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# **Investigation on the emission of Volatile Organic Compounds from heated vegetation and their potential to cause a forest fire flashover**

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## **Abstract**

An experimental study is conducted of the emission of Volatile Organic Compounds (VOCs) emitted by *Rosmarinus officinalis* plants when exposed to an external radiant flux. The thermal radiation heats the plant and causes the emission of VOCs. The thermal radiation simulates the radiant flux received by vegetation in a forest fire. The results of the experiments are used in a simplified analysis to determine if the emissions of VOCs in an actual forest fire situation could produce a flammable gas mixture and potentially lead to the onset of a forest fire flashover. The experiments consist in placing a plant in a hermetic enclosure and to heat it with a radiant panel. The VOCs produced are collected and analyzed with an Automatic Thermal Desorber coupled with a Gas Chromatograph/Mass Spectrometer (ATD-GC/MS). The effects of the fire intensity (radiant panel heat flux) and the fire retardant on the VOCs emission are then investigated. Two thresholds of the VOCs emission are observed. The first is for plant temperatures of around 120°C and appears to be caused by the evaporation of the water in the plant that carry with it a certain amount of VOCs. The second one is around 175°C which is due to the vaporization of the major parts of VOCs. The application of a fire retardant increases the emission of VOCs due to the presence of the water (80%) in the fire retardant. However the use of the retardant results in a lower production of VOCs than using water alone. The measurements are used to estimate the concentration of VOCs potentially produced during the propagation of a specific fire and compared to the flammability limits of  $\alpha$ -pinene. It is concluded that the quantities of VOCs emitted by *Rosmarinus officinalis* shrubs under certain fire conditions are capable of creating a forest fire flashover.

**Keywords:** VOCs emission, VOCs flammability, Fire Flashover.

## 1. Introduction

In forest fires it has been observed that occasionally the fire propagates at unusual speed. This type of fire propagation is known as eruptive fires for its continuous increase of the rate of spread (Viegas et al., 2008), or fires flashover for its sudden character (Dold et al. 2009). The phenomenon of eruptive fire has occurred several times in the United States of America. Indeed, the South Canyon fire of 1994, described by Butler et al. (1998), had 14 fatalities and the Thirtymile fire of 2001, analyzed by Furnish et al. (2001), had four fatalities. A similar accident, investigated by Viegas (2005), occurred in Portugal during the summer 2003 where two persons lost their life. Up to now, there are only two scientific explanations for this phenomenon in forest fires literature. The first one is based on the feedback effect of the convection induced by the fire that may occur naturally in steep terrain, (Viegas, 2005) and (Viegas, 2006). The second explanation indicates that the eruptive fire is a result of an interaction between the intensity and the rate of spread mediated by flow attachment (Dold and Zinoviev, 2009).

In France, over the last 15 years eleven cases of eruptive forest fires and/or forest fires flashover involving the death of thirteen fire-fighters have been reported (Barboni, 2006). Among these accidents, the forest fire of Palasca (Corsica Island) in September 2000 had two fatalities and five fire-fighters suffered severe burns. Survivors reported being surrounded by a hydrocarbon fire due to its rate of spread (about 5 m/s), homogeneous flame length and pool fire aspect. In a review of the accident, Dold et al. (2009) have written “*the apparent quenching of the head fire in the Palasca incident does suggest that the fire might not have developed as a continuous fireline but as a form of premixed flame spread or flashover*”. Up to now, it appears that the mechanisms that lead to a forest fire blow-up are not totally understood.

The previous explanations have been supported by laboratory experiments but it is very difficult to obtain a validation in the field. Another explanation that is regularly proposed by firefighters is that a combination of terrain could favor the accumulation of combustible volatiles emitted by fire heated vegetation (a canyon for example) and that has steep surfaces may favor the onset of a fire blow-up

Certain Mediterranean plants (e.g. *Rosmarinus officinalis*, *Cistus albidus*, *Pinus halepensis*) when heated produce and emit volatile substances related to their secondary metabolism, (Owen et al., 1997) and (Llusià and Peñuelas, 1999a). The composition of these Volatile Organic Compounds (VOCs) is flammable. An assumption used to explain some fires flashover encountered by fire-fighters is that these emitted compounds are found in concentrations close to the Lower Flammability Limit (LFL) at periods when the plants are themselves highly flammable. To obtain this critical situation, it is necessary that these chemical products accumulate in certain geographical zones (e.g. small valleys, canyons). The conjugation of these two effects (accumulation and flammability) may be capable of causing situations with potential for a gas phase flame propagation, which together with an adjacent steep terrain may result in an unusually fast fire propagation, i.e. a fire flashover. However, there is no experimental evidence that can confirm this point of view, except from a very preliminary studies conducted by (Raffalli et al. 2002) and (Ormeño et al. 2009). These last authors showed shorter combustion times and increasing spread rates under higher VOCs emissions. Their epi-radiator experiments indicated that VOCs concentration was positively correlated to flame height and negatively to ignition delay. However, further studies are needed to understand further the problem.

The aim of the present paper is to conduct some experimental work at laboratory scale to evaluate the interest of investigating this potential cause. the emission of VOCs by a representative vegetation of the Mediterranean basin such as *Rosmarinus officinalis*, when

exposed to thermal radiation representative of an adjacent fire, is conducted. The information is used to determine if such emission can produce a flammable mixture around the vegetation and consequently be a potential mechanism for the development of a fire flashover. For this purpose, experiments are conducted in which samples of vegetation are exposed to thermal radiation, simulating the impact from an ongoing fire. The VOCs produced are collected and tested to determine the effect of external parameters such as radiant flux, plant temperature and fire retardants on their concentration and flammability. An original experimental protocol which consists in placing a plant in a hermetic enclosure and to heat it with a radiant panel has been developed and used in the experiments. The qualitative and quantitative analysis of the VOCs produced is carried out with an Automatic Thermal Desorber coupled with a Gas Chromatograph/Mass Spectrometer (ATD-GC/MS).

The description of the experimental set-up, analysis method, and the experimental results and the associated discussions follows.

## **2. Experimental set-up and experimental methodology**

As indicated above, the different *Rosmarinus officinalis* plants are placed in a hermetic enclosure and are heated by a radiant panel. In our studies, we have two batches of 50 *Rosmarinus officinalis* plants, the first batch was used for the calibration of experimental parameters and the second one to determinate the plant temperature and the fire retardant effects. These experiments were realized at different seasons. The hermetic enclosure of dimensions 100 cm x 100 cm x 134 cm is manufactured in Siporex material of thickness of 7 cm and its volume is about 1.2 m<sup>3</sup>. The radiant panel is an assembly of 16 black ceramics plates of dimensions 12 x 12 cm<sup>2</sup> providing each one a thermal power of 1.2 kW. The maximal power emitted per unit of surface of this radiant panel is about 83 kW/m<sup>2</sup> (figure 1).

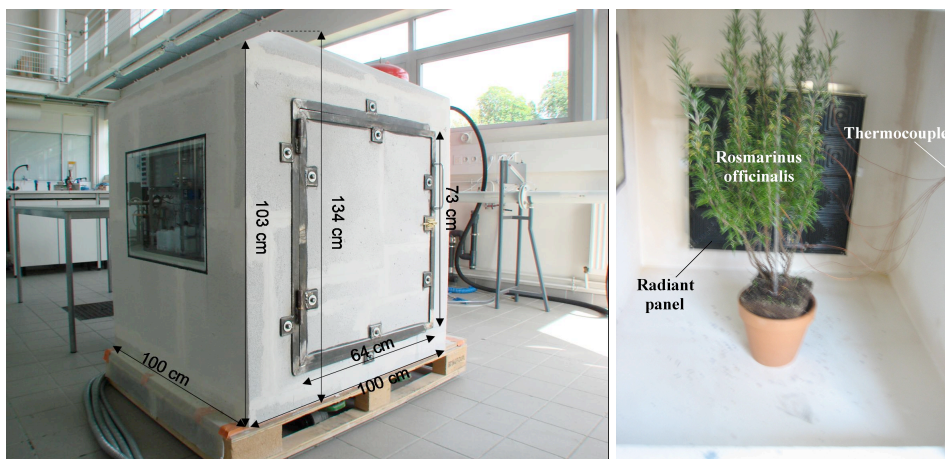


Figure 1: Photographs of the hermetic enclosure, the plant and the radiant panel.

The *Rosmarinus officinalis* plants of an average mass of 155 g and an average height of 30 cm are placed at the centre of the hermetic enclosure at a distance of 50 cm from the radiant panel. The moisture content of the different plants is about 70 % and they are heated during 30 min. The heat flux of the radiant panel is varied from 0.44 to 20.59 kW/m<sup>2</sup> for the study of the plant temperature (or heat flux) effect and was fixed to 15.50 kW/m<sup>2</sup> to study the effect of the quantity of the fire retardant. The trapping and the sampling of the VOC are ensured by sorbent tubes and a pump at a flow-rate of 150 mL/min. The sorbent tubes used were glass multibed tubes with dimensions of 11.5 cm x 6 mm o.d. x 4 mm i.d., Supelco® (Tenax TA®). These tubes were transferred in a freezing box into the laboratory and analysed by the ATD-GC/MS instrument. The sampling was carried out in triplicate. The experimental protocol is illustrated in figure 2. [Each sampling and analysis was performed in triplicate.](#)

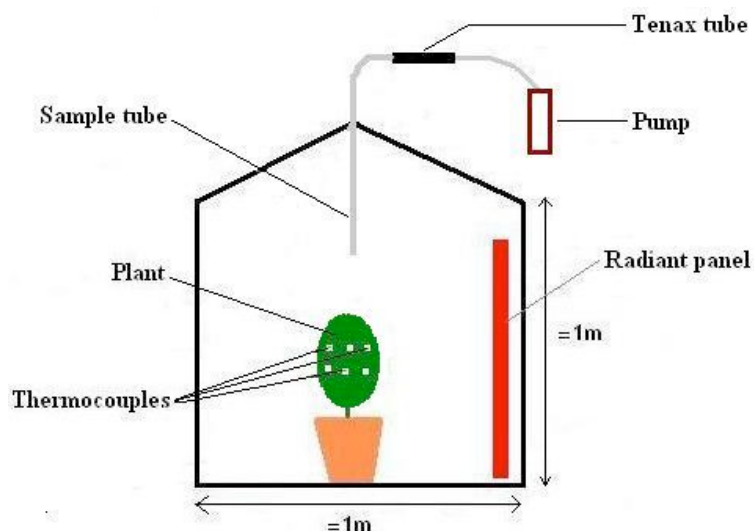


Figure 2: Diagram showing the experimental protocol.

The analyses were carried out using an Automatic Thermal Desorber Perkin Elmer® (Waltham, MA, USA) ATD 400 turbomatrix®. For the thermal desorption of volatile components, Helium flow was set at 30 mL/min. A sorbent (Tenax TA®) was brought to 280 °C for 10 min and a carrier gas flushed (Helium) the sample towards a cold trap (Tenax TA®, 22 cm, 0.53 mm i.d., Supelco® Co.) at -30 °C. In a second step, the cold trap was programmed from -30 to 280 °C at 40 °C/s then held isothermally at 280 °C for 3 min. The compounds were desorbed to the column of GC/FID and column of GC/MS by the transfer line temperature maintained at 280 °C.

GC/FID analyses were carried out using a Perkin-Elmer® apparatus equipped with Flame Ionization Detection (FID) system and a fused-silica capillary column Rtx-1 (polydimethylsiloxane, 60 m × 0.22 mm i.d., film thickness 0.25 μm). The oven temperature was programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C for 35 min. Retention indices (*I*) of compounds were determined relative to the retention times of series of *n*-alkanes (C<sub>5</sub>-C<sub>30</sub>) with linear interpolation, using Van den Dool and Kratz equation (Van den Dool and Kratz, 1963), and software from Perkin-Elmer®.



GC/MS analyses were carried out using Perkin-Elmer® apparatus equipped with a TurboMass® detector (quadrupole), and a fused-silica capillary column Rtx-1 (polydimethylsiloxane, 60 m × 0.22 mm i.d., film thickness 0.25 µm). Ion source temperature: 150 °C, Energy Ionization (EI): 70 eV, EI mass spectra were acquired over the mass range 35-350 Da (scan time: 1s). The oven temperature was programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C for 35 min.

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

1. on computer matching with commercial mass spectral libraries ([NIST/EPA/NIH, 1999](#)), and comparison of mass spectra with those of our own library of authentic compounds or literature data ([König et al., 2001](#)).
2. on comparison of calculated retention indices on apolar column, with those of authentic compounds or literature data ([NIST WebBook, 2005](#)).

The quantification of the different compounds is presented in  $\alpha$ -pinene equivalent. The quantification of this compound was carried out by direct liquid injection in the Tenax TA tubes and was calibrated in mass range 3.58 ng-17.16 µg.

### **3. Emission of Volatile Organic Compounds**

Some preliminary experiments were conducted in order to determine the range of experimental parameters such as the heat flux of the radiant panel and the height and time of sampling. The object of selecting the radiant panel heat flux is to explore the generation of a range of temperatures in the hermetic enclosure between 30 and 210 °C. The temperature range was selected in order to simulate the heating of plants by a fire front before the pyrolysis phase. Indeed, the pyrolysis temperature of *Rosmarinus officinalis* is about 250 °C. The table below presents the different radiant panel temperatures, the heat fluxes and the hermetic enclosure temperatures measured at the selected heating time of 30 min.

Table 1: Heating condition values for a heating time of 30 min.

Radiant panel temperature (°C)	100	150	225	350	375	400	450	500
Radiant panel heat flux $\phi$ (kW/m <sup>2</sup> )	1.10	1.82	3.49	8.54	10.00	11.63	15.49	20.24
Hermetic enclosure temperature (°C)	38	54	79	120	135	145	174	205

One of the parameters influencing the measurement of the quantities of VOCs emitted by the *Rosmarinus officinalis* is the sampling height inside the enclosure. For this reason the VOCs emission were measured at four heights from the hermetic enclosure base: H1=112 cm, H2=88 cm, H3=61 cm and H4=37cm. The results are presented in figure 3, they show that the VOCs emission is not homogeneous in the enclosure and that the  $\alpha$ -pinene compound represents 60-80% of the total VOCs emissions. An important quantity of VOCs is measured at the height H1. The gases emitted by the plant are hot and accumulate in top of the enclosure because of their low density. The emission at height H2 is lower than the emissions at the heights H3 and H4 because these heights are situated near the emission source (*Rosmarinus officinalis*). These results allowed us to set the height H1 as the sampling height for the parametric study.

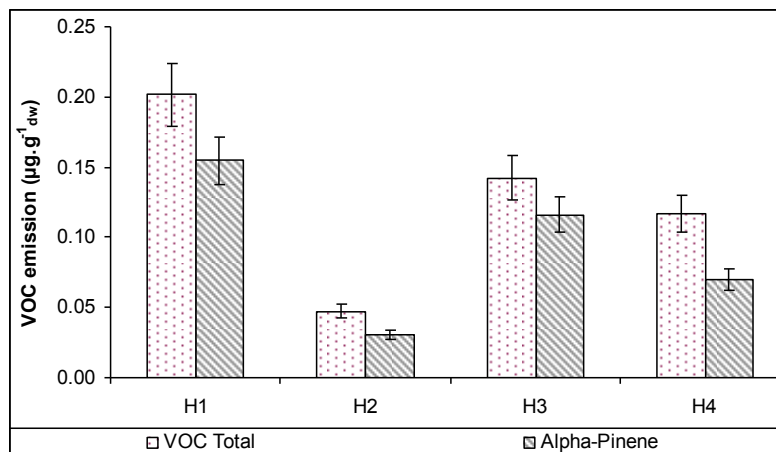


Figure 3: Emission of total VOCs and  $\alpha$ -pinene versus sampling heights (H1=112 cm, H2=88 cm, H3=61 cm and H4=37cm).

Another parameter such as the sampling time should be determined in order to know if the quantities of VOCs collected are sufficient to quantify volatile compounds. Figure 4 shows the amount of the total VOCs and the  $\alpha$ -pinene emitted by *Rosmarinus officinalis* at 150 °C for different sampling times. We observe that the amount of VOCs emitted is plenty for a sampling time of 10 min. Furthermore, this sampling time allows maintaining the temperature of enclosure at a constant value without thermal losses with the ambient.

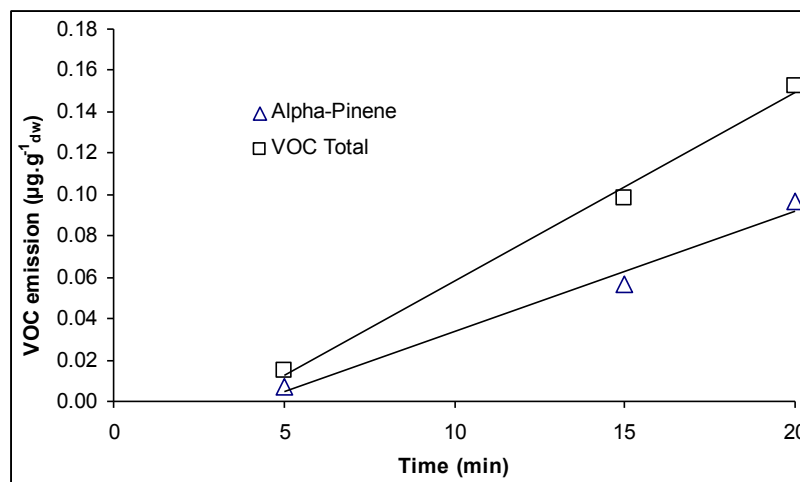


Figure 4: Evolution of VOCs emission depending on the sampling time.

### 3.1 Effect of plant temperature and radiant panel heat flux

The aim of these tests is to track the VOCs emission as a function of temperature in order to estimate the quantity emitted by vegetation during a forest fire. As indicated previously, we chose a range of radiant panel heat flux from 0.44 to 20.59 kW/m<sup>2</sup> corresponding to a range of temperature from 30 to 210 °C, a sampling height of H1=112 cm and heating and sampling times equal to 30 min and 10 min respectively. The VOCs analyses were carried out using ATD-GC/MS, 18 compounds were identified in the *Rosmarinus officinalis* (Lamiaceae family) and classified by ascendant order of the retention indices I (table 2).

Table 2: Identification of VOCs compounds emitted by the *Rosmarinus officinalis*.

N°	<sup>1</sup> I <sub>l</sub>	<sup>2</sup> I <sub>a</sub>	Name
1	936	931	α-pinene
2	950	943	camphene
3	964	952	thuja-2,4-(10)-diene
4	970	964	sabinene
5	978	970	β-pinene
6	982	979	myrcene
7	1013	1008	α-terpinene
8	1018	1012	para-cymene
9	1022	1020	1,8-cineol
10	1025	1020	limonene
11	1051	1047	γ-terpinene
12	1082	1079	α-terpinolene
13	1088	1085	filifolone
14	1128	1122	camphor
15	1149	1141	pinocarvone
16	1182	1176	estragol
17	1219	1210	verbenone
18	1270	1269	bornyl acetate

<sup>1</sup> retention indices calculated on apolar column.

<sup>2</sup> retention indices of authentic compounds or literature data (NIST WebBook, 2006).

The VOCs composition was characterized by high contents of monoterpenes hydrocarbons. The main components were α-pinene, limonene, camphene, myrcene, β-pinene, para-cymene and camphor. The same constituents were observed by Ormeño et al., (2007) for the study of the VOCs emissions by *Rosmarinus officinalis* under natural conditions. The total emission of these compounds represents a percentage varying with temperature from 88 to 100% of the total VOCs emissions. Figure 5 describes the evolution of the main constituents and the total VOCs emissions as a function of the enclosure temperature.

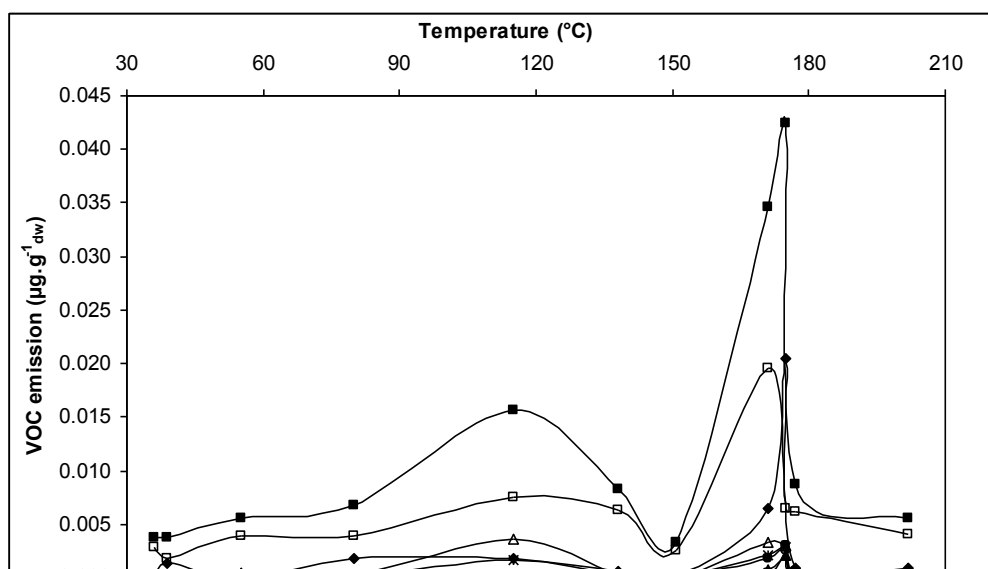


Figure 5: The VOCs emission as function of temperature and radiant heat flux.

Let notice that the VOCs quantity measured at the different temperatures is lower than the one presented in the previous section. These differences can be explained by the variation of the nature of the plants and their soils. Some studies have demonstrated that VOCs emission is influenced by numbers of biotic and abiotic parameters (Peñuelas and Lusià, 1999b). Indeed, the plants used in the previous section had more *Rosmarinus officinalis* needles which results in a more important emission. Lawrence (1995, 1997) shows the different composition of essential oil according to sampling sites and the emission of monoterpenes varied according to the seasonal period (Holzke et al., 2006). Ormeño et al. (2007) and Ormeño et al. (2008) showed that the emission of all major monoterpenes hydrocarbons released by *Rosmarinus officinalis* were higher in plants growing on calcareous soils than siliceous soils.

It was also observed that, when the temperature increases the VOCs emission increases until reaching a temperature of 175°C. This tendency was observed by Barboni (2006) for others Mediterranean vegetal species such as *Pinus nigra* ssp *laricio* and *Pinus pinaster*. The VOCs quantity at 175°C is 8 times higher than the one measured at 50°C.  $\alpha$ -pinene is the major compound in the *Rosmarinus officinalis*. The  $\alpha$ -pinene emission is five times higher at 175°C than at 50°C. Moreover, we observe an increase of VOCs emission around 120°C due to the transport of the VOCs by the water molecules during its evaporation process. Between the temperatures 120°C and 150°C, we observe a diminution of the VOCs quantity due probably to the lower influence from the water evaporation. Since the boiling temperature of monoterpenes is starting about 154°C, for the temperature below 150°C these molecules

would be in a liquid or in an equilibrium liquid-vapour state. Consequently, for the temperatures higher than 150°C the VOCs emission increases rapidly to reach a maximum at 175°C. The quantity of volatile compounds is 3.3 times more important in this range of temperature than in the range of temperatures 50°C to 120°C. Beyond 175°C, we notice a significant decrease of the quantity of VOCs that can be explained by the thermal degradation and/or polymerisation of the terpenic molecules (Barboni 2006).

### 3.2 Fire retardant effect

A great part of the fight against forest fires consists in dropping liquids from aircrafts. The dropped fluid can be water for direct attack or chemical retardant, which is in Europe a mixture of water (80%), polyphosphate, clay and gum. Several studies have been carried out for the effect of fire retardants on the forest fires behaviour (Giménez et al., 2006) and (Liodakis et al., 2006), but there are no works devoted to their effect on VOCs emission. In this work we conduct a study of the effect of applying different quantities of chemical fire retardant ( $\eta_1=6\text{ml}$ ,  $\eta_2=12\text{ml}$ ,  $\eta_3=18\text{ml}$ ,  $\eta_4=24\text{ml}$  and  $\eta_5=30\text{ml}$ ) on VOCs emission. We also used water (30ml) in order to compare its effects to the fire retardant effects on the VOCs emission. The enclosure temperature in this study corresponds to the maximum value of the VOCs emission previously found (175°C). The total emission of the seven main compounds presented above represents a percentage varying with the chemical fire retardant quantity from 92 to 98% of the total VOCs emissions. The different results are presented in figure 6.

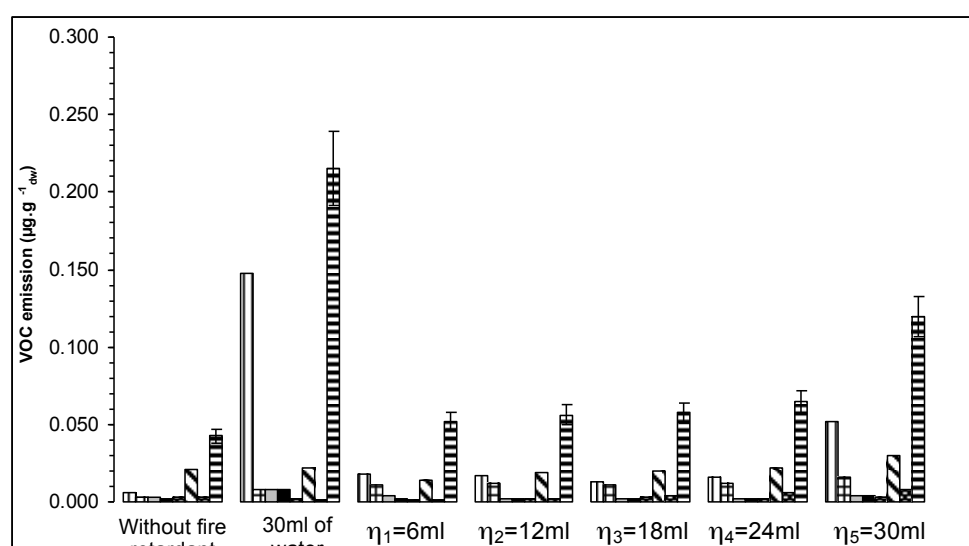


Figure 6: Effect of the fire retardant on the VOCs emissions at 175 °C.

In figure 6 it is observed that the application of fire retardant **favors** the VOCs emission. The total quantity of VOCs changes from the value of  $0.0424 \mu\text{g}\cdot\text{g}^{-1}_{\text{dw}}$  without fire retardant to the value of  $0.0522 \mu\text{g}\cdot\text{g}^{-1}_{\text{dw}}$  with quantity of  $\eta_1=6\text{ml}$ . Moreover, the VOCs emission increases while increasing the quantity of fire retardant and it reaches a value of  $0.1196 \mu\text{g}\cdot\text{g}^{-1}_{\text{dw}}$  for the saturation quantity of  $\eta_5=30\text{ml}$ . This result can be explained by the presence of water, which causes the transport of the VOCs molecules as it evaporates. Also, the comparison between the two cases with quantity of  $\eta_5=30\text{ml}$ , the one with water and fire retardant mixture and the other with water alone, shows that the total VOCs is about 2 times more important with water alone. Thus, the chemical fire retardant has a reducing effect on the VOCs emission. This reduction is due to the presence of clay in this substance which plays an adsorbent role as indicated by [Harti et al. \(2007\)](#) and [Zaitan et al. \(2008\)](#).

### **3.3 Effect of radiant panel heat flux, plant temperature and fire retardant**

As showed in the last section, the application of the fire retardant increases the VOCs emission due to the presence of water (80%), and for the same quantity the fire retardant reduce considerably the VOCs emissions (about 55%). To explain this result, we have analysed the behaviour of the VOCs emissions as a function of temperature with a presence of the fire retardant. We chose the maximal quantity of  $\eta_5=30\text{ml}$  and a range of radiant panel heat flux from  $0.44$  to  $20.59 \text{ kW/m}^2$  corresponding to a range of temperature from  $30$  to  $210$





Figure 7: Evolution of VOCs emission as function of temperature and heat flux with the presence of the fire retardant ( $\eta_5=30\text{ml}$ ).

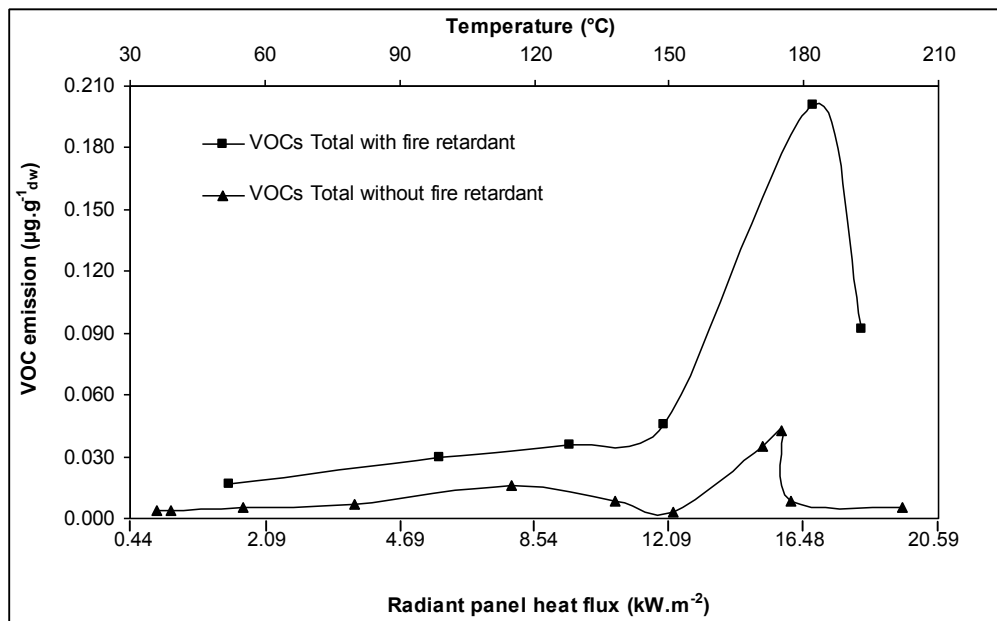


Figure 8: The total VOCs emission as function of plant temperature and radiant heat flux with and without fire retardant ( $\eta_5=30\text{ml}$ ).

#### 4. Flammability of Volatile Organic Compounds

After having studied the preheating and the fire retardant effects on the emission of VOCs, it becomes interesting to examine whether the gas mixture that would be produced by these emissions when mixed with surrounded air could be flammable or no. To proceed, the VOCs concentration in the plant surrounding must be calculated and compared with the Lower and the Upper Flammability Limits of  $\alpha$ -pinene as a function of temperature.

The concentration of volatile organic compounds,  $C_{\text{VOCs}}$ , at the sampling location and at different temperatures is given by the following relation:

$$C_{\text{VOCs}} [\text{g} \cdot \text{m}^{-3}] = m_i \frac{E_{\text{VOCs}}}{Q_v \tau} \quad (1)$$

Where  $m_i = 155 \text{ g}$  is the initial mass of *Rosmarinus officinalis* plants,  $E_{\text{VOCs}} [\mu\text{g} \cdot \text{g}_{\text{dw}}^{-1}]$  is the measured emission of VOCs per unit mass of plant,  $Q_v = 150 \text{ ml} \cdot \text{min}^{-1}$  is the flow-rate of gases extracted by the pump and  $\tau = 10 \text{ min}$  is the sampling time. In order to determine if the mixture is flammable it must be compared to the flammability limits of the VOCs at the corresponding temperature.

The Lower and Upper Flammability Limits, LFL and UFL, of  $\alpha$ -pinene can be expressed by:

$$LFL [\text{g} \cdot \text{m}^{-3}] = 10 \frac{LFL(\%)}{V_m} W \quad (2)$$

$$UFL [\text{g} \cdot \text{m}^{-3}] = 10 \frac{UFL(\%)}{V_m} W \quad (3)$$

where  $LFL(\%)$  and  $UFL(\%)$  are respectively the Lower and Upper Flammability Limits in volume percentage.  $W = 136.23 \text{ g} \cdot \text{mol}^{-1}$  is the molar weight of  $\alpha$ -pinene and  $V_m [l \cdot \text{mol}^{-1}]$  is the molar volume, that depends on the temperature as:

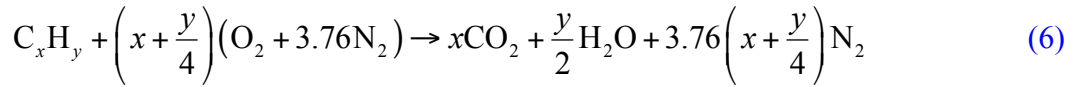
$$V_m [l \cdot \text{mol}^{-1}] = 8.205 \times 10^{-2} (T + 273) \quad (4)$$

with  $T$  ( $^{\circ}\text{C}$ ) is the temperature of VOCs. The dependence of the lower flammability limit on temperature is given by (Catoire and Naudet, 2005):

$$LFL(\%) = 519.957 X^{0.70936} n^{-0.197} (T + 273)^{-0.51536} \quad (5)$$

where  $X$  is the mole fraction of the hydrocarbon in the corresponding stoichiometric hydrocarbon/air mixture,  $n$  is the number of carbon atoms in this molecule, and  $T$  is the temperature (in  $^{\circ}\text{C}$ ).

The stoichiometric fuel/air mixture is defined as follows:



and

$$X = \frac{1}{1 + 4.76 \left(x + \frac{y}{4}\right)} \quad (7)$$

For  $\alpha$ -pinene hydrocarbon  $x = 10$ ,  $y = 16$ ,  $n = 10$  and  $X = 0.015$ . The temperature dependence of the upper flammability limit can be estimated by means of equation (Drysdale, 1999):

$$UFL(\%) = UFL_{25}(\%) \left[1 + 7.21 \times 10^{-4} (T - 25)\right] \quad (8)$$

where  $UFL_{25}(\%)=6.1$  and  $T$  ( $^{\circ}\text{C}$ ) is the temperature of fuel/air mixture. When we replace the relations (4)–(8) in the relations (2) and (3), the Lower and Upper Flammability Limits of  $\alpha$ -pinene can be written:

$$LFL \left[ \text{g} \cdot \text{m}^{-3} \right] = 2.7892 \times 10^5 (T + 273)^{-1.51536} \quad (9)$$

$$UFL \left[ \text{g} \cdot \text{m}^{-3} \right] = 10.128 \times 10^4 \frac{1 + 7.21 \times 10^{-4} (T - 25)}{T + 273} \quad (10)$$

The concentration of VOCs in experiments and in terrain (small valley or canyon of area of one hectare occupied by *Rosmarinus officinalis* shrubs of a load of  $1.5 \text{ kg/m}^2$ ) and the flammability limits of  $\alpha$ -pinene are plotted in figure 9. The VOCs concentrations at large scale in particular conditions (climatic: without wind and topography: canyon) are calculated, by extrapolation, using the experimental data obtained in the hermetic enclosure and the value of surface density of vegetation (equal to  $1.5 \text{ kg/m}^2$ ).

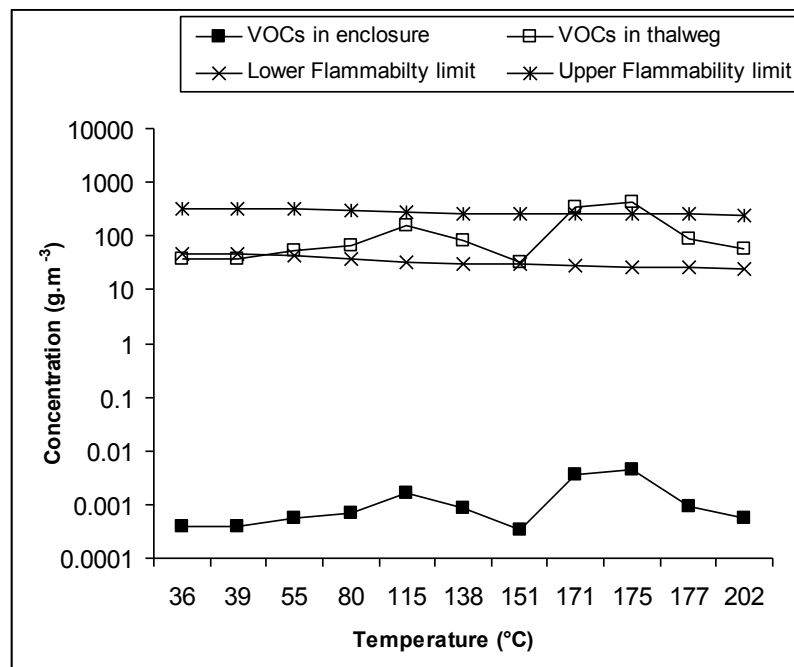


Figure 9: Concentration of VOCs and flammability limits.

This figure shows that the concentration of VOCs emitted by *Rosmarinus officinalis* plants in the hermetic enclosure at different temperatures before the onset of pyrolysis is lower than the Lower Flammability Limit of  $\alpha$ -pinene, and consequently the corresponding gas mixture is non flammable. Contrary to small scale, the concentrations of VOCs emitted by *Rosmarinus officinalis* at field scale (in terrain) are superior to LFL and inferior to UFL. We observe from the curves that the concentration of VOCs is in the flammability domain of  $\alpha$ -pinene except two temperatures 171 °C and 175 °C where the values of concentration exceed the Upper Flammability Limit. These results show that under certain conditions of vegetation type and density, climatic, topography, and fire characteristics, it could be possible to have a flammable gas mixture in the vicinity of the vegetation ahead of the fire that could lead to a gaseous flame propagation and to a potential development of a fire flashover triggered by this gaseous combustion process.

## 5. Conclusions

The present study, conducted on the effect of the plant temperature and external radiant heat flux on the emission of the VOCs by *Rosmarinus officinalis* plants as per their potential implication on forest fires can be summarized in three parts. The first part concerns the effect of temperature or heat flux effect on VOCs emission. For a temperature range of 30 to 210°C, corresponding to a heat flux range of 0.44 to 20.59 kW/m<sup>2</sup> in these tests, two peaks of the VOCs emission were recorded. One of the peaks is around 120°C (8.54 kW/m<sup>2</sup>) apparently due to the transport of the volatile compounds by the water molecules during their evaporation process. The other is around 175°C (15.50 kW/m<sup>2</sup>) due to the evaporation of the main part of the VOCs present in the plant.

The second part concerns with the fire retardant effect on VOCs emission. It was found that the application of the retardant (a mixture of water, polyphosphate, clay and gum) enhances the VOCs emission because of the presence of the water. However, its use in fire-fighting seems better than the use of water alone since it was observed a significant decrease in VOCs emission in the case with the fire retardant mixture compared with water alone.

The third part shows that the concentration of VOCs measured in the laboratory experiments is much lower than the Lower Flammability Limit of  $\alpha$ -pinene, and consequently was not flammable. However estimation of the potential concentration of VOCs in an uneven geographical area, such as a valley, may be flammable under certain fire conditions and consequently potentially leading to the development of a forest fire flashover. This estimation shows that the potential for forest fire blow-up investigated in this paper cannot be put aside and needs to be further investigated. Field sampling of VOC emissions in canyons under summer conditions will be necessary as well as the investigation of the flammability of VOC-smoke mixtures that are more realistic during actual fires.

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## **6. References**

Barboni T. (2006) Contribution de méthodes de la chimie analytique à l'amélioration de la qualité de fruits et à la détermination de mécanismes (EGE) et de risques d'incendie, Ph. D thesis of the université de Corse, France (In French).

Butler B.W., Bartlette R.A., Bradshaw L.S., Cohen J.D., Andrews P.L., Putnam T. and Mangan R.J. (1998) Fire behaviour associated with the 1994 South Canyon Fire on Storm King Mountain, Colorado, Research Paper, RMRS-RP-9, Ogden, UT: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, 82 p.

Catoire L. and Naudet V. (2005) Estimation of temperature-dependent lower flammability limit of pure organic compounds in air at atmospheric pressure, *Process safety progress*, vol. 24, pp. 130-137.

Dold J.W. and Zinoviev A. (to appear 2009) Fire eruption through intensity and spread rate interaction mediated by flow attachment, *Combustion Theory and Modelling*.

Dold J.W., Simeoni A., Zinoviev A. and Weber R. (to appear 2009) The Palasca fire, September 2000: Eruption or Flashover? In 'Some Forest Fire Related Accidents in Europe', D. Xavier-Viegas (Ed.) JRC, Ispra.

Drysdale D. (1999) An introduction to fire dynamics, 2ed., John Wiley & Sons, New York.

Giménez A., Arqués P. and Arnaldos J. (2006) Experimental study for characterizing the effectiveness of long-term forest fire retardants and the influence of fuel characteristics on the reduction of the rate of fire spread, *Forest Ecology and Management*, S234-S236.

Furnish J., Chockie A., Anderson L., Connaughton K., Dash D., Duran J., Graham B., Jackson G., Kern T., Lasko R., Prange J., Pincha-Tulley J. and Withlock C. (2001) Thirtymile fire investigation, Factual Report and Management Evaluation Report, USDA, Forest Service, October 2001.

Harti S., Cifredo G., Gatica J.M., Vidal H. and Chafik T. (2007) Physicochemical characterization and adsorptive properties of some Moroccan clay minerals extruded as lab-scale monoliths, *Applied Clay Science*, vol. 36, pp. 287–296.

Holzke C., Hoffmann T., Jaeger L., Hoppmann R., Zimmer W. (2006) Diurnal and seasonal variation of monoterpene and sesquiterpene emission from scotpin (*Pinus sylverstris L.*), *Atmospheric Environment*, vol. 40, pp. 3174-3185.

König W.A., Hochmuth D.H. and Joulain D. (2001) Terpenoids and Related Constituents of Essential Oils. Library of MassFinder 2.1. University of Hamburg, Institute of Organic Chemistry, Hamburg, Germany.

Lawrence B.M. (1995) Progress in essential oils, *Perfumer & Flavorist*, vol. 20(1), pp. 47-54.

Lawrence B.M. (1997) Progress in essential oils: Rosemary oil, *Perfumer & Flavorist*, vol. 22(5), pp. 71-75

Liodakis S., Vorisis D. and Agiovlasitis I.P. (2006) Testing the retardancy effect of various inorganic chemicals on smoldering combustion of *Pinus halepensis* needles, *Thermochimica Acta*, vol. 444, pp. 157–165.

Llusià J. and Peñuelas J. (1999a) *Pinus halepensis* and *Quercus ilex* terpene emission as affected by temperature and humidity, *Biologia Plantarum*, vol. 42, pp. 317-320.

Llusià J. and Peñuelas J. (1999b) Short-term responses of terpene emission rates to experimental changes of PFD in *Pinus halepensis* and *Quercus ilex* in summer field conditions, *Environmental and Experimental Botany*, vol. 42, pp. 61-68.

National Institute of Standards and Technology (1999). PC Version 1.7 of The NIST/EPA/NIH Mass Spectra Library. Perkin-Elmer Corp: Norwalk, CT.

National Institute of Standards and Technology. NIST WebBook (06/2005): <http://webbook.nist.gov/chemistry>.

Ormeño E., Baldy V., Ballini C. and Fernandez C. (2008) Production and diversity of volatile terpenes from plants on calcareous and siliceous soils: effect of soil nutrients, *Journal of chemical ecology*, vol. 34, pp. 1219-1229.

Ormeño E., Céspedes B., Sánchez I.A., Velasco-García A., Moreno J.M., Fernandez C. and Baldy V. (2009) The relationship between terpenes and flammability of leaf litter, *Forest Ecology and Management*, vol. 257, pp. 471-482.

Ormeño E., Fernandez C., Bousquet-Mélou A., Greff S., Morin E., Robles C., Vila B. and Bonin G. (2007) Monoterpene and sesquiterpene emissions of three Mediterranean species through calcareous and siliceous soils in natural conditions, *Atmospheric Environment*, vol. 41, pp. 629–639.



- Owen S., Boissard C., Strett A., Duckham S.C., Csiky O. and Hewitt C.N. (1997) Screening of 18 Mediterranean Plant Species for volatile organic compound emissions, *Atmospheric Environment*, vol. 31, pp. 101–118.
- Raffalli N., Picard C. and Giroud F. (2002) Safety and awareness of people involved in forest fires suppression, *Forest Fire Research & Wildland Fire Safety*, Viegas (ed.), ISBN 90-77017-72-0, Rotterdam.
- Van Den Dool H. and Kratz P.D. (1963) A Generalization of the retention index system including linear temperature programmed gas - liquid partition chromatography, *Journal of Chromatography A*, vol. 11, pp. 463-478.
- Viegas D.X. (2005) A Mathematical model for forest fires blow-up, *Combustion Sciences and Technology*, vol. 177, pp. 27-51.
- Viegas D.X. (2006) Parametric study of an eruptive fire behaviour model, *International Journal of Wildland Fire*, vol. 15, pp. 169-177.
- Viegas, D.X., Stipanicev, D., Ribeiro, L., Pita, L.P. and Rossa C. (2008) The Kornati fire accident – eruptive fire in relatively low fuel load herbaceous fuel conditions, *Modelling, Monitoring and Management of Forest Fires I*, WIT Transactions on Ecology and the Environment (ISSN: 1743-3541), Vol. 119, pp. 365-375.
- Zaitan H., Bianchi D., Achak O. and Chafik T. (2008) A comparative study of the adsorption and desorption of o-xylene onto bentonite clay and alumina, *Journal of Hazardous Materials*, vol. 153, pp. 852–859.