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INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Università degli Studi della Tuscia
Istituto di Biologia Agroambientale e Forestale (CNR-IBAF)

An overview on biogenic organic volatile compound (BVOC) emission and their release during biomass burning

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Tato akce se koná v rámci projektu:
Vybudování vědeckého týmu environmentální metabolomiky a ekofyziologie a jeho zapojení do mezinárodních sítí (ENVIMET; r.č. **CZ.1.07/2.3.00/20.0246**) realizovaného v rámci Operačního programu Vzdělávání pro konkurenceschopnost.

What are BVOCs?

Biogenic VOCs are volatile substances that include a large spectrum of compunds. They includes the isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids.

The carbon skeletons of isoprenoids are composed of characteristics C_5 units and they are subdivded into:

- Hemiterpenes (C_5, for example isoprene)
- Monoterpene (C_{10} , for example α-pinene, menthol, camphor)
- Sesquiterpenes (C_{15}, for example β-caryophyllene, abscisc acid)
- Diterpenes (C20, for example gibberellins, phytole)
- Triterpenes (C30, for example sterols)
- Tetraterpenes (C40, for example carotenoids)
- Prenols and Polyterpenses (>C45, for example plastochinone, ubichinone)

The more volatile compounds, isoprene and monoterpenes, are the most prominent compounds and the most important for atmospheric chemistry.

Biosynthesis

All isoprenoid are synthetized via a common C5 precursor, the isopentenyl pyrophosphate (**IPP**), called «active isoprene». IPP can be reversibily transformed to its isomer dimethylallyl pyrophosphate (**DMAPP**).

DMAPP is the substrate for **isoprene synthase**, a chloroplastic enzyme producing **isoprene** by cleaving pyrophosphate. Isoprene synthase is regarded to be active only in mature chloroplasts

By adding another IPP unit to DMAPP, the monoterpene geranylpyrophosphate (**GPP**)
is formed. GPP is the starting unit for other **monoterpenes**.
The production of monoterpenes takes place within the plastids.

The synthesis of the basic isoprenoid precursor **IPP** can be explained by two different biochemical pathways:

- The classical *mevalonate pathways* , into the cytosol, for the formation of sesquiterpenes, ubichinone, sterols and polyterpenses, through the metabolic intermediate of mevalonic acid.
- The novel *mevalonate-indipendent pathways* (*Rohmer pathway*) in chloroplasts of higher plants, for the formation of isoprene, monoterpene, phytole and carotenoids, through the metabolic intermediate of deoxyxylulose-5-phosphate.

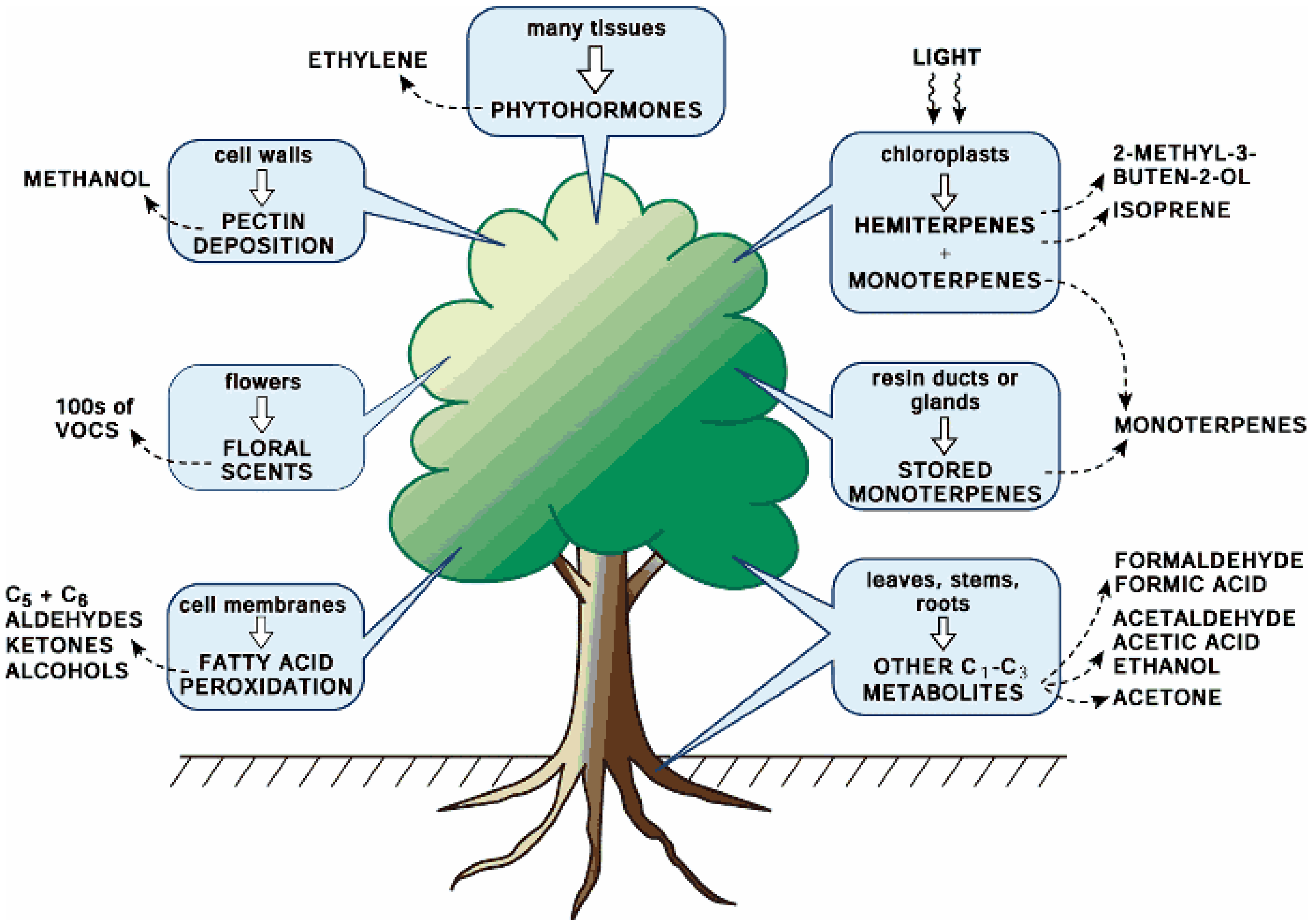
Who emits voc?

Monoterpenes constitute the main fraction of “essential oils” that are produced and stored in plant secretory organs like glandular trichomes and resin ducts. Monoterpene-storing plants are usually monoterpene emitters:

- Numerous coniferous plants
- *Lamicaceae* (e.g. *Rosmarinnus officinalis, Salvia officinalis, Thymus vulgaris*),
- *Apiaceae* (e.g. *Foeniculum vulgare*, *Petroselinum crispum*),
- *Myrtaceae* (e.g. *Eucalyptus*),
- *Asteraceae* ,
- *Rutaceae* (e.g. *Citrus*),
- *Quercus ilex* and *Quercus coccifera*

Isoprene is never stored in plants after production, but is rapidly lost by volatilization. Isoprene-emitting species are more often found in woody plant species than in herbs and crops:

- *Salicaceae* (e.g. *Salix*, *Populus*),
- *Fagaceae* (except *Quercus ilex*, *Q. coccifera* and *Q. suber*)
- *Palmae,*
- *Pinaceae* (e.g. ***Picea****)*



This figure, called the "tree of VOC“, highlights the potential of the plant to produce and release a wide variety of VOC (Fall 1999).

Influences of environmental factors on VOC emission

The emission of BVOC is highly dependent on environmental factors such as **radiation** and **temperature**.

If VOCs are emitted directly after their synthesis, as isoprene, the emission is mainly linked to photosynthesis, and consequently the radiation. The emission shows a saturation behavior similar to the light saturation of CO_2 assimilation. The temperature dependence of isoprene emission point to the necessary enzymatic production of isoprene, showing a temperature maximum and a subsequent decrease at higher temperatures owing to enzyme inactivation.

VOCs that are accumulated in storage organs, are regarded as light-independent. The emission is considered a simple process of volatilization from the pool reserve: it is strongly dependent on the temperature and related to the vapor pressure and to the transport resistance along the diffusion path. The emission response to temperature shows an exponential increase with temperature.

Temperature and light responses differ among plant species and can vary among shade- and sun-adapted leaves within the canopy of an individual tree.

Influences of environmental factors on VOC emission

Other factors can affect the BVOC emission :

- **water stress** and **saline**,
- **air humidity**,
- **high concentration of carbon dioxide** in the atmosphere,
- **mechanical stress** and **injury** (herbivore and pathogen attacks),
- **phenological stage** (budding, flowering, fruiting, leaf senescence and dormancy)
- **physiological changes** (mature leaves emit, while young leaves emit no or much lesser extent).

Ecophysiological functions of VOC productions and emissions

The ecophysiological function of **isoprene** production and emission:

- **protects the photosynthetic apparatus of leaves against nonbiotic stresses**: for example isoprene formation inside chloroplast could serve to prevent light damage by dissipating excessive energy; contributes to the regeneration of $NADPH^+$
- **protects membrane against heat stress**

The ecophysiological function of **monoterpenes** production and emission:

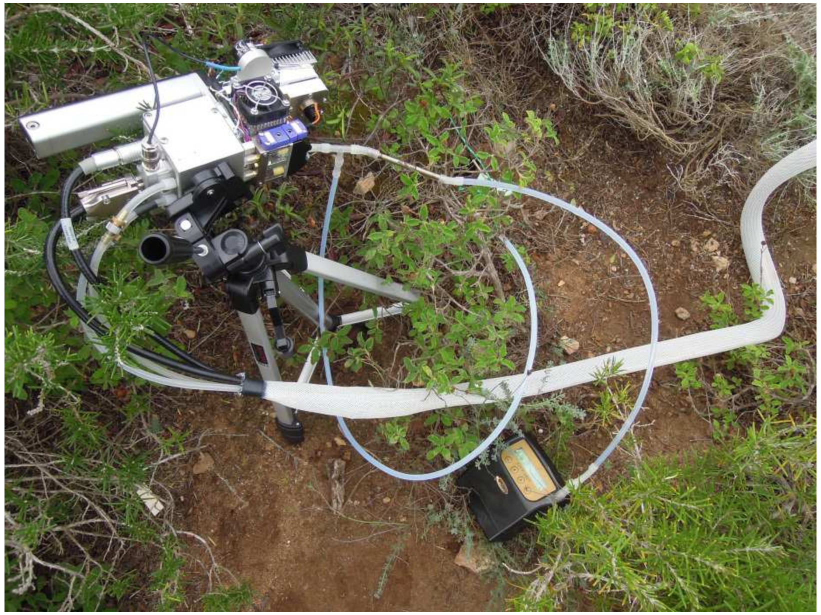
- **Signaling between plants and insect**: some monoterpenes can act as deterrents and repellent, may be attractive to pollinators or may attract predators of insects pests
- **Signaling within plants as well as between plants**: for example the release of methyl salicylate by infected tobacco plants acts as an atmospheric signal to warn and activate other plants against the tobacco mosaic virus.
- **Defense against pathogens and herbivores**: for example *β*-Pinene is an internal inhibitor of respiration and might limit fungal and microbial growth within the leaf tissue by flooding the inter-cellular gas space.

Methodological Aspects

The technique for the analysis of VOC analyzes the volatile compound, emitted by plants, present in the air surrounding a sample of plant material (single plant, branch, leaf, fruit, flower). The single plant or organ vegetative are enclosed in a specific cuvette and it is possible to set certain conditions of temperature, light and gas concentration in the incoming air into the cuvette.

The analysis of VOC can be conducted **in continuous** (**on-line**) by the **PTR-MS** providing immediately the results of the profile and emission rates, or **in the laboratory** (**off-line**) prior sampling of volatile compounds. In this case the cuvette is connected through a system of teflon tube to a Tenax trap (absorbent substrate) that absorbs volatile organic compounds through a portable pump. The chemical analysis is generally conducted by **gas-chromatography** (**GC**), associated with **mass spectrometry** (**MS**), which allows to identify and quantify the compounds released by the plants.

Emission factors are given in relation to leaf biomass and time and describe the release of a trace gas species under standard condition of temperature (30°C) and light (1000 μmol $m^{-2}s^{-1}$ photosynthetically active radiation (PAR)).



Why are we interested in biogenic VOCs?

VOCs play an important role in the chemistry of the atmosphere by influencing ozone and hydroxyl radical (OH) concentrations, and the conversion rates of nitrogen oxides (NO_x). Elevated levels of VOCs and NO_x have led to an approximate doubling of ozone in the lower troposphere over the past couple of centuries, making tropospheric ozone the third most important anthropogenic greenhouse gas after carbon dioxide (CO_2) and methane. Because of ozone's strong oxidizing properties, increases in tropospheric ozone are a concern for living systems on Earth.

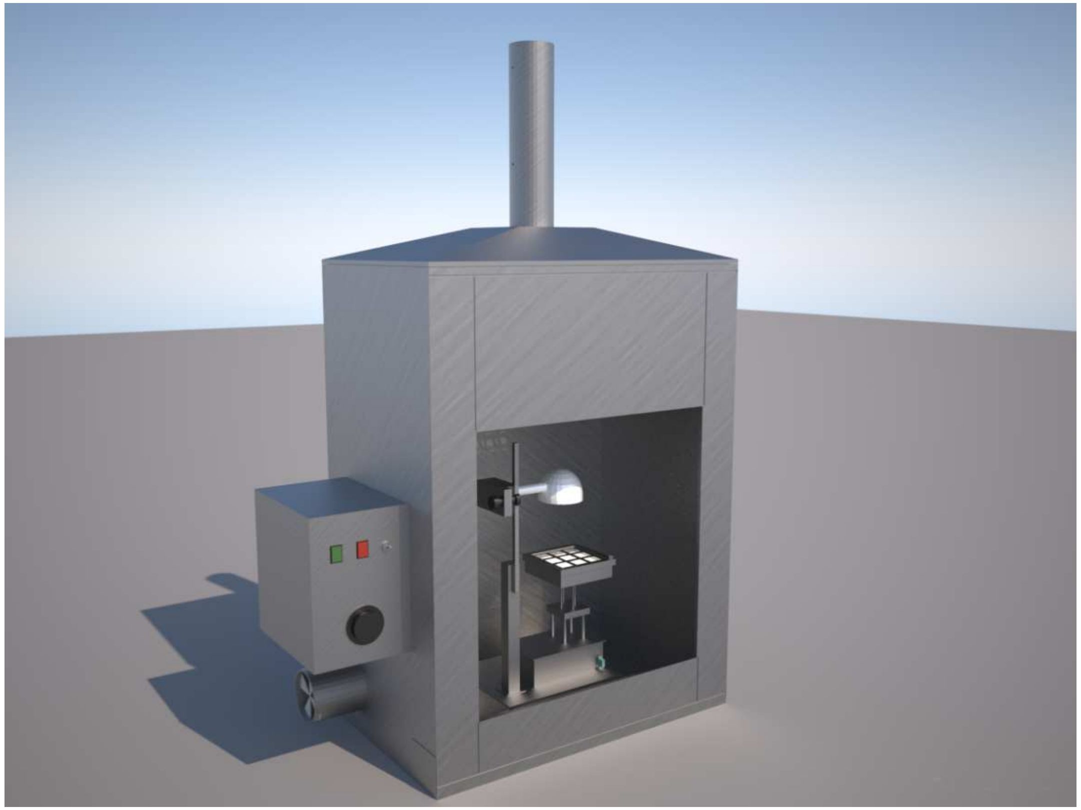
VOCs also serve as a source of atmospheric secondary organic aerosol (SOA), which influences the solar radiation budget and cloud droplet nucleation. Through these complex interactions, VOCs play an important role in air quality and climate and it is important to understand biochemical and physiological controls on the formation and release of these VOCs to the atmosphere, especially given man-made changes in global CO_2 levels and temperature, NOx emissions, and planting of large isoprene-emitting agriforests.

Laboratory experiment of emission from fire: combustion chamber

A combustion chamber was designed and installed in the laboratory of Institute of Agro-Environmental & Forest Biology (IBAF) of Porano.

Dimension of 106x80x50 cm

It is equipped with:
- High precision balance
- Epiradiometer to ignite
- Thermocouple
- Fan
- Sensors



The sensors

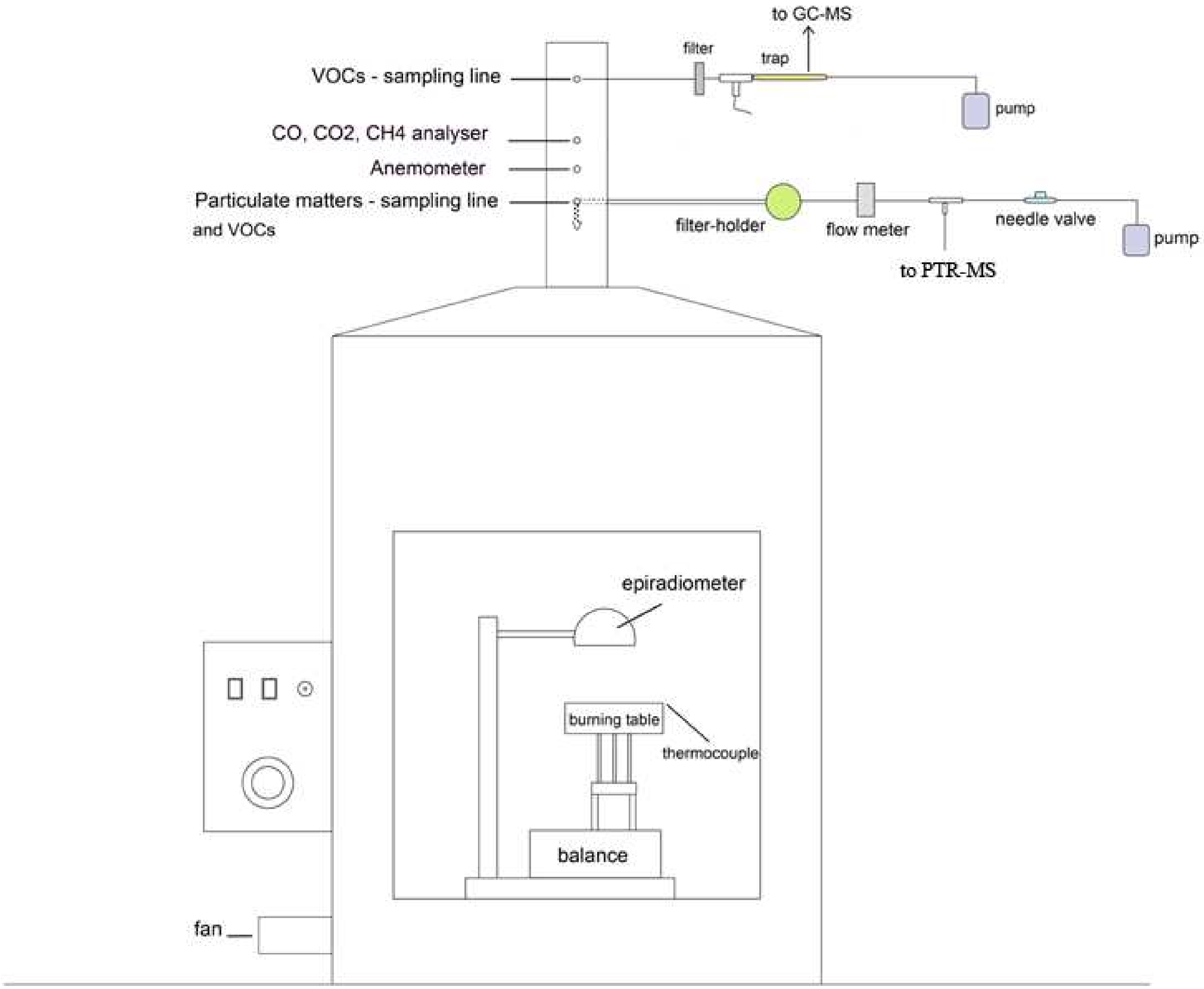
- **Gas chromatography–mass spectrometry** (GCMS-MSD 5975C, Agilent Technologies, California, USA) to identify different volatile organic compound absorbed into the tenax trap.

- **Proton-transfer-reaction mass spectrometer** (PTR-MS, Ionicon, Austria) real-time on-line measurements of volatile organic compounds in air with a high sensitivity and a fast response time.

- **Datalogger anemometer HD 2103.2** (Delta Hom srl, Italy) for the measurement of air flow rate through hot-wire anemometric probe AP471S1

- **Portable analyzer MRU NOVA PLUS** (MRU ITALIA srl, Italy) for the analysis of CO, CH_4 and CO_2 emission.

The sampling line

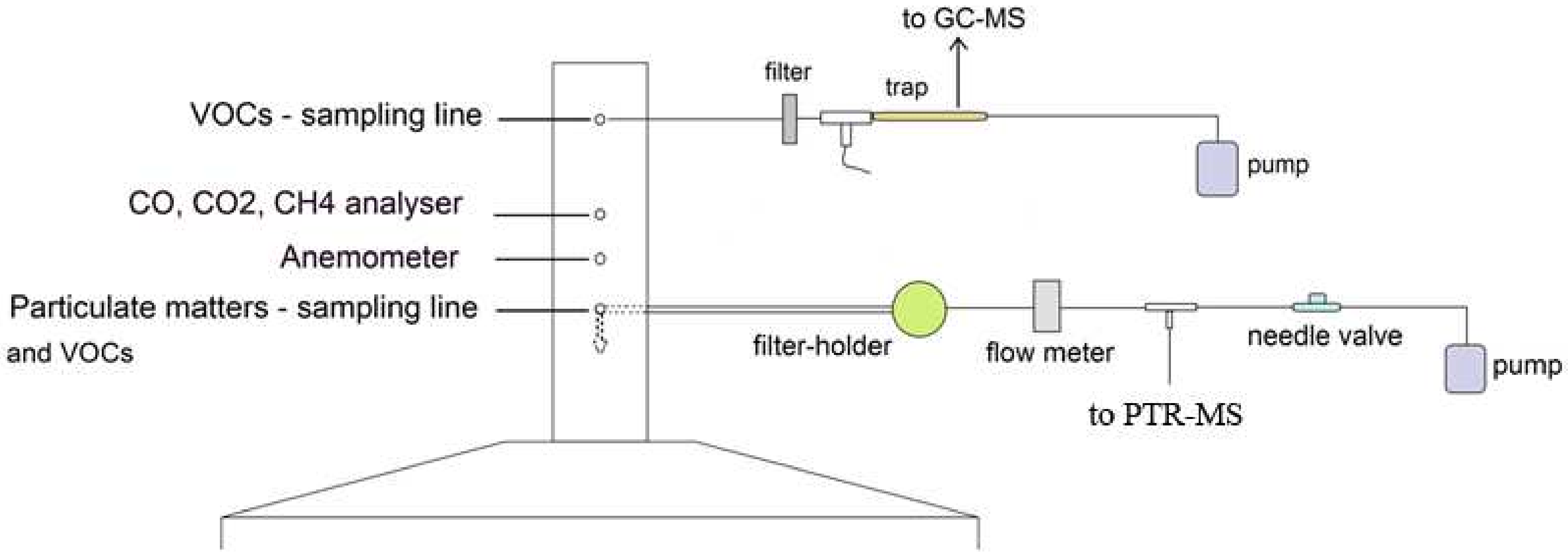


Sampling system for VOCs

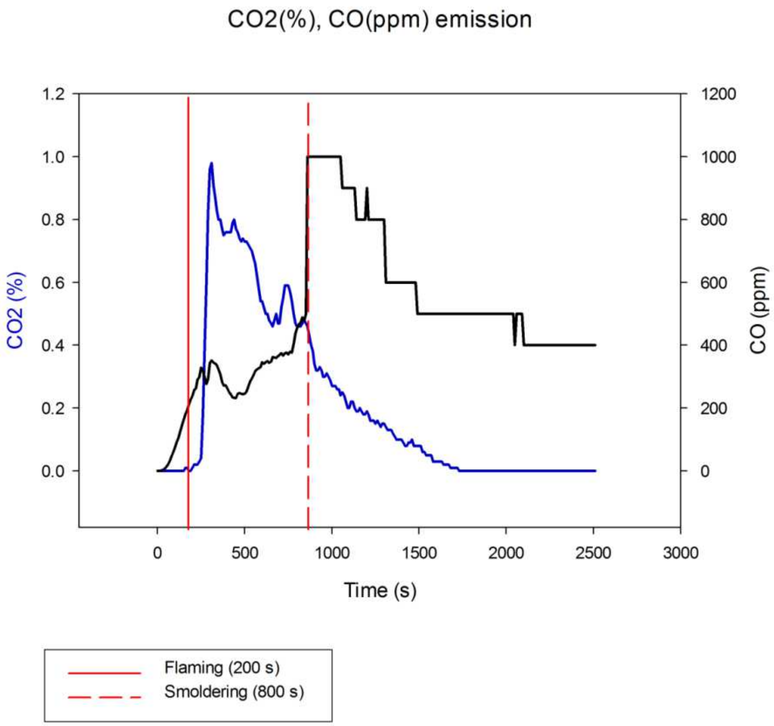
This system is composed by a filter to clean the air flow from the particulate matter, a T-system with an open tube for the escape of excess air, a tenax trap to absorbe the volatile organic compound and a pump to suck air from the chimney. Later the traps are desorbed and VOCs are analyzed through GC-MS.

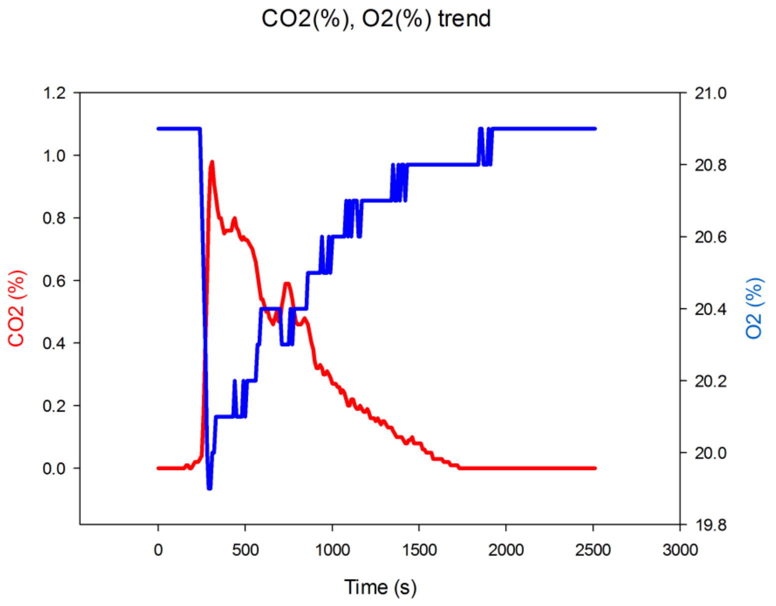
Sampling system for particulate measurement and VOCs

This system is composed by a stainless curve, equipped with nozzle (6 mm) for picking up the fumes, a stainless filter holder (47 mm), and quartz fiber and PTFE filters (provided by TCR Tecora srl., Italy) to trap the particulate matter. The flow is adjusted by a needle valve and monitored by a flow meter. Little portion of the fumes may be sent to PTR-MS for online monitoring of VOCs.



Preliminary results

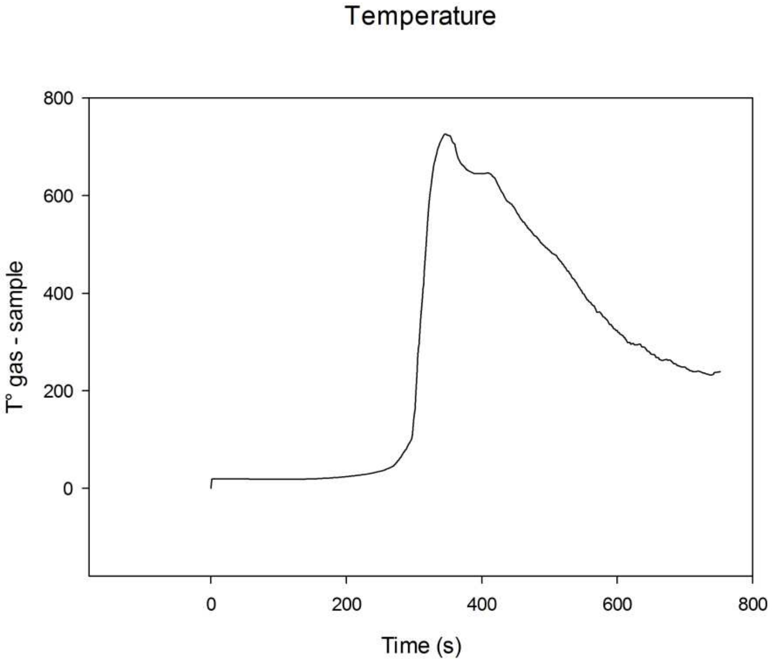


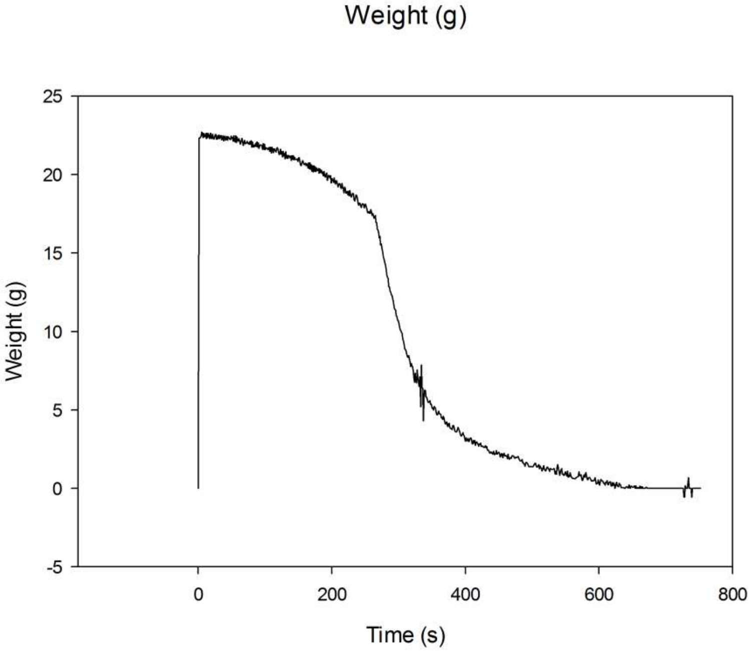


Flaming and smoldering are distinct combustion processes. During this experiment the emission of CO_2 reached its maximum during the flaming stage. A rapid rise of emitted CO, and an even more pronounced CO emission marked the transition from the flaming to the smoldering phase

Preliminary results

Temperature reached 700 °C and weight of sample decreased in a progressive mood

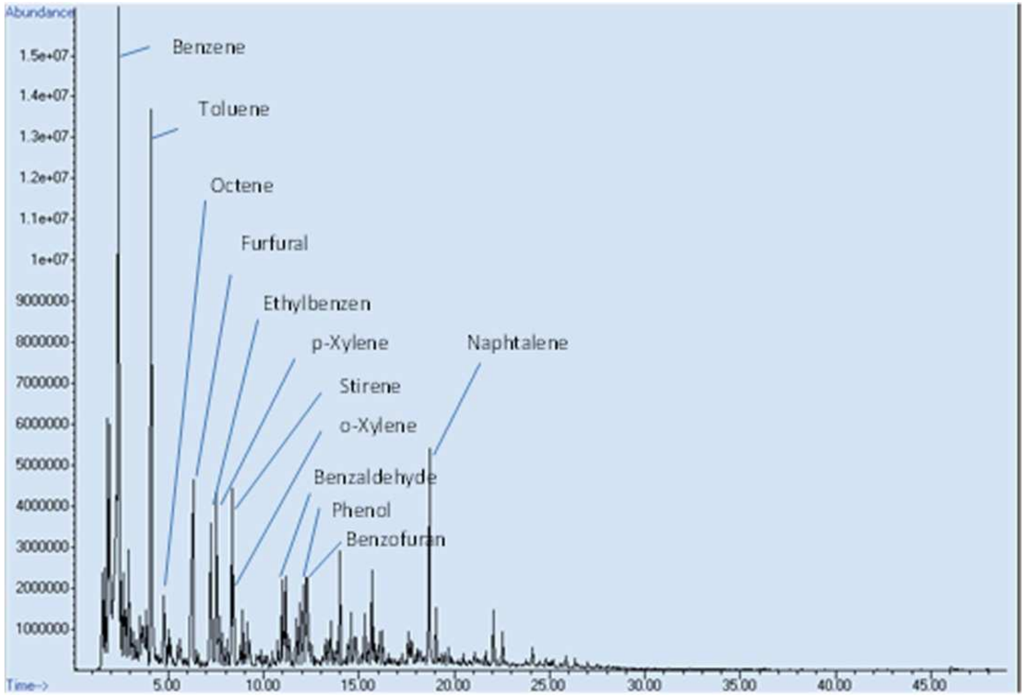




Preliminary results

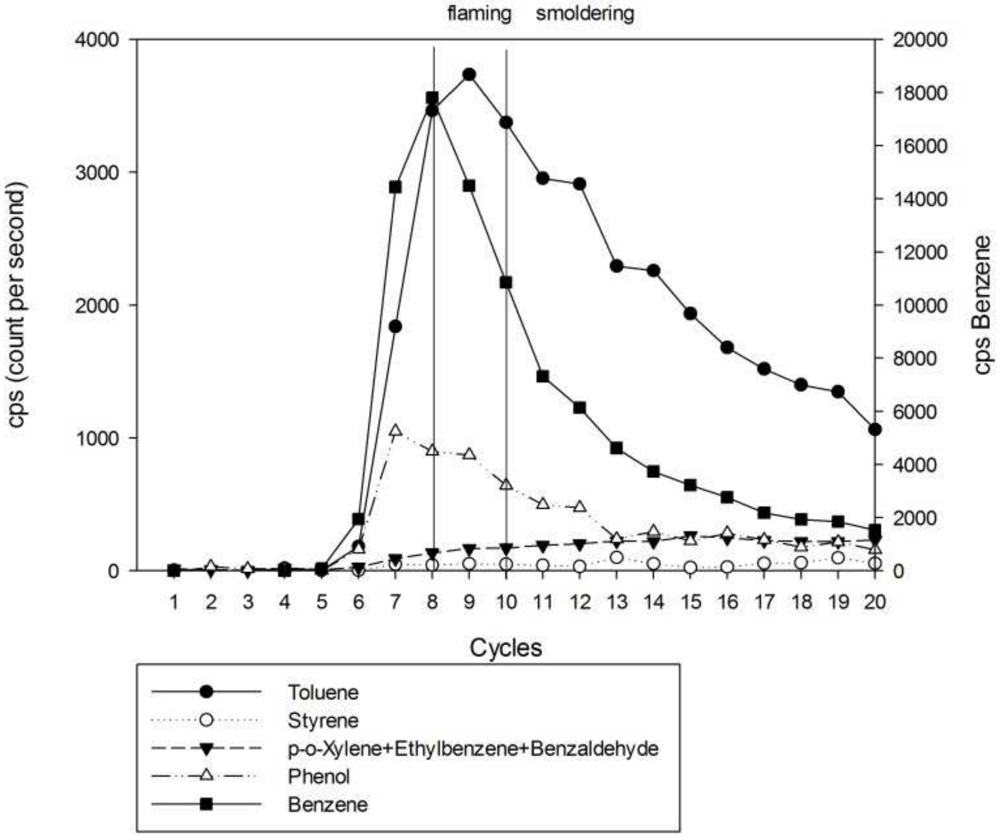
GC-MS analysis did not distinguish the VOCs emitted during the flaming phase from those emitted during the smoldering phase. We identified the main volatile organic compound emitted during the whole combustion. The identification of the various components was carried out by combining MS data with retention time information. We detected many aromatic compound emitted during the combustion. The most abundant were **benzene**, **toluene** and **naphthalene**. Other VOCs with lower peaks were **octenes**, **furfural**, **ethylbenzene**, **p-xylene**, **styrene**, **o-xylene**, **benzaldehyde**, **phenol** and **benzofuran**.

The figure reports the total ion current (TIC) profile of pyrogenic VOCs analyzed with GC-MS technique.

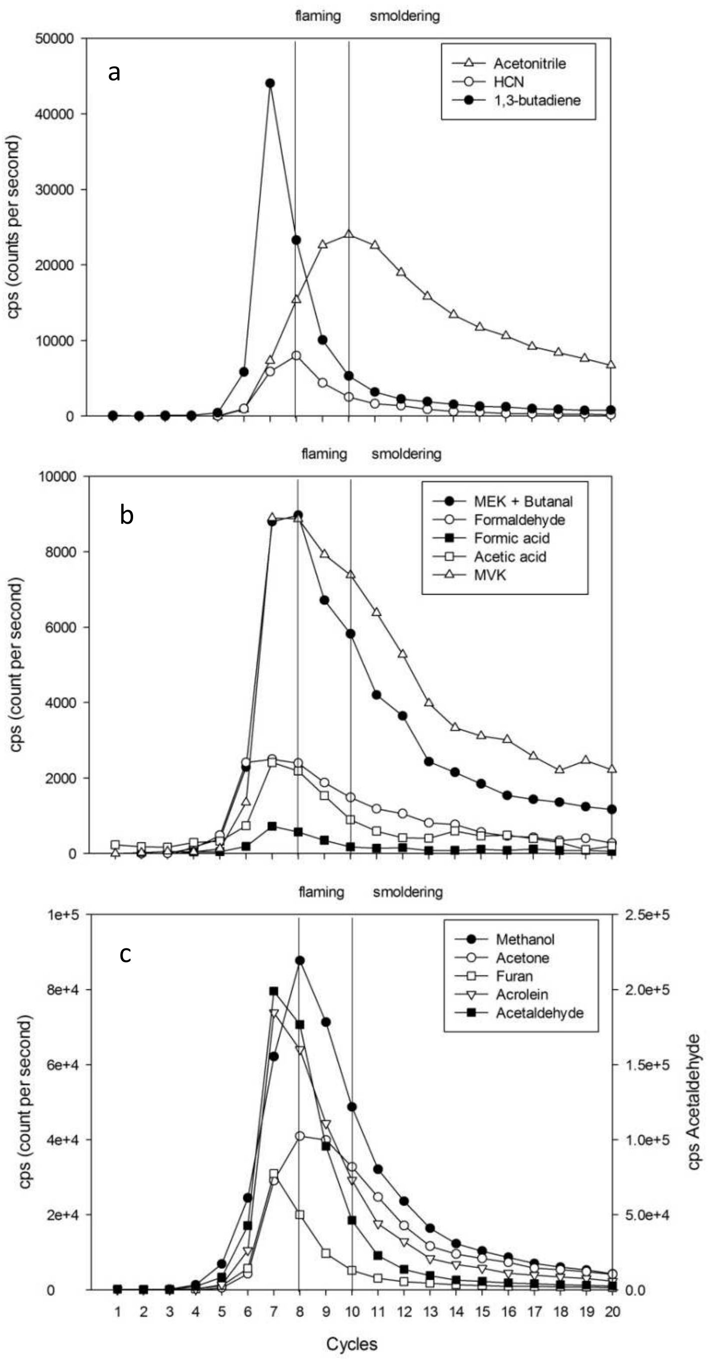


Preliminary results

The PTR-MS analysis allowed the on-line monitoring of VOC emission during the different phases of combustion. As the PTR-MS method gives only information on mass-to-charge ratio (m/z) data for VOCs and makes difficult to identify unambiguously released VOCS, we compared these results with those obtained with the results from GC-MS analysis and data from literature.



According to GC-MS analysis we identified many aromatics VOC. **Benzene** (m/z 79) and **toluene** (m/z 93) showed the highest emission. **Phenol** (m/z 95), **styrene** (m/z 105), **xylenes (p,o)**, **ethylbenzene** and **benzaldehyde** (m/z 107) were also identified.



As reported in literature, a great amount of VOC containing oxygen can be released from fire. Fig. b and fig. c showed the emission of **oxygenated VOCs** identified during combustion. **Acetaldehyde** (m/z 45) and **methanol** (m/z 33) that were released in great abundance from fire showed the highest peaks. Also **acrolein** (m/z 57), an important air toxic was released in great abundance. **Formaldehyde**, **formic acid**, **acetone**, **acetic acid**, and **furan** were also detected.

Some **nitrogen containing compound** showed were high released during burning as hydrocyanic acid **HCN** (m/z 28) and **Acetonitrile** (m/z 42) which is considered an useful marker for biomass burning because it is primarily emitted from vegetation fire (Fig a). A further important air toxic, **1-3 Butadiene**, was detected on mass 55.

Except for acetonitrile that reached its maximum emission at the beginning of smoldering phase, all others VOCs reached their maximum at the beginning of flaming phase or just before.

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Thanks for your attention !