactly 200 ml of smoke during the three different phase of burning (pre-ignition, flaming and smoldering). One trap for each stage of burning, for each combustion experiment, was collected. The background levels of VOCs in the exhaust chimney were determined by collecting a trap before each combustion experiment.

VOCs retained on the adsorption traps were first thermally desorbed using a thermal desorption unit (Markes International Limited, Llantrisant, UK) and then analyzed using a gas chromatographic-mass spectrometric unit (GC-MS-MSD 5975C).

On line VOC determinations were carried out by using proton-transfer-reaction mass spectrometer (PTR-MS, IONICON, Innsbruck, Austria). The analysis of VOCs by PTR-MS was performed in selected ion mode, by selecting the ions of the most important volatile and toxic components known to be emitted by biomass burning.

5.2.6 Calculation

The modified combustion efficiency (MCE) allows to assess the transition between the flaming and smoldering phases and it is defined as:

$$\mathrm{MCE} = \frac{[\mathrm{CO_2}]}{[\mathrm{CO_2}] + [\mathrm{CO}]}$$

The highest efficiency is observed in the flaming phase in which MCE=0.9-1 (Reid et al., 2005).

Emission factors (EFs) for a given compound is defined as the amount of that compound released per amount of fuel consumed (Scholes et al., 1996). It is expressed in unit of grams per kilogram fuel dry matter consumed. We calculated the EFs using the calibration curve of one standard compound for each class of carbon compounds (from C2 to C10) to quantify the emissions of all VOCs released.

The total amounts of particulate emitted during the combustions were calculated multiplying the amounts of particulate retained on the filter by the section of the chimney (78.5 cm^2) and dividing by the section of the pipe of the sampling line (0.2826 cm^2).

The total heat released during combustion was calculated as the area under the temperature-time curve during the burning experiment divided by the sample dry biomass (°C s g^{-1}).

5.2.7 GC-MS calibration

The calibration method is based on the determination of a relationship between the magnitude of a peak for a known amount of compound in a standard solutions, and the use of that relationship (the calibration curve) to estimate the amount of that compound in a sample of unknown concentration. Thirteen standards (1µl /ml methanol solution, 99% purity) were used for the GC-MS external calibrations (Fig. 14-19). For each class of carbon compounds, from one to three standard compounds were used, depending on their availability in our laboratories: acetic acid and ethanol (C2), acetone (C3), methyl ethyl ketone (C4), isoprene (C5), benzene (C6), toluene (C7), p-xylene and o-xylene (C8), nonane (C9), R(+)-limonene, linalool and α-pinene (C10). Three (0,1; 0.5; 1 µl) , or four (2 µl) different points of calibration at known concentrations were obtained depositing the standard on the mesh of the tenax trap and flowed inside through a 200ml/min of helium flow for one minute which allowed to retain more than 90% of the compounds into the tenax trap. The dilutions have been chosen in order to fall the concentration range of a calibration in the expected concentration range of the compounds in samples. The traps were immediately desorbed at the gas chromatograph. The calibration was performed by using the response (abundance) vs concentration (ng μl^{-1}) function that is then used to estimate concentration of compounds in a separately analyzed sample. The coefficient resulted from this function was used to quantify the volatile organic compounds identified thought the GC-MS analysis. If there are more than one standard compounds in a class, we used the standard that showed the best calibration curve.

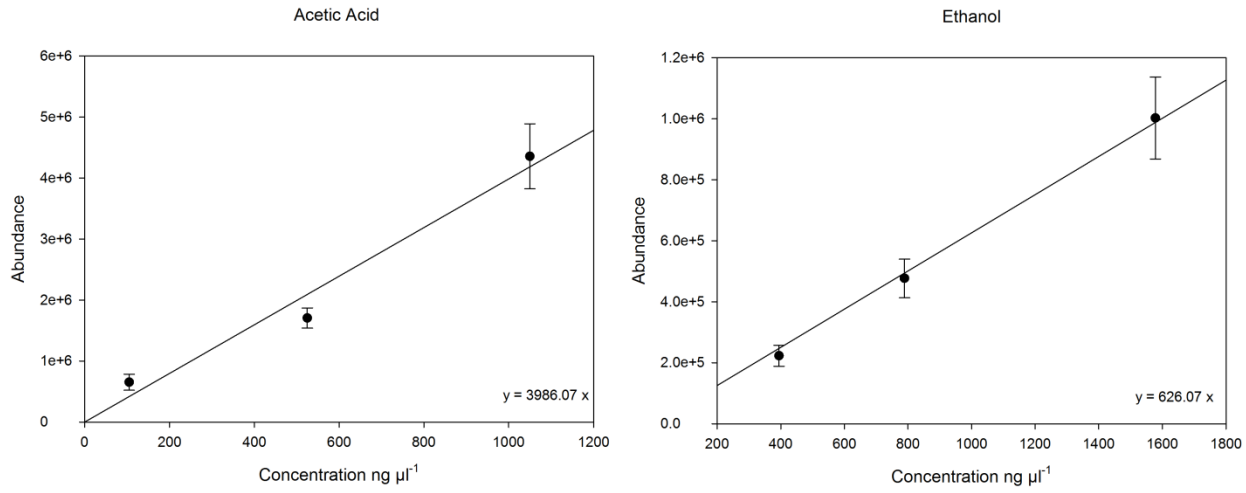

Fig 14 Calibration curve of acetic acid and ethanol for quantitative GC-MS analysis.

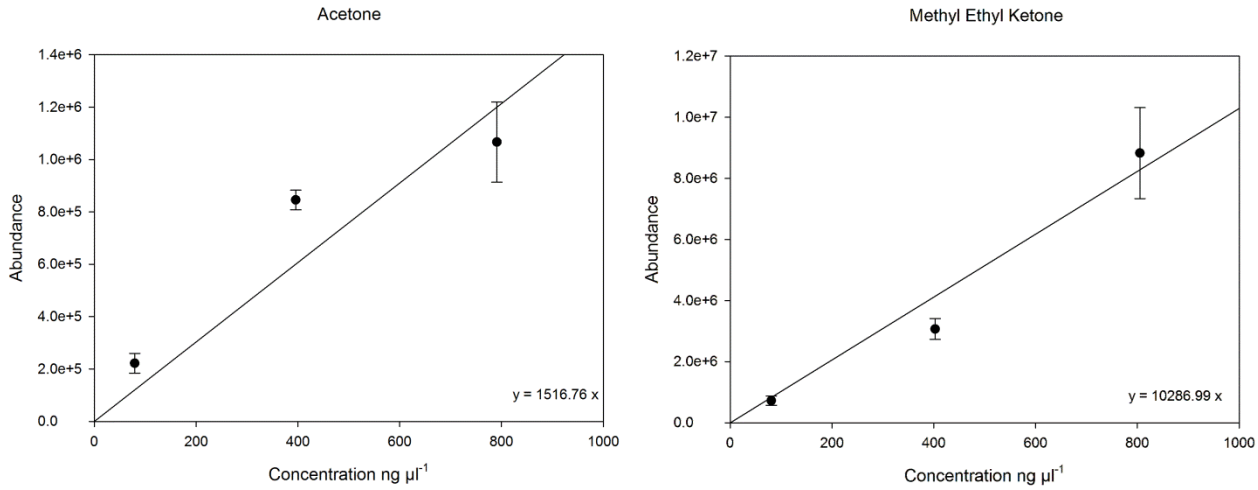

Fig 15 Calibration curve of acetone and methyl ethyl ketone for quantitative GC-MS analysis.

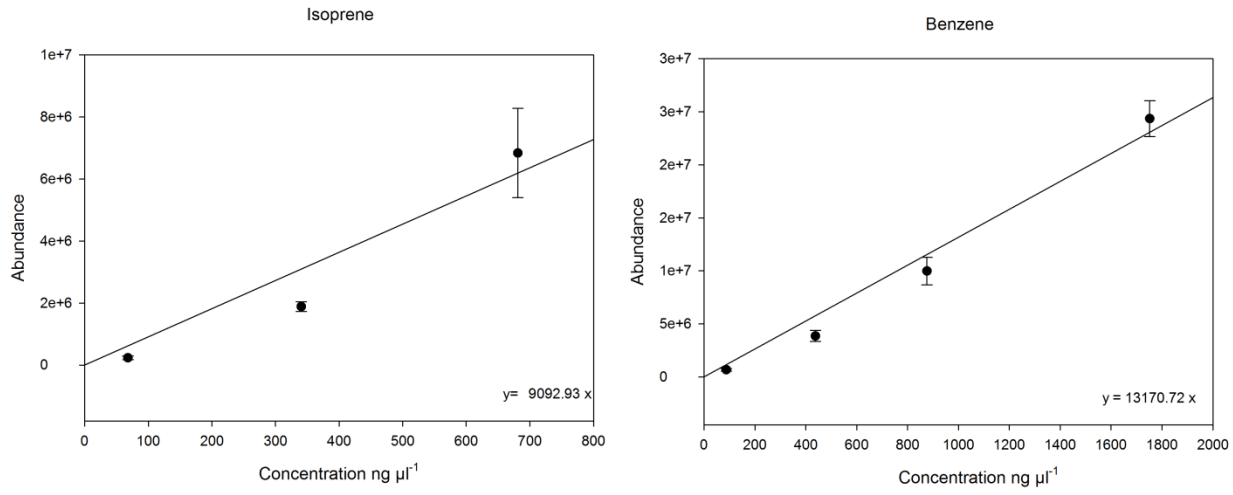

Fig 16 Calibration curve of isoprene and benzene for quantitative GC-MS analysis.

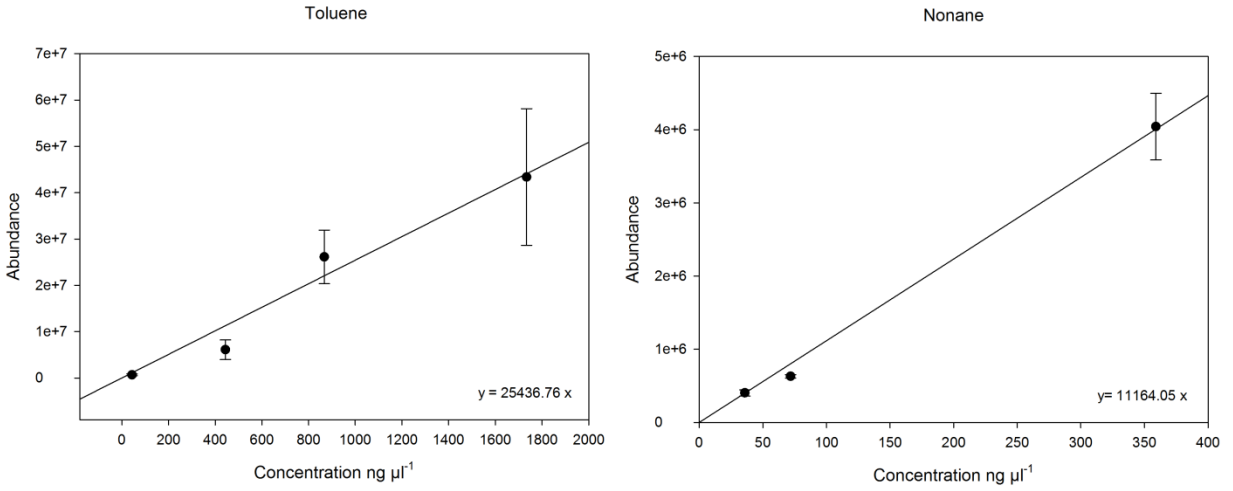

Fig 17 Calibration curve of toluene and nonane for quantitative GC-MS analysis.

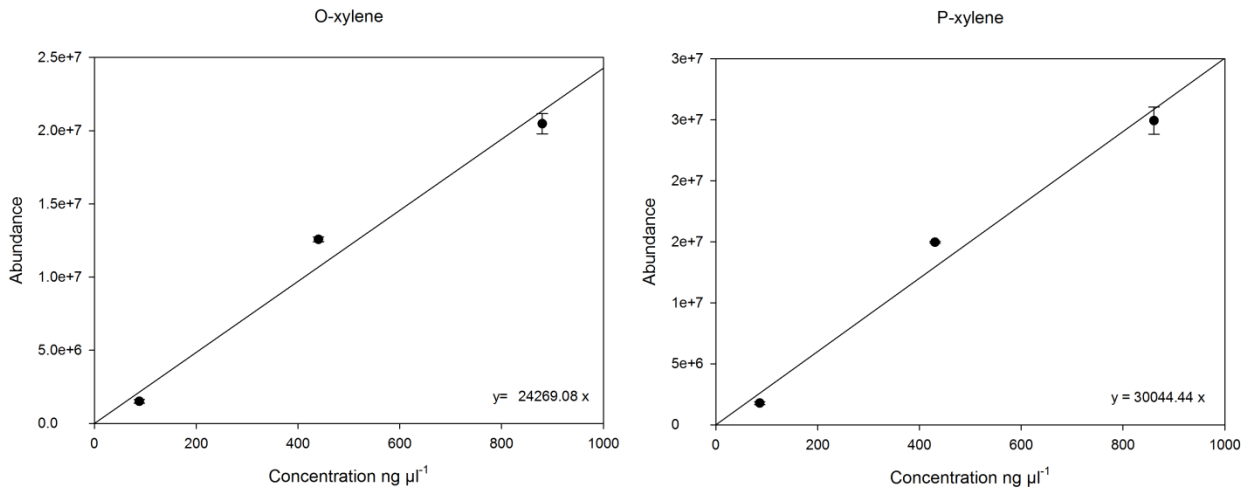

Fig 18 Calibration curve of o-xylene and p-xylene for quantitative GC-MS analysis.

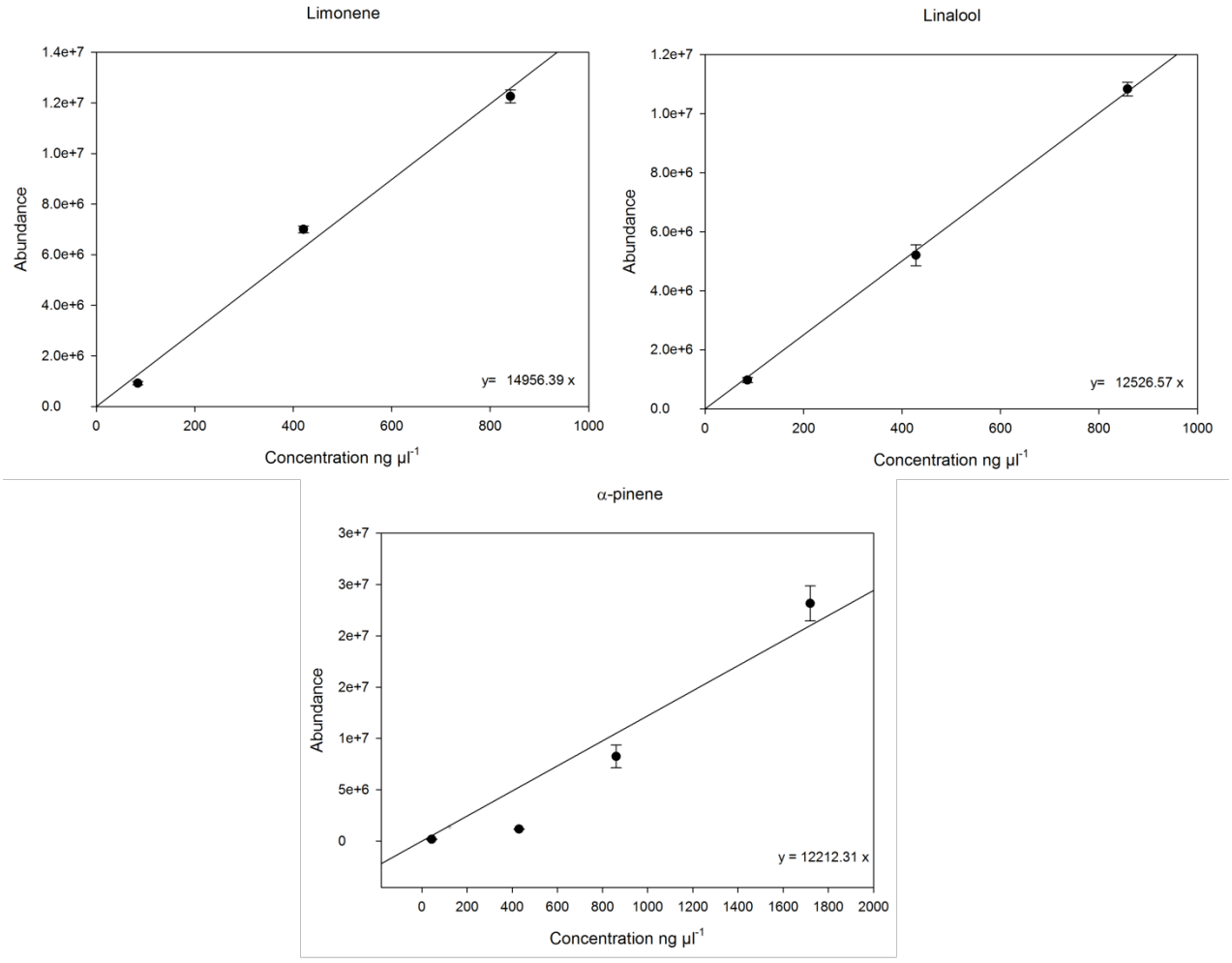

Fig 19 Calibration curve of limonene, linalool and α-pinene for quantitative GC-MS analysis.

5.2.8 Statistical analysis

Mean values and standard error were calculated on each parameter. Regression analysis were conducted among VOC emissions and the main features of fire as modified combustion efficiency (MCE) and the total heat released (°C).

Normality test (Shapiro-Wilk) were conducted on each fire parameters measured or calculated as duration of pre-ignition (s), duration of flaming (s), peak of heat (°C), the modified combustion efficiency (MCE), the total heat released (°C) and the total particulate matter (g kg^{-1}).

Two-way analysis of variance (Anova) were used to test the effect of each independent variable as different vegetable materials (leaves, branches and litter) and different species (*P. halepensis* and *Q. pubescens*) on each parameters and to test the interaction between them. These statistical analysis were conducted with Sigmaplot v. 12.5 software. Finally, a post-hoc test (Tukey test) were conducted on each Anova analysis to test if the comparison between each groups of samples are significant. This test were conducted with Systat v.12 software.

5.3 Results

The laboratory experiments revealed some differences in burning different tree species, especially between *storing* and *non-storing* species, namely *P. halepensis* and *Q. pubescens*, but also in burning different vegetable tissues. In Table 1 the significance of the comparison of values measured among tissues, among species and the interaction between tissues and species are reported. The total heat released and the total particulate matter did not show significant differences between species and tissues, whereas the duration of flaming, the peak of heat and the

modified combustion efficiency showed some significant difference, in some cases also extremely significant ($p \leq 0.001$).

	Duration of pre-ignition	Duration of flaming	Peak of heat	Total heat released	MCE	Total particulate matter
Tissues	**	***	***	-	**	-
Species	-	-	*	-	-	-
Tissues x Species	-	***	-	-	-	-

Table 1 The significance of values measured among tissues, among species, and the interaction between tissues and species. The levels of significance were indicated by * (P<0.05), ** (P<0.01), *** (P<0.001).

5.3.1 The features of fire

The average duration of pre-ignition phase (s), duration of flaming phase (s), the average peak of heat reached during the combustion (°C) and the total heat released (°C) were shown in Fig 20. The branches of oak reached the flame phase significant earlier then leaves of oak, while there is no difference in the duration of pre-ignition between branches and leaves of pine. The litter of pine showed a significant shorter pre-ignition phase then the leaves of both species. The combustions of little branches of both species showed the highest values for duration of flame and peak of heat, there are also a significant difference between them and the other tissues. There is significant differences in the duration of flaming also between leaves of *P. halepensis* and leaves of *Q. pubenscens*.

The values of the total heat released (°C s g^{-1}) during the combustion experiments did not show significant differences between tissue and species.

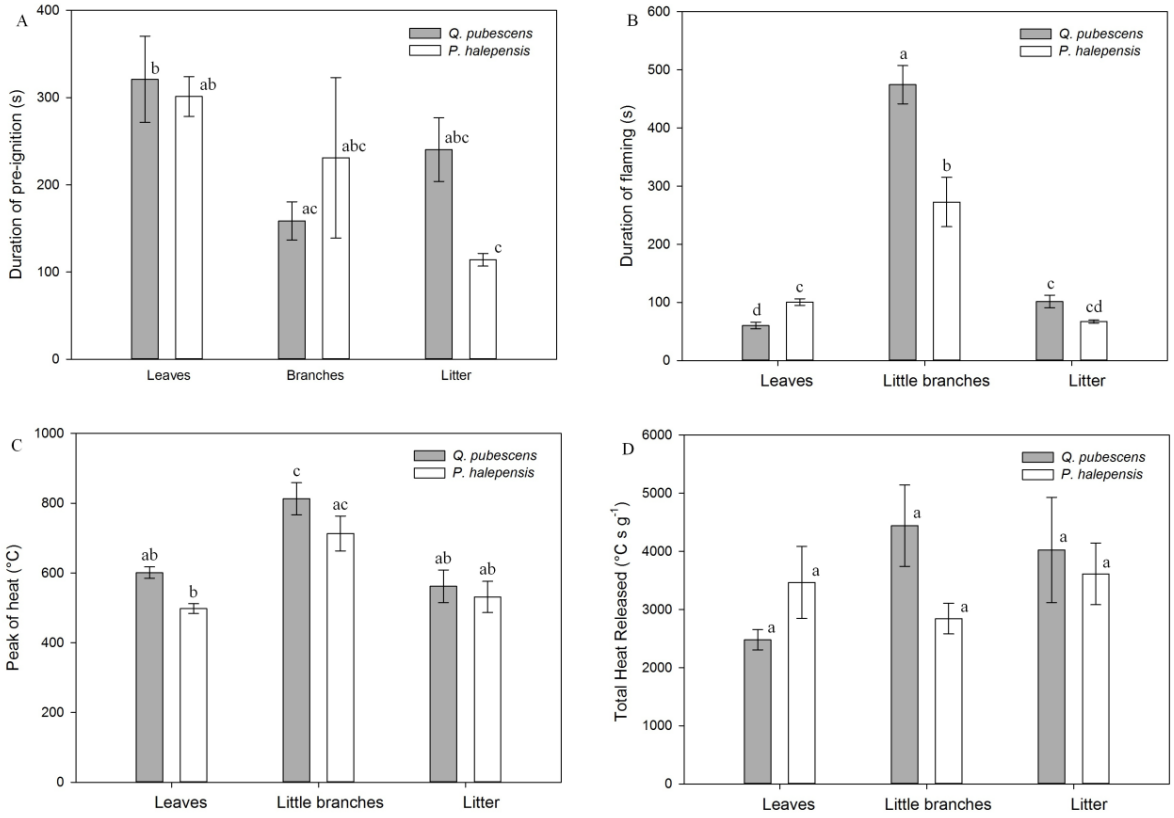

Fig 20 A) Duration of pre-ignition (s), B) durationf of flaming (s) ,C) peak of heat (°C) and D) total heat released (°C s g^{-1}) during the burning of leaves, little branches and litter of *Q. pubescens* and *P. halepensis*.

We tried to correlate the total heat released with the emission of the main important carcinogenic compounds as benzene and toluene but we didn't found significant relationship (values of p ranged from 0.18 to 0.80) even if there seems to be a negative trend suggesting that the emission of aromatic compound are favored at lower heat released values in both species (Fig. 21).

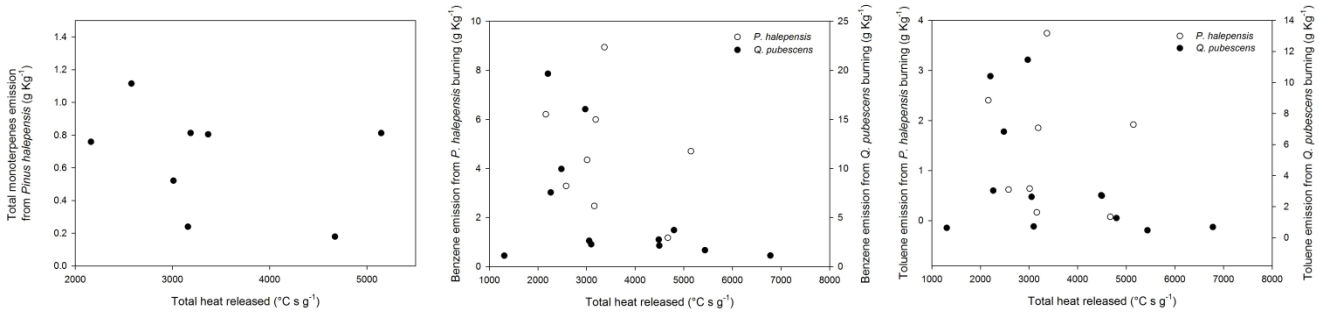

Fig 21 Total heat released (°C) during the combustion experiment and the correlation with benzene and toluene emission (mg hg^{-1}) during burning.

5.3.2 CO, CO_2 and CH_4 emissions

CO_2 and CO are the major gases emitted in both species. The values of CO_2 ranged from 984 to 1481 g kg^{-1}, the values of CO ranged from 124 to 166 g kg^{-1}. There is no significant differences between tissue and species both for CO and CO_2 emission even if it seems that CO_2 was released in major percentage from little branches burning. Methane emission instead showed significant highest value from some samples. In particular the CH_4 emissions from branches of pine are significant different from litter of oak and leave of pine, emission from branches of oak are significant different from both litter of pine and oak and finally emission from leaves of oak is significant different from litter of oak.

The data of carbon released in atmosphere from the combustion of 100 g of vegetal materials are reported in Table 2 and are referred to the carbon emitted as CO_2, CO and CH_4. The percentage of carbon released in atmosphere of the carbon initially present in the samples (assuming about 48% of the carbon content in vegetation) are also reported in Table 2.

The carbon emitted as these three gaseous compounds accounted for until 95% of the carbon content in vegetal materials as in the case of the combustion from little branches. The combustions from litter emitted lower carbon than the others, while the highest amount of carbon were released from the combustion of little branches in both species even if in a not significant way.

		Q. pubescens			*P. halepensis*		
		Leaves	**Little Branches**	**Litter**	**Leaves**	**Little Branches**	**Litter**
CO_2	**C (g hg^{-1})**	32.25 (±1.7)	40.42 (±2.2)	23.60 (±5.1)	32.56 (±2.3)	35.68 (±3.3)	25.97 (±8.9)
	C (%)	67.18	84.21	49.17	67.82	74.33	69.82
CO	**C (g hg^{-1})**	5.34 (±0.6)	5.55 (±0.4)	5.32 (±0.9)	6.41 (±0.4)	5.47 (±0.8)	5.56 (±1.9)
	C (%)	11.13	11.56	11.09	13.36	11.41	14.90
CH_4	**C (g hg^{-1})**	0.06 (±0.02)	0.08 (±0.01)	0.004 (±0.003)	0.03 (±0.02)	0.06 (±0.01)	0.02 (±0.005)
	C (%)	0.12	0.18	0.008	0.06	0.13	0.04
	Total C (g hg^{-1})	37.65 (±2.3)	46.05 (±2.7)	28.93 (±6.1)	39.00 (±2.8)	41.22 (±4.1)	31.55 (±10.8)
	Total C (%)	78.43	95.94	60.26	81.24	85.87	65.74

Table 2 The average amount of carbon and the relative percentage of the carbon initially present in the samples released in the atmosphere as CO, CO_2 and CH_4.

The trend of emission of these three main gaseous compounds during the burning was comparable in all experiments and a representative trend of one experiment was shown in Fig. 22.

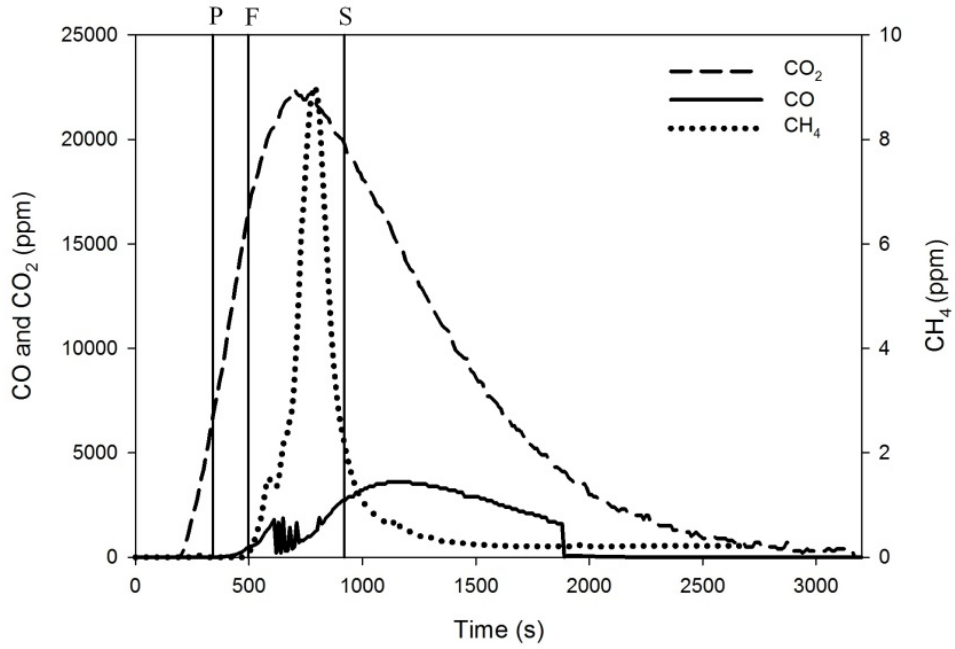

Fig 22 A representative trend of CO, CO_2 and CH_4 emission during the three stage of biomass burning (P = pre-ignition, F = flaming, S = smoldering).

CO_2 and CH_4 showed the peak of emission during the flaming stage, while CO showed the peak of emission during the smoldering phase. The mean MCE values ranged between 0,82 and 0,88 (Fig. 23).

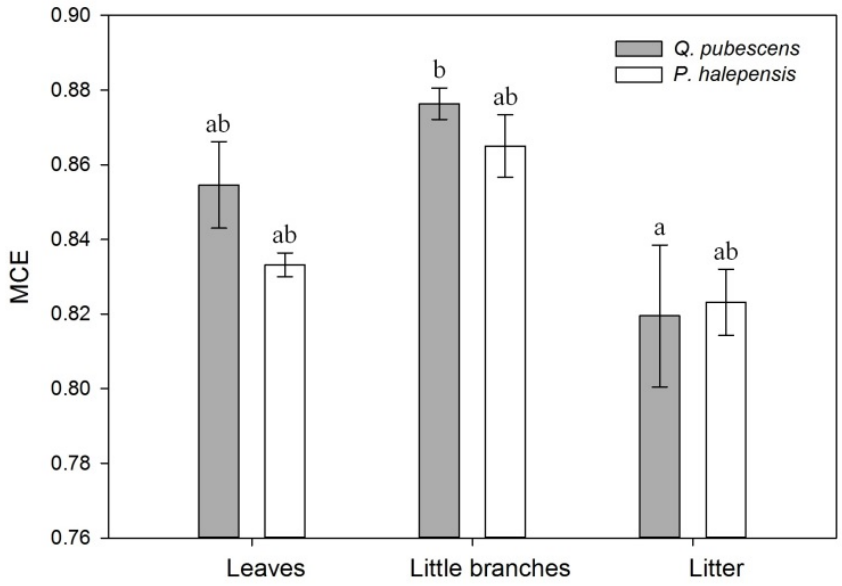

Fig 23 The modified combustion efficiency (MCE) from burning of leaves, little branches and litter of *Q. pubescens* and *P. halepensis*.

This is confirmed by the correlation between EFs and MCE showed in Fig. 24. The slope of the regression indicates the importance of flaming or smoldering phase in estimating the emission factor. Positive slopes point out that emission are promoted by flaming combustion, whereas negative slope suggest that emission is favored by the smoldering phase. The results showed that emission of CH_4 is favored by flaming combustion ($p=0.08$ and $p=0.05$ for pinus and oak respectively) as CO_2 ($p=0.24$ and $p=0.001$ for pinus and oak respectively) in both species while CO emission is favored by smoldering combustion ($p= 0.004$ for pine and $p= 0.02$ for oak). α-pinene emission from *P. halepensis* burning is favored during the flaming phase ($p=0.03$), the same also for the total monoterpene emission even if in a not significant way ($p=0.14$). If we

considered only D-limonene, it showed that it is favored by the smoldering combustion from *Q. pubescens* burning (p=0.04).

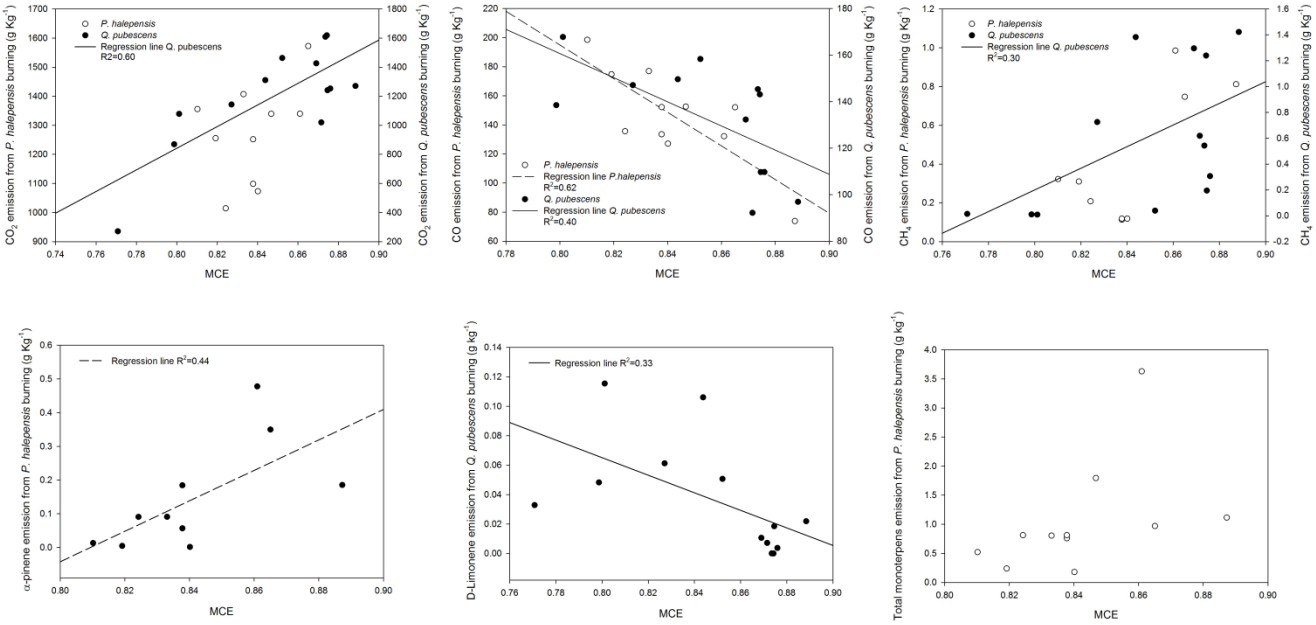

Fig 24 Correlation between some gaseous compounds (g Kg^{-1}) emitted during burning experiment and MCE. Significant linear regression were indicated ($p<0.05$).

5.3.3 VOCs emissions

We identified and quantified 83 volatile organic compounds emitted from the vegetation material burning. The average emission factors of gaseous emitted during the burning of leaves, little branches and litter of *Q. pubescens* and *P. halepensis* and the relative percentage of emissions during the three stage of burning (pre-ignition, flaming and smoldering) are shown in Table 3. The comparison between the two tree species showed that many oxygenated VOCs as methacrolein, methyl vinyl ketone (MVK), methyl ethyl ketone (MEK), 2-methylfuran and 2-furladehyde, but also many aromatic compounds as benzene, toluene, styrene, ethylbenzene, m-p-xylene, o-xylene, naphthalene are emitted in greater quantity from leaves burning than little branches and litter burnig, both from *Q. pubescens* and *P. halepensis*.

Compounds emitted	*Quercus pubescens*											
	Leaves (gr Kg^{-1})	P (%)	F (%)	S (%)	**Little branches (gr Kg^{-1})**	P (%)	F (%)	S (%)	**Litter (gr Kg^{-1})**	P (%)	F (%)	S (%)
Carbon dioxide (CO2)	**1181.61 (64.10)**	22.95	6	71.06	**1481.08 (82.97)**	10.84	33.69	55.47	**984.45 (203.26)**	23.72	6.01	70.27
Carbon monoxide (CO)	**124.64 (14.15)**	1.1	0.44	98.47	**129.40 (11.20)**	0.64	16.94	82.42	**124.09 (21.86)**	4.41	3.5	92.08
Methane (CH4)	**0.76 (0.23)**	23.52	18.8	57.67	**1.12 (0.2)**	0.64	66.49	32.87	**0.05 (0.03)**	14.23	26.06	59.72
Ethanol (CH3CH2OH)	**10.90 (6.55)**	17.89	10.52	71.59	**1.39 (1.18)**	37.61	62.39	0	**0.17 (0.11)**	100	0	0
Acetic Acid (CH3COOH)	**0.05 (0.03)**	100	0	0	**0.34 (0.3)**	33.87	66.13	0	**0.16 (0.05)**	100	0	0
Disulfide, dimethyl-(C2H6S1)	**0.50 (0.13)**	0	29.4	70.6	-	-	-	-	**0.2 (0.01)**	2.38	0	97.62
Methane, isothiocyanato- (C2H3NS)	**0.21 (0.06)**	0	100	0	-	-	-	-	**0.11 (0.06)**	0	0	100
Acrylonitrile (C3H3N)	-	-	-	-	-	-	-	-	-			
Acetone (C3H6O)	-	-	-	-	**6.93 (3.37)**	21.63	38.87	39.5	**3.44 (1.11)**	8.52	41.33	50.15
Acetic acid, methylester (C3H6O2)	-	-	-	-	**0.42 (0.18)**	0	27.28	72.72	**4.46 (0.67)**	1.84	26.84	71.33
1-Butyne (C4H6)	**0.20 (0.08)**	0	67.55	32.45	**0.12 (0.04)**	0	19.33	80.67	**0.18 (0.03)**	0	49.49	50.51
Pyrrole (C4H5N)	**1.09 (0.32)**	0	31.53	68.47	**0.07 (0.01)**	0	22.59	77.41	**0.25 (0.07)**	0	26.4	73.6
Methacrolein (C4H6O)	**0.60 (0.13)**	1.89	46.4	51.71	**0.10 (0.03)**	11.92	43.15	44.93	**0.19 (0.03)**	0	35.3	64.7
Methyl Vinyl Ketone (MVK, C4H6O)	**3.21 (0.57)**	0	46.77	53.23	**0.34 (0.09)**	0	45.46	54.54	**2.29 (0.43)**	0	37.63	62.37
Methyl Ethyl Ketone (MEK, C4H8O)	**1.74 (029)**	0.44	46.03	53.53	**0.24 (0.06)**	11.75	39.48	48.77	**1.41 (0.2)**	0.86	27.47	71.67
Acetic acid, ethylester (C4H8O2)	-	-	-	-	-	-	-	-	-	-	-	-
2-Butenal (C4H6O)	**0.34 (0.08)**	0	39.75	60.25	**0.03 (0.007)**	0	28.21	71.79	**0.18 (0.05)**	0	37.44	62.56
1,3-Cyclopentadiene (C5H6)	**3.08 (0.52)**	0	63.39	36.61	**0.23 (0.05)**	0	30.51	69.49	**0.5 (0.1)**	0.7	34.06	65.24
Pyridine (C5H5N)	**0.66 (0.3)**	0	0	100	**0.03 (0.01)**	0	0	100	-	-	-	-
Isoprene (C5H8)	**1.57 (0.2)**	0	57.43	42.57	-	-	-	-	**0.52 (0.08)**	0	41.67	58.33
cis-1,3-Pentadiene (C5H8)	-	-	-	-	-	-	-	-	-	-	-	-
Cyclopentene (C5H8)	**0.58 (0.08)**	0	51.18	48.82	**0.02 (0.007)**	0	24.42	75.58	**0.28 (0.03)**	0.65	25.66	73.69
1-Pentene (C5H10)	**1.33 (0.37)**	0	66.06	33.94	-	-	-	-	-	-	-	-
3-Methyl-1-Butene (C5H10)	**0.37 (0.05)**	0	66.92	33.08	-	-	-	-	**0.06 (0.008)**	0	0	100
cis-2-Pentene (C5H10)	-	-	-	-	-	-	-	-	-	-	-	-
3-Butene-2-one, 3-methyl (C5H8O)	-	-	-	-	-	-	-	-	**0.23 (0.04)**	0	22.49	77.51
2-Methylfuran (C5H6O)	**1.50 (0.25)**	0.17	40.66	59.17	**0.17 (0.02)**	6.82	38.23	54.95	**0.91 (0.12)**	0.98	19.52	79.5
2-Furaldehyde (C5H4O2)	**1.49 (0.51)**	0	17.96	82.04	**0.20 (0.06)**	0.39	23.44	76.18	**1.19 (0.45)**	1.5	21.93	76.56
2-Furanmethanol (C5H6O2)	**0.02 (0.01)**	0	0	100	**0.02 (0.009)**	11.47	26.87	61.66	-	-	-	-
Benzene (C6H6)	**13.30 (2.77)**	0	56.47	43.53	**2.38 (0.46)**	0.02	18.42	81.56	**1.95 (0.35)**	0.21	37.26	62.53
cis-1,4-Hexadiene (C6H10)	**0.02 (0.01)**	0	100	0	-	-	-	-	-	-	-	-
trans-1,4-Hexadiene (C6H10)	-	-	-	-	-	-	-	-	-	-	-	-
1,4-Cyclohexadiene (C6H8)	**0.50 (0.08)**	0	55.43	44.57	**0.02 (0.006)**	0	25.4	74.6	**0.08 (0.01)**	0	0	100
1,3-Cyclohexadiene(C6H8)	-	-	-	-	-	-	-	-	**0.07 (0.01)**	0	0	100
2,4-Hexanediene (C6H10)	**0.30 (0.02)**	0	57.17	42.83	-	-	-	-	**0.08 (0.01)**	0	0	100
Cyclopentene,3-methylene (C6H8)	-	-	-	-	-	-	-	-	-	-	-	-
Cyclohexene (C6H10)	**0.31 (0.06)**	0	50.2	49.8	-	-	-	-	**0.13 (0.02)**	0	27.23	72.77
1,3-Pentadiene,3-methyl- (C6H10)	**0.21 (0.04)**	0	71.74	28.26	-	-	-	-	**0.04 (0.01)**	0	0	100
2-Methyl-3-Pentene (C6H12)	-	-	-	-	-	-	-	-	-	-	-	-
1-Hexene (C6H12)	-	-	-	-	-	-	-	-	-	-	-	-
Phenol (C6H5OH)	-	-	-	-	-	-	-	-	-	-	-	-
Toluene (C6H5CH3)	**7.93 (1.91)**	0.04	45.54	54.42	**0.77 (0.17)**	0	17.42	82.58	**1.87 (0.49)**	0.21	27.46	72.33

2-Ethylfuran (C6H8O)	**0.12 (0.03)**	0	55.06	44.94	-	-	-	-	**0.05 (0.01)**	0	18.26	81.74
2,5-Dimethylfuran (C6H8O)	**0.21 (0.04)**	0	37.3	62.7	**0.05 (0.02)**	0	16.19	83.81	**0.14 (0.02)**	3.26	17.93	78.81
Ethanol-2-butoxy (C6H14O2)	**0.01 (0.003)**	52.35	47.65	0	**0.01 (0.007)**	0	100	0	**0.03 (0.005)**	19.49	41.09	39.43
1-Heptene (C7H14)	-	-	-	-	-	-	-	-	**0.11 (0.02)**	0	30.85	69.15
n-Heptane (C7H16)	-	-	-	-	-	-	-	-	-	-	-	-
Benzenenitrile (C7H5N)	**0.31 (0.15)**	0	21.99	78.01	**0.01 (0.003)**	0	10.68	89.32	**0.05 (0.01)**	0	32.8	67.2
Benzaldehyde (C7H6O)	**0.44 (0.19)**	0	28.35	71.65	**0.03 (0.008)**	0	16.24	83.76	**0.13 (0.04)**	0.3	47.22	52.48
Heptane, 3-methyl- (C8H18)	-	-	-	-	-	-	-	-	-	-	-	-
Ethynyl Benzene (C8H6)	**0.09 (0.03)**	0	49.43	50.57	**0.03 (0.01)**	0	15.42	84.58	**0.009 (0.003)**	0	47.44	52.56
Styrene (C8H8)	**0.75 (0.26)**	0.08	43.31	56.62	**0.06 (0.03)**	0	16.67	83.33	**0.12 (0.04)**	0.31	34.4	65.3
Ethylbenzene (C8H10)	**0.43 (0.12)**	0	42.9	57.1	**0.03 (0.007)**	0	18.69	81.31	**0.09 (0.03)**	0.26	31.56	68.18
m,p-Xylenes (C8H10)	**0.36 (0.1)**	0.05	38.23	61.71	**0.02 (0.009)**	7.7	17.47	74.84	**0.14 (0.05)**	0	36.31	63.69
o-Xylene (C8H10)	**0.16 (0.05)**	0.03	37.27	62.7	**0.01 (0.003)**	0	15.55	84.45	**0.07 (0.02)**	0	32.24	67.76
1-Octene (C8H16)	-	-	-	-	-	-	-	-	**0.06 (0.01)**	0	32.81	67.19
Benzofuran (C8H6O)	**0.29 (0.12)**	0	33.01	66.99	**0.02 (0.01)**	0	11.11	88.89	**0.05 (0.02)**	0	30.37	69.63
Octanal (C8H16O)	-	-	-	-	-	-	-	-	-	-	-	-
1-Hexanol,2-ethyl- (C8H18O)	-	-	-	-	-	-	-	-	-	-	-	-
Acetophenone (C8H8O)	**0.05 (0.02)**	0	12.96	87.04	**0.004 (0.001)**	0	25.2	74.8	**0.02 (0.008)**	0	49.82	50.18
Indene (C9H8)	**0.84 (0.34)**	0	41.13	58.87	**0.13 (0.07)**	0	10.3	89.7	**0.12 (0.04)**	0	30.46	69.54
alpha-Methylstyrene (C9H10)	-	-	-	-	-	-	-	-	-	-	-	-
1-Ethyl-3-Methylbenzene (C9H12)	**0.15 (0.05)**	0	42.25	57.75	**0.01 (0.006)**	0	0	100	**0.02 (0.01)**	0	0	100
1-Ethyl-4-Methylbenzene (C9H12)	-	-	-	-	-	-	-	-	-	-	-	-
1-Ethyl-2-Methylbenzene (C9H12)	**0.08 (0.03)**	0	49.58	50.42	**0.004 (0.002)**	0	0	100	**0.04 (0.01)**	0	31.58	68.42
1,2,3-Trimethylbenzene (C9H12)	**0.07 (0.03)**	0	29.76	70.24	-	-	-	-	**0.02 (0.008)**	0	0	100
Isopropenylbenzene (C9H10)	**0.07 (0.02)**	0	33.31	66.69	-	-	-	-	-	-	-	-
n-Propylbenzene (C9H12)	**0.12 (0.03)**	0	35.58	64.42	-	-	-	-	**0.04 (0.01)**	0	30.96	69.04
1-Nonene (C9H18)	-	-	-	-	-	-	-	-	-	-	-	-
α-Pinene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
Naphthalene (C10H8)	**0.89 (0.47)**	0	21.33	78.67	**0.23 (0.11)**	1.35	4.22	94.43	**0.09 (0.02)**	0	36.26	63.74
n-Butylbenzene (C10H14)	**0.02 (0.01)**	0	0	100	-	-	-	-	**0.02 (0.01)**	0	38.1	61.9
β-Cymene (C10H14)	-	-	-	-	-	-	-	-	-	-	-	-
β-Pinene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
cis-Linalool oxide (C10H18O2)	-	-	-	-	-	-	-	-	-	-	-	-
Sabinene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
3-Carene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
Terpinolene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
Camphene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-
n-Decane (C10H22)	-	-	-	-	-	-	-	-	-	-	-	-
D-Limonene (C10H16)	**0.04 (0.02)**	27.77	6.4	65.83	**0.01 (0.005)**	30.98	69.02	0	**0.05 (0.01)**	8.37	37.96	53.67
Myrcene (C10H16)	-	-	-	-	**0.01 (0.006)**	27.2	72.8	0	-	-	-	-
β-Linalool (C10H18O)	**0.14 (0.07)**	27.31	0	72.69	**0.42 (0.19)**	22.27	53.91	23.82	-	-	-	-

Compound emitted	*Pinus halepensis*											
	Needles (gr Kg^{-1})	P (%)	F (%)	S (%)	Little branches (gr Kg^{-1})	P (%)	F (%)	S (%)	Litter (gr Kg^{-1})	P (%)	F (%)	S (%)
Carbon dioxide (CO2)	**1192.9 (86.68)**	23.1	9.33	67.57	**1307.34 (122.80)**	15.19	20.45	64.36	**1228.01 (82.74)**	22.18	7.07	70.75
Carbon monoxide (CO)	**149.60 (10.03)**	0.25	0.89	98.87	**127.68 (18.57)**	4.07	5.73	90.2	**166.77 (21.01)**	0.06	0.51	99.44
Methane (CH4)	**0.35 (0.2)**	5.85	11.45	82.7	**0.85 (0.07)**	0.98	72.92	26.1	**0.25 (0.06)**	51.49	29.86	18.63
Ethanol (CH3CH2OH)	**0.49 (0.47)**	100	0	0	**5.75 (3.03)**	5.11	62.23	32.66	**0.88 (0.45)**	42.06	0	57.94
Acetic Acid (CH3COOH)	-	-	-	-	-	-	-	-	-	-	-	-
Disulfide, dimethyl-(C2H6S1)	**5.81 (0.82)**	0.86	21.83	77.31	-	-	-	-	**0.9 (0.08)**	0	14.79	85.21
Methane, isothiocyanato- (C2H3NS)	-	-	-	-	-	-	-	-	-	-	-	-
Acrylonitrile (C3H3N)	-	-	-	-	**0.52 (0.32)**	0	100	0	-	-	-	-
Acetone (C3H6O)	-	-	-	-	**14.22 (11.88)**	0.64	65.72	33.64	-	-	-	-
Acetic acid, methylester (C3H6O2)	-	-	-	-	-	-	-		-	-	-	-
1-Butyne (C4H6)	**0.16 (0.03)**	0	66.17	33.83	**0.09 (0.06)**	0	100	0	**0.32 (0.09)**	0	82.59	17.41
Pyrrole (C4H5N)	**0.35 (0.03)**	0	18.09	81.91	**0.03 (0.01)**	0	0	100	-	-	-	-
Methacrolein (C4H6O)	**0.96 (0.17)**	0	35.89	64.11	**0.42 (0.15)**	0	39.79	60.21	**0.23 (0.05)**	0	31.13	68.87
Methyl Vinyl Ketone (MVK, C4H6O)	**3.54 (0.65)**	0	32.73	67.27	**0.82 (0.31)**	3.09	35.5	61.41	**0.84 (0.11)**	0	21.11	78.89
Methyl Ethyl Ketone (MEK, C4H8O)	**1.87 (0.3)**	1.26	26.29	72.45	**0.56 (0.26)**	1.18	29.3	69.52	**0.4 (0.05)**	0	17.22	82.78
Acetic acid, ethylester (C4H8O2)	-	-	-	-	**0.16 (0.04)**	4.28	36.49	59.23	-	-	-	-
2-Butenal (C4H6O)	-	-	-	-	-	-	-	-	-	-	-	-
1,3-Cyclopentadiene (C5H6)	**1.91 (0.41)**	0	46	54	**0.89 (0.46)**	0	53.85	46.15	**0.65 (0.07)**	0	34.37	65.63
Pyridine (C5H5N)	-	-	-	-	-	-	-	-	-	-	-	-
Isoprene (C5H8)	**6.97 (1.49)**	0	34	66	**0.87 (0.5)**	0	33.22	66.78	**1.30 (0.2)**	0	29.69	70.31
cis-1,3-Pentadiene (C5H8)	**1.05 (0.3)**	0	32	68	**0.04 (0.01)**	0	0	100	**0.23 (0.03)**	0	26.58	73.42
Cyclopentene (C5H8)	**0.68 (0.18)**	0	31	69	**0.1 (0.04)**	0	0	100	**0.15 (0.02)**	0	22.53	77.47
1-Pentene (C5H10)	-	-	-	-	-	-	-	-	-	-	-	-
3-Methyl-1-Butene (C5H10)	**0.66 (0.2)**	0	34	66	-	-	-	-	**0.12 (0.02)**	0	33.88	66.12
cis-2-Pentene (C5H10)	**2.83 (0.82)**	0	32	68	-	-	-	-	-	-	-	-
3-Butene-2-one, 3-methyl (C5H8O)	-	-	-	-	-	-	-	-	-	-	-	-
2-Methylfuran (C5H6O)	**1.56 (0.19)**	0	25.63	74.37	**0.45 (0.23)**	0	21.98	78.02	**0.4 (0.08)**	0	13.71	86.29
2-Furaldehyde (C5H4O2)	**0.27 (0.013)**	0.77	16.8	82.43	**0.15 (0.04)**	0	21.94	78.06	**0.006 (0.0009)**	0	0	100
2-Furanmethanol (C5H6O2)	**0.1 (0.02)**	0	6.08	93.92	-	-	-	-	-	-	-	-
Benzene (C6H6)	**6.46 (0.89)**	0	46.48	53.52	**7.58 (2.34)**	0	39.7	60.3	**2.66 (0.92)**	0	31.7	68.3
cis-1,4-Hexadiene (C6H10)	**0.11 (0.02)**	0	28.08	71.92	-	-	-	-	**0.02 (0.002)**	0	21.54	78.46
trans-1,4-Hexadiene (C6H10)	**0.07 (0.01)**	0	25.82	74.18	-	-	-	-	**0.01 (0.005)**	0	0	100
1,4-Cyclohexadiene (C6H8)	**0.72 (0.17)**	0	35.23	64.77	**0.10 (0.03)**	0	27.79	72.21	**0.15 (0.03)**	0	24.62	75.38
1,3-Cyclohexadiene(C6H8)	**0.77 (0.19)**	0	35.24	64.76	**0.1 (0.03)**	0	27.89	72.11	**0.17 (0.03)**	0	25.7	74.3
2,4-Hexanediene (C6H10)	**0.4 (0.09)**	0	29.68	70.32	**0.04 (0.01)**	0	0	100	**0.06 (0.005)**	0	20.33	79.67
Cyclopentene,3-methylene (C6H8)	**0.68 (0.2)**	0	30.88	69.12	-	-	-	-	**0.07 (0.01)**	0	0	100
Cyclohexene (C6H10)	**0.32 (0.08)**	0	25.55	74.45	**0.03 (0.01)**	0	0	100	**0.04 (0.004)**	0	20.75	79.25
1,3-Pentadiene,3-methyl- (C6H10)	**0.44 (0.1)**	0	32.54	67.46	-	-	-	-	**0.07 (0.009)**	0	0	100
2-Methyl-3-Pentene (C6H12)	**0.1 (0.02)**	0	0	100	-	-	-	-	-	-	-	-
1-Hexene (C6H12)	**1.08 (0.2)**	0	31.84	68.16	-	-	-	-	-	-	-	-
Phenol (C6H5OH)	**0.66 (0.05)**	0	19.49	80.51	**0.1 (0.03)**	5.06	40.02	54.92	**0.03 (0.02)**	0	4.66	95.34
Toluene (C6H5CH3)	**2.47 (0.43)**	0	28.35	71.65	**1.08 (0.23)**	1.41	22.38	76.2	**0.29 (0.17)**	0	35.44	64.56

2-Ethylfuran (C6H8O)	**0.11 (0.04)**	0	24.99	75.01	-	-	-	-	-	-	-	-	-	-	-	-
2,5-Dimethylfuran (C6H8O)	**0.18 (0.01)**	0	20.52	79.48	**0.04 (0.02)**	0	16.8	83.2	**0.03 (0.001)**	0	15.87	84.13				
Ethanol-2-butoxy (C6H14O2)	**0.01 (0.007)**	19.99	46.78	33.22	**0.03 (0.004)**	0	50.51	49.49	**0.009 (0.001)**	0	0	100				
1-Heptene (C7H14)	**0.2 (0.05)**	0	26.35	73.65	**0.03 (0.01)**	0	0	100	**0.03 (0.002)**	0	21.49	78.51				
n-Heptane (C7H16)	**0.42 (0.38)**	0	95.2	4.8	**0.02 (0.004)**	3.94	31.33	64.73	**0.008 (0.001)**	0	0	100				
Benzenenitrile (C7H5N)	-	-	-	-	**0.01 (0.004)**	0	21.63	78.37	-	-	-	-				
Benzaldehyde (C7H6O)	**0.06 (0.008)**	0	30.51	69.49	**0.07 (0.01)**	1.71	36.03	62.25	**0.007 (0.001)**	0	44.43	55.57				
Heptane, 3-methyl- (C8H18)	**0.02 (0.001)**	0	13.34	86.66	**0.01 (0.003)**	10.04	40.75	49.22	**0.004 (0.002)**	0	26.98	73.02				
Ethynyl Benzene (C8H6)	-	-	-	-	**0.04 (0.01)**	0	31.76	68.24	-	-	-	-				
Styrene (C8H8)	**0.18 (0.02)**	0	29.7	70.3	**0.14 (0.03)**	0	30.8	69.2	**0.02 (0.01)**	0	43.94	56.06				
Ethylbenzene (C8H10)	**0.16 (0.02)**	0	27.86	72.14	**0.05 (0.006)**	0	25.57	74.43	**0.007 (0.005)**	0	0	100				
m,p-Xylenes (C8H10)	**0.32 (0.05)**	0	23.78	76.22	**0.08 (0.01)**	0	23.24	76.76	**0.007 (0.005)**	0	0	100				
o-Xylene (C8H10)	**0.09 (0.01)**	0	24.19	75.81	**0.02 (0.003)**	0	25.22	74.78	**0.002 (0.001)**	0	0	100				
1-Octene (C8H16)	**0.08 (0.01)**	0	23.74	76.26	-	-	-	-	**0.004 (0.0008)**	0	0	100				
Benzofuran (C8H6O)	-	-	-	-	-	-	-	-	-	-	-	-				
Octanal (C8H16O)	**0.003 (0.0004)**	13.2	45.71	41.09	**0.009 (0.002)**	11.04	56.88	32.08	**0.001 (0.0006)**	0	51.85	48.15				
1-Hexanol,2-ethyl- (C8H18O)	**0.002 (0.0009)**	0	69.8	30.2	**0.02 (0.002)**	7.43	52.98	39.59	**0.002 (0.001)**	0	38.5	61.5				
Acetophenone (C8H8O)	**0.01 (0.001)**	0	36.46	63.54	**0.01 (0.004)**	6.26	41.3	52.45	**0.002 (0.0002)**	0	40.75	59.25				
Indene (C9H8)	**0.11 (0.004)**	0	35.61	64.39	**0.1 (0.04)**	0	21.98	78.02	-	-	-	-				
alpha-Methylstyrene (C9H10)	**0.24 (0.13)**	0	9.71	90.29	-	-	-	-	-	-	-	-				
1-Ethyl-3-Methylbenzene (C9H12)	**0.08 (0.01)**	0	27.98	72.02	**0.009 (0.003)**	0	0	100	-	-	-	-				
1-Ethyl-4-Methylbenzene (C9H12)	**0.17 (0.02)**	0	27.86	72.14	**0.03 (0.005)**	0	21.72	78.28	-	-	-	-				
1-Ethyl-2-Methylbenzene (C9H12)	**0.06 (0.006)**	0	25.68	74.32	**0.007 (0.002)**	0	0	100	-	-	-	-				
1,2,3-Trimethylbenzene (C9H12)	-	-	-	-	-	-	-	-	-	-	-	-				
Isopropenylbenzene (C9H10)	-	-	-	-	-	-	-	-	-	-	-	-				
n-Propylbenzene (C9H12)	**0.04 (0.005)**	0	22.81	77.19	**0.01 (0.003)**	0	34.91	65.09	-	-	-	-				
1-Nonene (C9H18)	**0.09 (0.02)**	0	24.19	75.81	**0.007 (0.003)**	0	0	100	-	-	-	-				
α-Pinene (C10H16)	**0.11 (0.03)**	4.92	16.68	78.4	**0.55 (0.22)**	3.2	36.93	59.87	**0.006 (0.003)**	0	39.83	60.17				
Naphthalene (C10H8)	**0.21 (0.009)**	0	38.48	61.52	**0.12 (0.05)**	0	14.79	85.21	-	-	-	-				
n-Butylbenzene (C10H14)	-	-	-	-	-	-	-	-	-	-	-	-				
β-Cymene (C10H14)	**0.13 (0.007)**	0.2	20.99	78.82	**0.05 (0.02)**	0	41.29	58.71	**0.01 (0.006)**	0	36.04	63.96				
β-Pinene (C10H16)	**0.33 (0.05)**	1.7	25.95	72.35	**0.27 (0.07)**	2.34	38.15	59.51	**0.02 (0.01)**	0	0	100				
cis-Linalool oxide (C10H18O2)	-	-	-	-	**0.005 (0.003)**	0	0	100	-	-	-	-				
Sabinene (C10H16)	**0.05 (0.02)**	0	15.74	84.26	-	-	-	-	-	-	-	-				
3-Carene (C10H16)	**0.04 (0.01)**	1.24	25.57	73.19	**0.02 (0.005)**	2.98	52.93	44.08	-	-	-	-				
Terpinolene (C10H16)	-	-	-	-	**0.004 (0.002)**	0	0	100	-	-	-	-				
Camphene (C10H16)	**0.005 (0.003)**	0	0	100	**0.01 (0.003)**	0	35.22	64.78	-	-	-	-				
n-Decane (C10H22)	**0.02 (0.002)**	8.17	13.02	78.81	**0.01 (0.005)**	0	100	0	**0.003 (0.002)**	0	0	100				
D-Limonene (C10H16)	**0.14 (0.01)**	1.61	34.88	63.51	**0.06 (0.01)**	0	59.82	40.18	**0.008 (0.004)**	0	33.45	66.55				
Myrcene (C10H16)	-	-	-	-	-	-	-	-	-	-	-	-				
β-Linalool (C10H18O)	-	-	-	-	**0.89 (0.49)**	0.32	41.99	57.69	**0.26 (0.09)**	0	48.92	51.08				

Table 3 The average emission factors from leaves, little branches and litter of *Quercus pubescens* and *Pinus halepensis* burning, and the relative percentage of emissions during the three stage of burning (P= pre-ignition, F= flaming and S= smoldering).

Benzene and toluene are the aromatic compounds emitted in greater quantities. Depending on species we showed different amounts of emissions from different tissue. For instance, if we considered the emission of ethanol, it is emitted in greater quantity from the combustion of leaves in the case of *Q. pubescens* while, in the case of *P. halepensis*, the combustion of branches showed the highest emissions.

Some gaseous species characterized the emission of a specific species, or are emitted in lower quantity from the other. Benzenenitrile, ethynilbenzene, benzofuran are emitted from the burning of all tissue of *Q. pubescens*, while they are absent (e.g. leaves and litter) or emitted in low quantity (e.g. little branches) from *P. halepensis* burning.

On the other hand, most of monoterpenes as α-pinene, β-pinene, β-cymene, sabinene, Δ^3-carene, terpinolene and camphene are emitted only from the burning of pine in different amounts depending on the tissues combusted. Only D-limonene are present in all experiments of combustion. The percentage of VOCs emission during the three different phase of combustions suggested that most of compounds are emitted in greater quantity during the smoldering phase. Fig. 25 showed the trend of monoterpenes (m/z 137) emissions during the combustions of leaves, little branches and litter of *P. halepensis* analyzed by PTR-MS. Little branches showed the greater quantities of emission and the peak of emission occurred earlier (just after the flaming phase) than the others tissues. The combustion of litter showed the lower quantity emission, while the combustion of leaves showed the major delay in emissions.

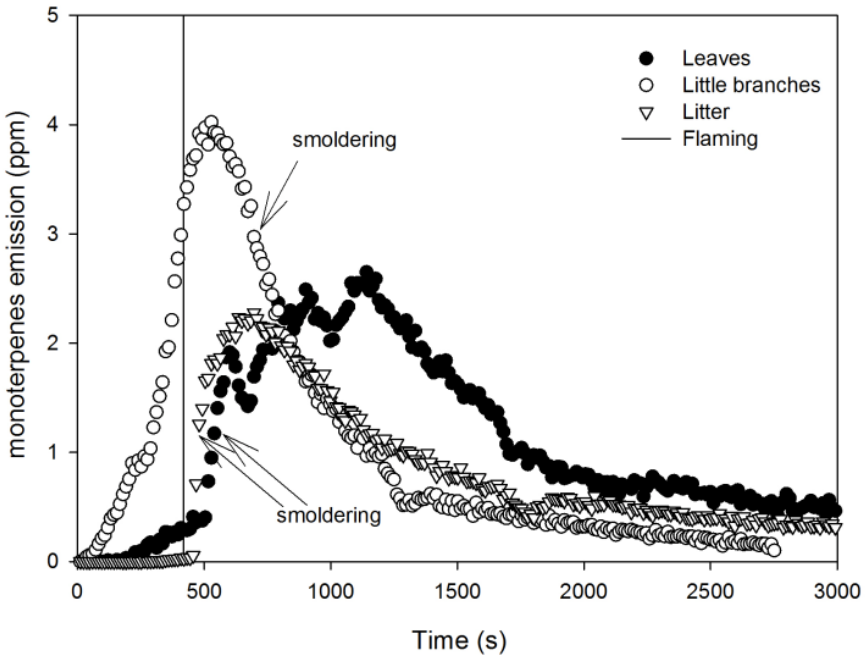

Fig 25 Trend in real time of monoterpenes emission analyzed by PTR-MS from the combustion of leaves, little branches and litter of *Pinus halepensis* . The time of the phases are aligned in order that the beginning of flaming phase (indicated by the vertical line) is equal for all three experiments. The darts indicated the beginning of smoldering phase for each experiment.

Some oxygenated VOCs as methanol and acetaldehyde were not efficiently detected by the GC-MS analysis, we reported only the trend of their emission without the quantitative analysis. Fig. 26 showed a representative trend of emission of methanol (m/z 33), acetaldehyde (m/z 45) and acetone (m/z 59) in real time during the combustion of leaves of oak. These compound are largely emitted during the pre-ignition phase, drastically decreased during the flame and finally slightly raised again during the smoldering phase.

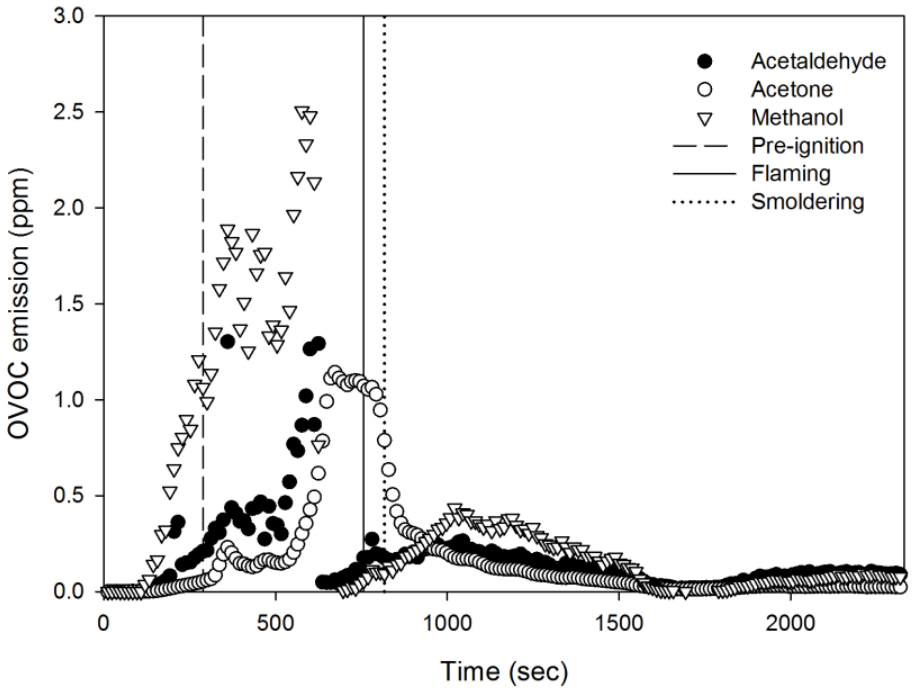

Fig 26 Trend in real time of oxygenated VOCs (acetaldehyde, methanol and acetone) emission analyzed by PTR-MS from the combustion of leaves of *Quercus pubescens* during the three phase of biomass burning (P = pre-ignition, F = flaming, S = smoldering).

5.3.4 Particulate emissions

The values of the total particulate matters released during the combustion experiments are reported in Fig. 27. The particulate matters emissions are homogeneous , ranging from 8.61 to 11.60 g Kg^{-1}. There is no significant difference between the emissions from different species and tissue.

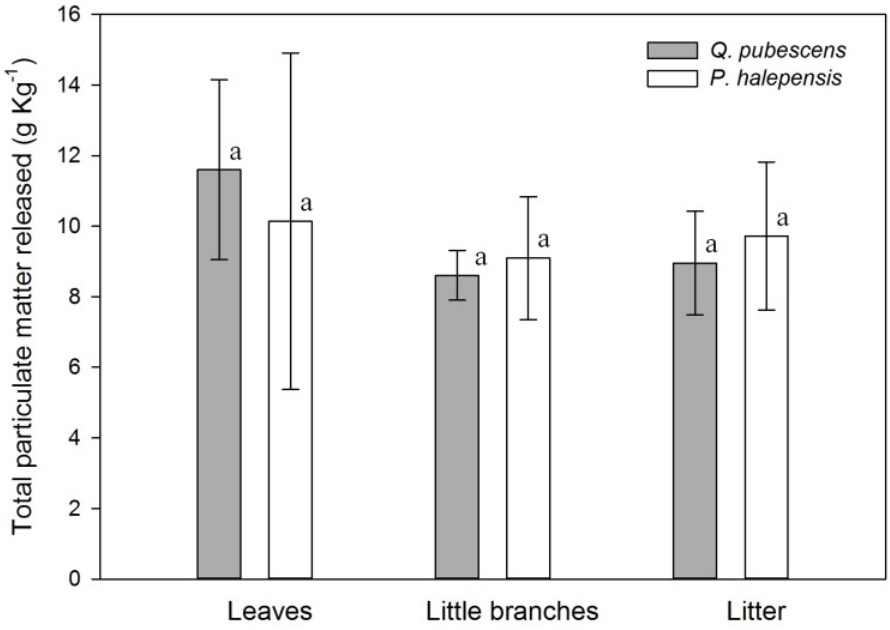

Fig 27 Total particulate matter (g Kg^{-1}) released during the combustion of leaves, little branches and litter of *Q. pubescens* and *P. halepensis*.

5.4 Discussion

5.4.1 The combustion process

Until now, there are very few works in the literature that have investigated the emissions from the combustion of litter and other components of the tree, as leaves and branches, separately (Courty et al., 2012, Alessio et al., 2008). As expected, branches, which may be considered as high-density fuels (Lobert and Warnatz, 1993), are much harder to ignite respect leaves and litter. The duration of flaming and the peak of heat reached during the combustion of branches are significantly higher than for the other materials in both species. The branches of pine reached the flame phase in the same time than the branches of oak but they burned significantly faster than the branches of oak (Fig 20A, 20B). This fact could be attributed to the emissions of VOCs that increase with the

temperature (Barboni et al., 2011) and can influence the intrinsic flammability of vegetation (Owens et al., 1998) due to the flammable character of VOCs. For these reasons VOCs, especially monoterpenes as limonene and α-pinene in pine, that are accumulated over the branches due to the stagnation condition that is present into a combustion chamber respect to a field, could cause the acceleration of the combustion of pine branches (Courty et al., 2012). The difference between the two species become significant only at the flame phase and this could be explained by the fact that isoprenoids pool in conifers are tightly sealed into the resin ducts/glandular reservoirs and they are broken only when temperature reach very high values (as could be the flame temperature) (Ciccioli et al., 2014).

Also the leaves of pine reached the flame phase in the same time than the leaves of oak but they burned significantly slower, despite the higher quantity of monoterpenes emitted from pine. This is in contrast with it was found by Alessio et al. (2008) who, investigating the influence of isoprenoids on flammability, showed that the needles of *P. halepensis* burn more rapidly than *Q. ilex* leaves. Our results are probably explained by the morphological structure of leaves of *Q. pubescens* which are wider and thinner than needle of *P. halepensis* and *Q. ilex* leaves, so they may have favoured the spread of fire (Tartaglini et al., 1992). In other experiments, it was demonstrated that, if leaves were directly and sudden exposed to flame, high isoprenoids contents could facilitate flammability (Ciccioli et al., 2014). In this case instead, as suggested by Greenberg et al. (2006), the intrinsic flammability of isoprenoid may be masked by the dynamics of the combustion, as pre-ignition temperature, which depleted the isoprenoids pool that have evaporated without favoring the ignition of pine needles. Interestingly, for oak, the branches reached the flame phase significantly early than the leaves.

Courty et al. (2012) studied the combustion of *Pinus pinea* and found that the VOCs emissions increase with the temperature of needle until only 160 °C, above which they decrease due to the

thermal degradation of the emitted terpenoids. This is probably the reason that explain the negative trend, even if it is not significant, of total monoterpenes emission correlated to the total heat released (Fig. 21).

5.4.2 The modified combustion efficiency

The majority of the compounds investigated in this study showed the highest percentage of emission during the smoldering phase. It is probably justified by the insufficient conversion of the products during the flaming stage due to a deficiency of air supply during the combustion, or probably due to an excess of biomass used during the experiments which made the combustion less efficient (Soares Neto et al., 2009). The modified combustion efficiency (MCE) values calculated in our experiments confirmed this. All MCE values were < 0.9, suggesting that the burning experiments were dominated by the smoldering phase and that more than 50% of the emissions were produced by smoldering combustion (Ward and Hardy, 1991). The MCE values reported here were lower than it has been reported in other studies, for instance the MCE of coniferous canopy (0.92 ±0.036) and pine-forest understory (0.936 ±0.025) by Yokelson et al. (2013). It is well known that fire emission factors strongly depend on the modified combustion efficiency (Soares Neto et al., 2009; Yokelson et al., 2013). The correlation between the MCE values and the emission factors of VOCs may reveal if the VOCs emissions present a weak or strong dependence from the combustion process. In our experiments we saw that D-limonene emission was associated with smoldering combustion in *Q. pubescens* burning as shown by its increasing EF at lower MCE, while α-pinene and the total monoterpenes emissions were associated with flaming combustion in *P. halepensis* burning (Fig. 18). As reported in the literature, the CO_2 emission is associated with the flaming phase during which it reaches the

highest peak, while CO is mainly emitted during the smoldering phase (Lobert et al., 1991; Ward and Hardy, 1991) (Fig.22 and Fig.24).

5.4.3 CO, CO_2, CH_4 emissions and the C budget

The amount of compounds emitted from burning of vegetation material and their emission factors reported here were reasonably consistent with those found by other studies in the Mediterranean ecosystem (Evytugina et al., 2013; Vincent et al., 2013) and were considerably higher than those from tropical and savannah fires reported by Akagi et al. (2011), Andreae et Merlet (2001) and Urbanski (2009). However, it should be kept in mind that the high variability of combustion process and the different sampling strategies may render difficult the comparison of data.

The amount of CO and CO_2 emitted during our combustion experiments are similar to what found by Vincent et al. (2013) who studied the wildfire forest emission in open air in Portugal founding values from 67 to 383 g kg^{-1} for CO and from 1029 to 1655 g kg^{-1} for CO_2. The CO_2 emissions registered in our study are indeed slightly lower than what Akagi et al. (2011) presented for tropical forest, savanna, boreal forest, temperate forest and extratropical forest that ranged from 1489±121 g kg^{-1} to 1686±38 g kg^{-1}. CO_2 emission factors are also lower than the values reported by Andrea and Marlet (2001) for the same ecosystem. The CO emission are similar to what found by Akagi et al. (2001) for boreal (127 ±45 g kg^{-1}) and extratropical (122 ±44 g kg^{-1}) forest.

During burning the largest fraction of carbon content into the plant materials is emitted in atmosphere as CO and CO_2, as shown in Table 3. The combustion of leaves releases lower carbon in the form of CO and CO_2 than the combustion of little branches and this is explained by the fact that the combustion from leaves release greater quantities of the other volatile organic compounds (even if in a not significant way).

The direct carbon emission from biomass burning depend primarily on pre-fire characteristics and burning conditions during the fire itself (Amiro et al., 2001). Our data are consistent with the data from literature that reported the carbon released in the same percentage namely 90%, 9% and 1% respectively in the form of CO_2, CO and CH_4 (Cofer et al., 1998; Kasischke and Bruhwiler, 2002). Our percentage (Table 2) were slightly different, with a lesser amount of C released as CO_2 and a greater amount in the form of CO, probably due to a lower combustion efficiency.

In some cases it was shown that the type of forest stand, or fuel type, has a strong influence on carbon emission rate as in the case of burning of jack pine and black spruce (Quintilio et al., 1977). In our study the differences in physical fuel structures of oak and pine materials did not influence the amounts of carbon released. It is however to be taken into account that the two type of results are extrapolated from two different scale, the previous results came from field study (stand-level) while our results were from laboratory experiment.

Contrary to what found by Garcia-Hurtado et al. (2013) who showed relatively high emission of CH_4 during the smoldering phase, in the present study the methane emission was significantly associated with the flaming phase ($p=0.08$, $p=0.05$) (Fig.24) during which it showed the peak of emission (Fig.16) then it rapidly decreased. Methane is a low-oxidized compound that begin to be emitted as soon as the embers start to be ardent before the onset of the flames. The percentages of the methane emission during the three combustion phases are highly variable, in the case of *P. halepensis* litter the largest amount of emission is emitted during the pre-ignition phase. In both tree species, the CH_4 emission from the combustions of branches showed the highest percentage of emission during the flaming stage and were higher than for the others tissues. The values of methane emission obtained in this study are generally lower than what is found by Akagi et al. (2011) and Yokelson et al. (2013) for the combustion of several ecosystem types (tropical forest, boreal forest, savanna, temperate forest and extratropical forest).

5.4.4 Emissions of Aromatic VOCs

According to Faix et al. (1991) and Struppe et al. (1996) aromatic compounds are emitted upon thermal degradation of biomass, essentially from wood lignin. Benzene is the dominant aromatic VOC in fire plume and represent an environmental concern, whether due to its known carcinogenic effect on human health (U.S. EPA, 1995) or as a precursor of PAH (Warnatz et al., 1999). The combustion of leaves released twice the quantity of benzene than the combustion of needles, on the contrary the combustion of branches and litter of pine released greater quantity than those of the respective component of oak. Also for toluene the emission from leaves burning is about twice the value of emission from needle.

Some compounds as acetonitrile and NO_x, even if they are important related to wildfire, were not assessed in this study owing the unavailability of analytical equipment for their measurement.

5.4.5 Emissions of Oxygenated VOCs

Among measured OVOCs, acetone is an important source of HO_x radicals in the upper troposphere (Singh et al.,1995). Our results showed that it was not always present during the combustion. For instance, the combustion of oak leaves and pine needles did not show emission of acetone, while it was emitted in high amount during the combustion of branches in both species. Oxygenated VOCs as ethanol, acetic acid, methacrolein, methyl ethyl ketone (MEK), 2-methylfuran, 2-furaldeyde, ethanol-2-butoxy are the main compounds emitted during the pre-ignition, at temperature between 250 and 500 °C, during which more water is released by the progressive dehydration of the –OH and –COOH functional groups (Greenberg et al., 2006;

Ciccioli et al., 2014). This is confirmed by the trend of some OVOCs emission in real time analyzed by the PTR-MS (Fig. 26) that showed the main emission of acetaldehyde, methanol and acetone during the pre-ignition phase. It showed also a slightly increase of these compounds, in particular methanol during the smoldering phase. This could be explained by the fact that these compound may derive from other sources. For example methanol is both present initially as a dissolved component in leaf water and also is released in the de-ethylation of pectin at higher temperature during the smoldering phase (Fall, 1999; Greenberg et al., 2006). Some oxygenated VOCs as ethanol and acetic acid have also reach a percentage of 100% of emission during the pre-ignition phase, as in the case of oak litter. The emission of 2-furaldehyde from pine needle are similar to what found by Evtyugina et al. (2013) in pine and eucalyptus wildfire (0.337 ±0.25 g kg^{-1}).

5.4.6 Isoprene and monoterpenes emissions

Isoprene is a volatile species that is generally immediately emitted after its production, without storing. Nevertheless, isoprene emissions were detected during the biomass burning, especially from the combustion of needle of pine. It is know that isoprene are highly dependent on temperature (Guenther et al., 1993) so its emission during the combustion could be promoted by the heating of sample but it was also detected as pyrolysis product from wildfire (Bajus, 2010). The EFs of isoprene detected here, were higher than what is found in the plume of a Mediterranean wildfire by Evtyugina (2013) and in other studies (Andreae et Merlet, 2001; Akagi et al., 2011; Simpson et al., 2011) but are more consistent with the average of isoprene emission from the experiments in the biomass-fire simulation facility by Yokelson et al. (2008), crop residue fires (Yokelson et al., 2011) and prescribed fire (Burling et al., 2011) that ranged from

3.69 to 3.81 g Kg^{-1}. Isoprene is a very reactive species that react rapidly with the OH radicals, promoting the formation of tropospheric ozone (Ciccioli et al., 2014).

The large quantity of monoterpenes as α-pinene, β-cimene, β-pinene, sabinene, Δ^3-carene, terpinolene, camphene emitted during the combustion of pine tissue is due to the distillation of large amount of terpenes, stored in the form of liquid micelles into specialized organs, such as glands or resine ducts (Fall, 1999,), during the heating of vegetation (Simpson et al., 2011). Contrary to what reported by Alessio et al. (2008), who did not show limonene emission from burning of *Pinus halepensis* leaves, in this study we detected a notable emission of limonene that ranged from 0.008 g kg^{-1} from litter to 0.14 g kg^{-1} from needle combustion. Most of monoterpenes as β-cymene, β-pinene, sabinene, Δ^3-carene, limonene are emitted in larger amounts from needle than branches. This is consistent with what found by Greenberg et al. (2006) and it could be the result of a lower percentage of terpenes in woody tissue compared to leaf tissue. In particular α-pinene and β-pinene were the major BVOC emitted, as it is reported in the literature (Barboni et al., 2011).

The combustions of *Q. pubescens* tissues did not release all these type of biogenic compound, except for limonene and myrcene.

Isoprenoids emissions receive a lot of attention because they are involved in the flammability of vegetable material and probably are the first compounds ignited in the spread of fire (De Lillis et al., 2009), but also because most of them, for instance many monoterpenes, react rapidly with the OH radicals (Ciccioli et al., 2014) and increase photochemical pollutants in the presence of anthropogenic compounds (Kita et al., 2000; Miranda and Borrego, 2002).

The morphology of the Mediterranean landscape that favoured the photochemical formation of ozone and SOA and the high frequency of wildfire expecially in the summer period, make the

identification of highly reactive VOCs emitted from the biomass burning a very important topic to be investigated.

This is justified by the fact that there are many important chemical processes that occur into the fire plume, particularly during the day time when UV light, acting on fire-induced VOC/NO_x mixture, induced photochemical reaction (Ciccioli et al., 2014). The OH radicals drive the photochemical processes reacting with VOCs and they can induce the formation of ozone and a series of pollutant called photochemical oxidants at different rates depending on the composition of VOCs (Fishman et al., 1991; Andreae et al., 1994; Finnlayson-Pitts and Pitts, 2000, Yokelson et al., 2009; Heringa et al., 2011).

5.4.7 Particulate matters emissions

Into this dynamic system the particulate matter play an important role because they can remove VOCs and their oxidation products from the gas phase either by adsorption into hydrophobic carbon particles or by partition into the water layer covering the hygroscopic ones (Ciccioli et al., 2014). The increase of ozone, for instance generated by photochemically polluted urban plumes, brings a rapidly depletion of BVOCs within the combustion plume through the ozonolysis process that decomposes these compounds generating the same products that are formed by the reaction with OH radicals (Atkinson & Arey, 1998; Ciccioli et al., 2014). Particularly, the reaction of monoterpenes with ozone produce acidic species that are able to form SOA by condensation between themselves or through interaction with fine particles (Hoffmann and Warnke, 2007; Ciccioli et al., 2014).

The total particulate matter estimated in our study included fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulate. It ranged from 8.60 to 11.6 g kg^{-1} and it is consistent with the total particulate matter

emitted from the combustion of savanna and grassland (8.3±3.2 g kg^{-1}), tropical forest (6.5-10.5 g kg^{-1}) and agricultural residues (13 g kg^{-1}) (Andrae and Merlet, 2001). The particulate matter emitted by the biomass combustion can alter the climatic condition of the burned area, exacerbating the harmful effects of wildfire. Particles with a diameter smaller than 0.1 μm act as cloud condensation nuclei (CCN) (Andreae and Crutzen, 1997) and, when they mix with marine clouds, they decrease the diameter of the water droplets preventing the precipitation phenomena until the clouds reach an higher altitude where the temperature allow the droplets to grow (Ramanathan et al., 2001; Ciccioli et al., 2014). For this reason, the hydrogeological cycle of the burned area can be modified, promoting the desertification process (Ramanathan et al., 2001). Fine particle could also promote the formation of SOA from the oxidation products of some VOCs (Hoffman and Warnke, 2007).

5.5 Conclusion

The chamber experiments are a valid support to the field studies even if they are less representative of the real complexity of wildfire events. Our laboratory experiments provide the quantitative emission estimations of 83 volatile organic compounds from the combustion of three different vegetation material (foliage, small branches and litter) of *Pinus halepensis* and *Quercus pubescens* two tree species spread in the Mediterranean basin. In particular we characterized the compounds of the emissions spectrum from these species, for instance the great amount of monoterpenes that are only emitted from the pine materials. We also provided a comprehensive overview on the main features of the process of the fire: the peak of heat, the duration of pre-ignition and flaming phase, the total heat released and the modified combustion efficiency and we investigated the correlations between some of these parameters and the emissions of compounds.

In particular, we observed that the duration of flaming are significantly different between foliage and branches and between the species and we suggest that it could be the consequence not only of the different morphology of the vegetation material but also of the amount and type of VOCs emitted that favour the flaming event. We integrated the GC-MS data analysis with the PTR-MS data analysis to provide the real-time trend of the main gaseous species of interest as CO, CO_2, CH_4 and monoterpenes but also to identify some oxygenated species as acetaldehyde and methanol that are not detected by the GC-MS. Finally we reported the total amount of particulate matter emitted during the whole combustion.

The data from this work could be useful to improve the knowledge about the wildfire, particularly in the Mediterranean area where the fire event are very frequent in summer, also to promote a better fire management plan. The emission factors of compounds released from combustion reported in this study could be also useful to modelling the emissions factors expected from burning of large forested areas.

6 Implications

The large percentage of human-caused fire in Italy's Mediterranean ecosystems suggests the critical importance of fire management and fire suppression for maintaining ecologically sustainable fire regimes and preventing shortening in fire return intervals and loss of ecosystem biodiversity, ecosystem structural complexity and carbon storage in these ecosystem.

Temporal and spatial variation in fire intensity in Mediterranean peninsula can be known from ex-post inventory, however, the release of carbon and of other compounds by fires is poorly documented. Accurate estimates of the extent and severity of fire in Italy and their effects on biogenic emissions in field conditions are needed. Thus it is critical to validate and support the

laboratory measurement with field campaigns for consistent monitoring of extent and effect of fires in Mediterranean forests, woodlands, and scrub systems.

Fire from Mediterranean ecosystem could become in a near future of potential importance to the global carbon cycle.

The data obtained about the amount of carbon emitted from fire could be useful to evaluate the effect of forest fire on the carbon cycle providing direct estimates of C released from a certain amount of biomass burning. Firstly, it is possible to predict the amount of carbon that approximately could be emitted into the atmosphere following a forest fire of a specific area of which it can be estimated the amount of biomass. Secondly, combining these results with the annual net primary production of the ecosystem, for instance, it could be possible estimate how much carbon would be lost due to forest fires and, lastly, combining these data with C sequestered and stored in the new vegetation assemblage in the area burned during field experiment, it could be possible to estimate the C balance more accurately. Furthermore, as the greatest uncertainty in modelling carbon emissions from wildland fire is estimating the forest floor source (French et al., 2004), the estimation of the carbon released from litter obtained with the measurements in the combustion chamber can provide important information useful to modellers.

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