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### Influence of water and terpenes on flammability in some dominant Mediterranean species

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**Abstract.** In the Mediterranean basin, fires are a major concern for forest and shrubland ecosystems. We studied flammability, its seasonality and its relationship with leaf moisture and volatile terpene content and emission in the dominant species of a Mediterranean shrubland and forest in Catalonia (NE Iberian Peninsula). We measured temperatures and time elapsed between the three flammability phases: smoke, pyrolysis and flame, for four seasons. We sampled twice in spring because of an occasional drought period during this season. Flammability had a significant relationship with leaf hydration, in the shrubland and in the forest. Few and only weak correlations were found between terpene content and flammability. In the future, arid conditions projected by climatic and ecophysiological models will increase fire risk through decreased hydration and subsequent increased flammability of the species.

Additional keywords: Arbutus unedo, Cistus albidus, emission and content of volatile compounds, Erica multiflora, Globularia alypum, Phillyrea latifolia, Pinus halepensis, Pistacia lentiscus, Quercus ilex, Rosmarinus officinalis.

#### Introduction

Mediterranean shrublands and forests are subjected yearly to a drought period in summer time. The lack of water due to limited or non-existent rainfall, the low air humidity and high temperatures with corresponding high evaporative demands increase vegetation fire risks (Rambal and Hoff 1998). Fire has an important presence and influence in these Mediterranean ecosystems, its damage mostly depends on fire intensity and frequency. The reconstruction of vegetation is slow, and repetitive fire events may seriously endanger revegetation (Francis and Thornes 1990; Ferran *et al.* 1992; Bautista *et al.* 1994; Moench and Fusaro 2003).

Climate change during the 20th century has been reported to influence the increase in frequency and magnitude of fires (Piñol *et al.* 1998). Climatic and ecophysiological models such as GOTILWA (IPCC 2001; Sabaté *et al.* 2002; Peñuelas *et al.* 2005) project drier and warmer conditions and therefore higher fire risks.

But fire's appearance does not only depend on meteorological conditions; it also depends on the flammability of vegetation. Flammability is thought to be dependent on the foliar hydration of plants and leaves (Trabaud 1974, 1976; Cappelli *et al.* 1983; Massari and Leopaldi 1998). Trabaud (1976) described a trend where leaves with a lower percentage of water burst into flame easily, whereas leaves with high foliar hydration rarely ignited. Although this was true for most species, an exception was found in the case of *Quercus pubescens*, which rapidly flamed even at an elevated hydration content. The dependence of flammability on the hydric condition of plants and leaves is thus also linked to other environmental factors, life history and ecophysiology of the plant. Some species are more flammable than others even at the same water content (Massari and Leopaldi 1998).

In addition to leaves' moisture, volatile organic compounds such as monoterpenes constitute another possible factor driving flammability. These compounds are present and emitted by most Mediterranean plants (Llusià and Peñuelas 2000) but their actual effects on flammability are still controversial (Cappelli *et al.* 1983). White (1994) claimed that flammability was positively correlated with monoterpenoid content. Owens *et al.* (1998) confirmed and reinforced White's results.

The objective of the present paper is to characterise the different flammability of various species in two distinct Mediterranean ecosystems in Catalonia (NE Spain): first, in a typical Mediterranean dry shrubland, and second, in a typical Mediterranean forest, where we aimed to observe the possible seasonal changes in flammability, and the relationship of leaves' flammability with foliar hydration and with foliar terpene content and emissions. In addition, with the current study, we were also interested in providing information on possible changes in flammability in response to changes in soil water availability similar to those projected by global change modelling (GCM) and ecophysiological models such as GOTILWA (IPCC 2001; Sabaté *et al.* 2002; Peñuelas *et al.* 2005).

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**Fig. 1.** Mean monthly precipitation (mm) and air temperature (°C) during the period October 2004–August 2005 in the study site located in a shrubland in Central Catalonia and in a holm oak forest in Southern Catalonia.

#### Materials and methods

#### Shrubland study site and species analysed

The Garraf Natural Park (Garraf hereafter) is located  $\sim 30$  km south of Barcelona (on the central coast of Catalonia, 41°18'N, 1°49'E). The study site reaches 600-m altitude above sea level with a south-south-east slope (13°). The area went through two fire events in the summers of 1982 and 1994. At the moment, the vegetation covers 60–70% of the surface, and species are not taller than 70–100 cm. The vegetation is characteristic of a Mediterranean shrubland (*Rosmarino–Ericion*). The species analysed were evergreen and sclerophyllous shrubs: *Erica multiflora, Globularia alypum, Pistacia lentiscus, Rosmarinus officinalis* and tree saplings of *Pinus halepensis*.

The climate is typically Mediterranean, with mild temperatures and abundant rains during spring and autumn, cool winters, and hot, dry summers. Generally, the mean precipitation is 580 mm and the mean temperature  $15.1^{\circ}$ C. However, during the year the experiment took place, the precipitation was only 321 mm, almost 50% of normal rainfall (Fig. 1*a*).

#### Forest study site and species analysed

The flammability study was also carried out in a natural holm oak forest in the Prades mountains in Southern Catalonia (NE Spain 41°13′N, 0°55′E). The mean annual temperature is 12°C and the average annual rainfall is 658 mm, but, during the year the measurements took place, total precipitation was only 347 mm. The vegetation is dominated by *Quercus ilex*, but *Phillyrea latifolia*, *Arbutus unedo* and *Cistus albidus* are also abundant (Ogaya *et al.* 2003). These were the four species analysed. Plant sampling was conducted at the same altitude (930 m above the sea level) along the slope.

Temperature, rainfall, relative air humidity, wind speed, and radiation were recorded using a datalogger (Campbell CR10X, Campbell Scientific, Logan, UT, USA) located at the experimental site. However, during the year of study (October 2004–July 2005), rainfalls strongly decreased (Fig. 1*b*). Soil water content was assessed using a time domain reflectometry device (Zegellin *et al.* 1989) every 2 weeks. Four probes were randomly placed on each plot at 25-cm soil depth.

#### Leaf sampling

Fully and well-expanded current-year leaves were sampled for flammability on sunny days for each one of the studied species in five campaigns, from November 2004 to August 2005. Three to five leaves were used for water status analysis and three to five leaves more for terpene emission and content analyses. All collected leaves in the shrubland were oriented south-south-east and in the forest to the south.

#### Water status

Fresh leaves were promptly weighed and afterwards oven-dried for 24 h at 80°C. The foliar hydration (H) was determined as  $100 \times (FW - DW)/DW$ , where FW is the fresh weight and DW the dry weight after oven-drying the leaves.

#### Flammability measurements

Foliar flammability was measured with an infrared quartz epiradiator (Trabaud 1976; Cappelli et al. 1983; Massari and Leopaldi 1998). The instrument was coupled to a digital thermometer equipped with a probe partially in contact with the leaves sampled, and partially directly exposed to the heat of the lamp ( $\sim$ 50% of the probe was always in contact with leaves). A digital timer was used to record the time at which the following phases appeared: smoke, pyrolysis (incandescence), and flame. Time started to be counted at a temperature of 60°C. The epiradiator released heat and induced the first phase, and afterwards the temperature progressively increased through the phases until leaves flamed. All tests were conducted in a closed environment avoiding any wind influence. Previous to the analysis of flammability, up to 10 g of leaves were accurately weighed; then the amount was placed on a iron wire mesh, at 4-cm distance to the source of the epiradiator. Each species was tested from three to five times.

#### Terpene emission and content analyses

Terpene emissions were measured with a portable gas exchange system ADC LCA4, with a PLC4B chamber (ADC Inc., Hoddesdon, Hertfordshire, UK), where volatile compounds were collected. Part of the air exiting this chamber flowed through a 'T' system to a glass tube (11.5 cm long and 0.4-cm internal diameter) manually filled with terpene adsorbents Carbotrap C (300 mg), Carbotrap B (200 mg), and Carbosieve S-III (125 mg) (Supelco Inc., Bellefonte, PA, USA) separated by plugs of quartz

wool. Before use, these tubes were conditioned for 3 min at 350°C with a flow of purified helium. The sampling time was 5 min, and the flow varied between 100 and  $200 \,\mathrm{cm^3 \, min^{-1}}$ depending on the glass tube adsorbent and quartz wool packing. The flow passing through the volatile organic compound (VOC) adsorbents was measured with a bubbler flowmeter. The trapping and desorption efficiency of liquid and volatilised standards such as  $\alpha$ -pinene,  $\beta$ -pinene or limonene was practically 100%. After VOC sampling, the adsorbent tubes were stored at -30°C until analysis (within 24-48 h), and an absence of changes in terpene concentrations after storage of the tubes was proved, as checked by analysing replicate samples immediately and after 48-h storage. Isoprene and terpene analyses were conducted in a gas chromatographer-mass spectrometer (GC-MS) (Hewlett Packard HP59822B; Palo Alto, CA, USA). For detailed description of the analysis, see Peñuelas et al. (2005) and Llusià and Peñuelas (2000).

The analysis of foliar VOCs was performed on all species studied except in *E. multiflora*, *P. latifolia*, *Q. ilex* and *A. unedo*. Each leaf collected was immediately frozen in liquid nitrogen and then kept in a fridge at  $-30^{\circ}$ C until the analysis was carried out. For the analysis, each leaf was powdered in liquid nitrogen and afterwards diluted with 1 mL of pentane. The extraction was then injected automatically into the GC and compounds detected through the MS. All the process has been previously described in detail above and in Peñuelas *et al.* (2005) and Llusià and Peñuelas (2000).

#### Statistical analyses

Repeated-measure analyses of variance (ANOVA) and regression analyses were conducted using STATISTICA Version 6.0 for Windows (StatSoft Inc., Tulsa, Oklahoma). Regression analyses were conducted between the temperatures and times for the three phases of flammability and H, terpene content and terpene emission in all species. They were considered significant when P < 0.05. Regressions between leaf hydration and the different phases of flammability were considered as regression type II, when mean values of plots were regressed.

#### Results

#### Species and seasonal variation in leaf flammability

All species sampled in shrubland showed a decrease in the temperature at which flammability phases appeared during early spring, coinciding with minimum foliar hydration (Figs 2 and 4a). P. halepensis showed in most cases the greatest temperatures and time elapsed for smoke to appear. It was followed by R. officinalis. The other three species presented much lower temperature values for the appearance of smoke and in less time (Fig. 2). However, in the case of the Prades forest, the smoke phase did not show any relevant trend (data not shown). In this site, plant pyrolysis temperatures and elapsed time between phases were quite similar and did not show clear seasonal trends in A. unedo, Q. ilex and P. latifolia. Nevertheless, the shrub C. albidus reached pyrolysis at lower temperatures and faster than any of the other species and presented a clear seasonal trend with even lower temperatures and faster pyrolysis in the dry summer (Fig. 3). This species did not flame. Q. ilex and P. latifolia showed lower temperatures and shorter flame times than A. unedo (Fig. 3). All these species, except C. albidus, showed seasonal variation in pyrolysis temperature, which went from 325-328°C to a maximum of 364-382°C. The pyrolysis temperature of C. albidus showed a gradual increase from November 2004 to May 2005 (243-276°C) and after, decreased to lower values in summer (222-227°C). The temperature of flame appearance ranged between 377 and 450°C in Q. ilex and P. latifolia, and between 407 and 528°C in A. unedo, with no clear consistent seasonal trend. The time to reach pyrolysis was shorter for C. albidus (from 269s in winter to 142s in summer) than for the other three species, which went from 310-333 s in winter to 256-284 s in summer. Strong decreasing trends in time elapsed to flame were found in all three tree species. Among them, the shortest times were found for P. latifolia (419 s in winter and 299-313 s in summer) and the longest times for A. unedo (477 s in winter and 341-391 s in summer) (Fig. 3).

Similar results were found in shrubland samples where flame was observed only in *P. halepensis* and *E. multiflora*. In February, higher temperatures and elapsed time values denoted a lower flammability; in May, both species presented comparable temperatures for flame appearance. The time until flame reached its highest values was in autumn and winter and had a low variability from May to August. Higher temperatures and especially longer times to catch alight were found in *E. multiflora* compared with *P. halepensis* (Fig. 2).

#### Species and seasonal variation in leaf water hydration

Lower foliar hydration values were observed in the Garraf site. Prades forest species, growing in a more humid site, were more hydrated.

A clear pattern was observed in Garraf from November 2004 to May 2005. *R. officinalis* was the species that had a higher hydration through all the periods analysed (values ranged from 75 to 144%). *C. albidus* and *A. unedo* were the other species with higher hydration (from November to May, values ranged respectively from 149 to 162% and 126 to 111%). *E. multiflora* was found to be the species with the lowest foliar hydration (values ranged from 45 to 90%). The driest species in Prades was *Q. ilex* (values ranged from 76 to 84%). *E. multiflora, P. halepensis* and *G. alypum* followed the same trend during the seasons. Their foliar hydration decreased in May and had a partial or complete recovery during the following months. In *P. lentiscus*, no seasonal variability along the year was found (values ranged from 83 to 102%, Fig. 4a).

During the year, only *C. albidus* and *P. latifolia* showed a clear seasonal pattern in their foliar hydration (H) (see Fig. 4b). *C. albidus* foliar hydration increased from November 2004 to May 2005, and afterwards dramatically decreased to 61%. *Q. ilex* showed lower foliar hydration during the whole sampling period and *A. unedo* higher than the other two species, *P. latifolia* and *Q. ilex*. All species presented a trend towards decreasing foliar hydration in summer, *P. latifolia* decreased to 53%, *Q. ilex* to 59% and *A. unedo* to 90%. Among the treatments in Prades, none of the species selected demonstrated significant differences.



**Fig. 2.** Seasonal trend of temperatures and elapsed time to reach the three flammability phases (smoke, pyrolysis and flame) in the five species studied in the shrubland site: *Rosmarinus officinalis* ( $\Diamond$ ); *Globularia alypum* ( $\Box$ ); *Pinus halepensis* ( $\nabla$ ); *Erica multiflora* ( $\bigcirc$ ); and *Pistacia lentiscus* ( $\triangle$ ) (mean  $\pm$  s.e.; n = 3-4). Effect of the species and the seasons are depicted in each panel.



**Fig. 3.** Seasonal trend of temperature and time to reach the pyrolysis and flame phases of *Cistus albidus* ( $\mathbf{V}$ ), *Phillyrea latifolia* ( $\bigcirc$ ), *Quercus ilex* ( $\mathbf{\Phi}$ ) and *Arbutus unedo* ( $\nabla$ ) in the forest site. Statistical significances of the studied factors, species and seasons are given inside the panels.



**Fig. 4.** Seasonal trend of foliar hydration (H) in the species studied in (*a*) the shrubland site: *Rosmarinus officinalis* ( $\Diamond$ ); *Globularia alypum* ( $\Box$ ); *Pinus halepensis* ( $\nabla$ ); *Erica multiflora* ( $\bigcirc$ ); and *Pistacia lentiscus* ( $\triangle$ ) (mean  $\pm$  s.e.; n = 3-5), and (*b*) the forest site: *Cistus albidus* ( $\triangledown$ ); *Phillyrea latifolia* ( $\bigcirc$ ); *Quercus ilex* ( $\spadesuit$ ); and *Arbutus unedo* ( $\nabla$ ). Statistical significances of the studied factors, species and seasons are given inside the panels.

Table 1. Seasonal pattern of monoterpene emission rates (µg g<sup>-1</sup> DW h<sup>-1</sup>) and contents (mg g<sup>-1</sup> DW) in *Rosmarinus* officinalis, Globularia alypum, Pinus halepensis, Erica multiflora and Pistacia lentiscus growing in a shrubland of the Garraf natural park, central coast of Catalonia (Spain)

Emissions were only detected in *Globularia alypum*, *Pinus halepensis* and *Erica multiflora*. <sup>A,B</sup>, significant differences (P < 0.05) between seasons; n.d., not detected; DW, dry weight

| Total monoterpene emission | G. alypum                | P. halepensis          | E. multiflora            | Isoprene emission<br>E. multiflora    |
|----------------------------|--------------------------|------------------------|--------------------------|---------------------------------------|
| November 2004              | $1.74 \pm 1.08^{\rm A}$  | n.d.                   | $3.30\pm3.08^{\rm B}$    | $2.49\pm2.37^{A,B}$                   |
| January 2005               | $0.69\pm0.23^{\rm A}$    | $32.50\pm9.70^{\rm A}$ | $0.53\pm0.49^{\rm A}$    | $0.39\pm0.39^{\rm A}$                 |
| May 2005                   | $3.02\pm2.23^{\rm A}$    | 3.89                   | $7.88 \pm 3.92^{\rm B}$  | $5.50\pm3.51^{\mathrm{A},\mathrm{B}}$ |
| August 2005                | $0.18\pm0.04^{\rm A}$    | $7.43\pm6.20^{\rm B}$  | $6.30\pm2.29^{\rm B}$    | $6.17\pm2.31^{\rm B}$                 |
| Total monoterpene content  | R. officinalis           | G. alypum              | P. halepensis            | P. lentiscus                          |
| November 2004              | $10.11 \pm 1.67^{\rm A}$ | $1.63\pm0.46^{\rm B}$  | $14.95\pm5.73^{\rm A}$   | $2.59\pm0.90^{\rm A}$                 |
| January 2005               | $12.12\pm2.01^{\rm A}$   | $1.53\pm0.33^{\rm B}$  | $12.91 \pm 1.8^{\rm A}$  | $2.70\pm0.60^{\rm A}$                 |
| May 2005                   | $9.49 \pm 4.28^{\rm A}$  | $0.81\pm0.09^{\rm A}$  | $15.19\pm7.02^{\rm A}$   | n.d.                                  |
| June 2005                  | n.d.                     | $0.91\pm0.03^{\rm A}$  | $21.21 \pm 1.54^{\rm B}$ | $16.84\pm3.37^{\rm B}$                |
| August 2005                | $5.84 \pm 2.05^{\rm A}$  | $0.37\pm0.26^{\rm A}$  | $14.86\pm8.04^{\rm A}$   | $1.80\pm0.37^{\rm A}$                 |

Table 2. Seasonal pattern of monoterpene emissions ( $\mu g g^{-1} DW h^{-1}$ ) in *Cistus albidus, Phillyrea latifolia*and *Quercus ilex* growing in Prades holm oak forest (Southern Catalonia, Spain) and foliar monoterpene<br/>content (mg g<sup>-1</sup> DM) in *Cistus albidus* 

<sup>A,B</sup>, significant differences (P < 0.05) between seasons; n.d., not detected; DW, dry weight; DM, dry matter. Values are mean  $\pm$  s.e.

|               | Cistus albidus $(\mu g g^{-1} DW h^{-1})$ | Phillyrea latifolia $(\mu g g^{-1} DW h^{-1})$ | Quercus ilex<br>( $\mu$ g g <sup>-1</sup> DW h <sup>-1</sup> ) | Cistus albidus<br>(mg g <sup>-1</sup> DM) |
|---------------|---|--|--|---|
| November 2004 | $4.09\pm3.48^{\rm A}$                     | $3.53\pm3.06^{\rm A}$                          | $10.82\pm3.76^{\rm A}$   | n.d.                                      |
| January 2005  | $4.40\pm0.80^{\rm A}$                     | $2.95\pm0.62^{\rm A}$                          | $1.88\pm0.46^{\rm B}$  | $0.28\pm0.03^{\rm A}$                     |
| May 2005      | $2.23\pm0.80^{\rm A}$                     | $2.08 \pm 1.09^{\rm A}$                        | $16.86\pm2.31^{\rm A}$   | $0.25\pm0.06^{\rm A}$                     |
| June 2005     | n.d.                                      | n.d.   | n.d.   | $0.55\pm0.16^{\rm A}$                     |
| July 2005     | $1.13\pm0.08^{\rm A}$                     | $1.75\pm0.98^{\rm A}$                          | $10.51\pm0.75^{\rm A}$   | $0.25\pm0.05^{\rm A}$                     |



**Fig. 5.** Relationships between hydration (H), temperature and elapsed time for the three phases of flammability (smoke, pyrolysis and flame) in *Rosmarinus officinalis* from the shrubland site (Central Catalonia).

# Seasonal variation in leaves' volatile isoprenoid emission and content

In the shrubland, monoterpene emissions were detected in *P. halepensis*, *G. alypum* and *E. multiflora*. Emissions dramatically decreased to zero during the summer in *G. alypum*. However, a slight increase was observed in *E. multiflora* and *P. halepensis*. In *E. multiflora*, isoprene emissions were also detected (Table 1). They showed a typical trend depending on the mean seasonal temperatures. During the winter, isoprene emission was very low  $(0.39 \,\mu g \, g^{-1} \, DW \, h^{-1})$  but during the summer, it rose up to  $6.17 \,\mu g \, g^{-1} \, DW \, h^{-1}$ .

In the forest, leaf monoterpene emissions were detected in *Q. ilex, P. latifolia* and *C. albidus* but not in *A. unedo*. Leaves of *C. albidus* and *P. latifolia* emissions (Table 2) decreased in summer, whereas no clear trend was found in *Q. ilex* except for a decrease during the winter period.

In the shrubland, monoterpene content was detected in all species except in *E. multiflora*. It decreased from November

to August. However, in *P. halepensis*, values remained constant during the entire year of the experiment, except in June 2005, where a significantly high concentration was observed. The lowest values among the different species were found in *G. alypum*. In contrast, *P. halepensis* showed the highest values, close to those of *R. officinalis*.

Foliar monoterpene content was analysed in the only terpenestoring species of the forest site, *C. albidus*, and values were much lower than all other species analysed in Garraf and in most cases with no consistent differences through the year (Table 2).

#### Correlation of flammability with foliar hydration and monoterpene emission and content

In *R. officinalis* and *P. halepensis*, for all three flammability phases there was a positive correlation with foliar hydration and both temperature and time elapsed. However smoke did not



Fig. 6. Relationships between temperature, elapsed time and hydration (H) for the three phases of flammability (smoke, pyrolysis and flame) in *Globularia alypum* from the shrubland site (Central Catalonia).

correlate significantly (Figs 5 and 7). *G. alypum* showed a positive correlation only with temperature (Fig. 6). *E. multiflora* showed a significant correlation only in time to reach pyrolysis, in temperature and time elapsed until flame (Fig. 8). *P. lentiscus* was found to be the least flammable species. There was no flame phase and there was a weak but significant correlation between time elapsed until pyrolysis and hydration (Fig. 9).

No significant relationships were found between flammability variables (pyrolysis) and leaf isoprenoid emissions or content (Table 3) except for the time elapsed to pyrolysis, which was positively correlated, and for flame in *G. alypum*, negatively correlated with monoterpene content (Table 3).

In the forest ecosystem, no significant correlations between foliar hydration and both pyrolysis and flame temperatures and elapsed times were found in *A. unedo* (Fig. 10). But there was a positive correlation in the time required to reach flame in *Q. ilex* (Fig. 11) and in both phases, pyrolysis and flame, in *P. latifolia* (Fig. 12). *C. albidus*, which did not flame, also showed a positive correlation in the time elapsed to reach pyrolysis (Fig. 13).

There was no significant correlation between temperatures and elapsed times for the different flammability phases and the total monoterpene emissions (or content in *C. albidus*) (Table 4).

#### Discussion

For each shrubland species analysed, higher foliar hydration decreased flammability as shown in Figs 7-9, and in agreement with most studies linking the low risk of flammability to high water presence (Trabaud 1976; Owens et al. 1998; Massari and Leopaldi 1998; McKenzie et al. 2004). However, R. officinalis was the species with the highest hydration and still it reached pyrolysis at lower temperatures and in a shorter time than the other shrubland species, thus increasing the risk of fire for other plants. In the forest, C. albidus reached the pyrolysis phase at much lower temperatures and in a shorter time than the other species and thus presented the highest risk of initiating and propagating fire. R. officinalis showed lower temperatures in the pyrolysis phase than C. albidus (176 and 222°C respectively). Conversely, C. albidus reached pyrolysis earlier than R. officinalis (139 v. 209 s). Both species had the highest percentage of hydration in leaves during almost all the period sampled.



Fig. 7. Relationships between temperature, elapsed time and hydration (H) for the three phases of flammability (smoke, pyrolysis and flame) in *Pinus halepensis* from the shrubland site (Central Catalonia).

On the flammability scale among forest species, *P. latifolia* was more sensitive to flame than *Q. ilex*, and finally *C. albidus* was the least flammable of the four species studied in the forest. In fact, it did not reach the flame phase. *E. multiflora* and *P. halepensis* were the only shrubland species where leaves reached the flame phase. Interestingly, *E. multiflora* presented the lowest values of leaf hydration during all the period sampled when compared with other species at the same site. This species' water content is close to *Q. ilex* (84%) and *P. latifolia* (92%) and this confirms and reinforces the role of water availability and its importance regarding leaf flammability.

The time required to reach flame presented a clear seasonal trend in both sites (Figs 2f, 3d). During the warm and dry seasons, the time until flame appeared became shorter, increasing the plant fire risk. This seasonal variation in flammability has also been reported by Rodriguez Añón *et al.* (1995). Under wet conditions, species were less flammable, whereas in the summer, when water demands and transpiration were higher and plant hydration decreased, flammability increased. The seasonality of temperature and elapsed time for pyrolysis was clearer in *C. albidus* than in all other species. This species varied its leaf hydration quite severely, with a reduction of almost 70% from winter to the summer season (Fig. 4b). *E. multiflora* and

G. alvpum's seasonality showed a comparable decrease in hydration of  $\sim$ 50%, but other species did not show such strong differences even though their pyrolysis was related to their hydration. However, a decrease in hydration in a species such as P. latifolia was not influential for pyrolysis. A strong seasonality was found in the time to reach flame for the other three forest species, but not in flame temperatures. This is in accordance with the progressive increase in temperatures and water demand. During autumn and winter, there is high water availability provided by rainfall, lower temperatures and less evaporative demands, whereas during summer, Mediterranean plants are continuously subjected to high temperatures and lack of water. The lower summer leaf hydration increases foliar flammability. A. unedo had a lower flammability than C. albidus, which is in line with other reported observations (Massari and Leopaldi 1998). There was no clear relationship between these species-specific differences in flammability and their foliar hydration, so there must be some other factors influencing flammability. A. unedo was the least flammable species in the forest. The two shrubland species E. multiflora and P. halepensis presented similar elapsed times to reach flame as the forest species A. unedo during the summer period (August 2005). This makes P. latifolia and Q. ilex the most flammable species.



Fig. 8. Relationships between temperature, elapsed time and hydration (H) for the three phases of flammability (smoke, pyrolysis and flame) in *Erica multiflora* from the shrubland site (Central Catalonia).

Most plants in the Mediterranean basin are known to emit volatile terpenes. Those plants that emit terpenes may or may not have specialised structures where big pools of these volatile compounds are stored (Staudt et al. 1993; Seufert et al. 1995; Loreto et al. 1996; Llusià and Peñuelas 1998). In species that do not have such structures, these compounds are formed and emitted almost simultaneously. White (1994) suggests that leaves' organic volatile compounds may play a role in flammability. According to our observations (Fig. 2f), P. halepensis was more flammable than E. multiflora. The former species has large amounts of volatiles stored in resin ducts in its leaves. In contrast, E. multiflora does not have any kind of structures to store volatile compounds. This difference may suggest that plants with a high volatile content (generally storing species) are prone to fire, in particular as regards how quickly flame appears. In the case of the forest species, C. albidus may reach pyrolysis before other species. This could be because volatile compounds stored in the leaves decrease the time required. The other studied forest species do not store VOCs. No significant correlation was found between the annual changes in VOC emission and the annual changes in flammability for any of the species; therefore, the role of VOCs emissions in flammability seems to be limited. Although Owens *et al.* (1998) reported a relationship between flammability and volatile compounds, our results indicate uncertainties in this relationship in accordance with Cappelli *et al.* (1983).

P. halepensis and G. alypum presented larger volatile emissions than E. multiflora. The temperatures and time to reach the three flammability phases of E. multiflora were found to have a trend towards a negative correlation with monoterpenes and isoprene emissions. Flames appeared at lower temperatures whereas emissions of isoprenoids were high. Trabaud (1976) reported that a species like Quercus pubescens, which later proved to be an isoprene emitter, flamed quickly, even though hydration was high. White (1994) put forward the hypothesis that volatile compounds contained in leaves are implicated in leaf flammability; this presence may increase the risk of fire. Table 3 shows the correlations of terpene content and the phases of the flammability in the species analysed. The only significant relationship was with the time to reach flame in G. alypum. P. halepensis, the species with the highest monoterpene content, and the isoprene emitter E. multiflora were the most flammable species and this, as reported before, is consistent with White's (1994) expectations. However, these results of higher flammability of the species with



Fig. 9. Relationships between temperature, elapsed time and hydration (H) for the three phases of flammability (smoke, pyrolysis and flame) in *Pistacia lentiscus* from the shrubland site (Central Catalonia).

Table 3. Correlation coefficients of flammability variables with total monoterpene content and emissions in theshrubland species Rosmarinus officinalis, Globularia alypum, Pinus halepensis, Erica multiflora and Pistacia lentiscusSignificant correlations (P < 0.05) are highlighted in bold

| Total monoterpene content  | R. officinalis | G. alypum     | P. halepensis | P. lentiscus                       |
|----------------------------|----------------|---------------|---------------|------------------------------------|
| Smoke temperature (°C)     | 0.09           | -0.005        | 0.24          | -0.26                              |
| Smoke elapsed time (s)     | 0.07           | 0.01          | 0.10          | -0.37                              |
| Pyrolysis temperature (°C) | 0.22           | 0.41          | 0.09          | -0.43                              |
| Pyrolysis elapsed time (s) | 0.32           | 0.61          | 0.00          | -0.41                              |
| Flame temperature (°C)     | 0.19           | -0.36         | 0.01          | -0.72                              |
| Flame elapsed time (s)     | 0.44           | -0.85         | -0.11         | -0.66                              |
| Total monoterpene emission | G. alypum      | P. halepensis | E. multiflora | Isoprene emission<br>E. multiflora |
| Smoke temperature (°C)     | -0.5           | 0.27          | -0.45         | -0.29                              |
| Smoke elapsed time (s)     | -0.14          | 0.25          | -0.44         | -0.31                              |
| Pyrolysis temperature (°C) | -0.48          | 0.36          | -0.46         | -0.31                              |
| Pyrolysis elapsed time (s) | 0.02           | -0.02         | -0.55         | -0.48                              |
| Flame temperature (°C)     | -0.59          | 0.65          | -0.52         | -0.37                              |
| Flame elapsed time (s)     | -0.19          | 0.49          | -0.65         | -0.61                              |

the highest monoterpene content and emission were only found in shrubland, and not in the forest.

Climatic and ecophysiological models project more arid conditions in coming decades in the Mediterranean region (IPCC 2001; Sabaté *et al.* 2002; Peñuelas *et al.* 2005). Therefore, according to the results of the present study, the lack of water availability may increase flammability and fire risks. According to our measurements, those leaves with lower hydration may accelerate the appearance of flames, consequently increasing the propagation of fires (McKenzie *et al.* 2004). Water status depends on water availability, and on the extension of plant root systems to reach water available in deeper soil layers when shallow reserves dry out during the summer season. Those species that keep their levels of foliar hydration and suffer less water stress (Alessio *et al.* 2004) are certainly less prone to fire.

#### Conclusions

The most flammable species in the two studied ecosystems, the shrubland and the forest, were *P. halepensis*, *E. multiflora* and *P. latifolia* followed by *Q. ilex*. The impact of the increase in



Fig. 10. Relationship of temperature, elapsed time until pyrolysis and flame phases and foliar hydration (H) in *Arbutus unedo* from the holm oak forest in Prades (Southern Catalonia). Each value is the mean of n = 3 measurements.



**Fig. 11.** Relationship of temperature, elapsed time until the pyrolysis and flame phases and foliar hydration (H) in *Quercus ilex* from the holm oak forest in Prades (Southern Catalonia). Each value is the mean of n = 3 measurements.



Fig. 12. Relationship of temperature and elapsed time until the pyrolysis and flame phases and foliar hydration in *Phillyrea latifolia* from the holm oak forest in Prades (Southern Catalonia). Each value is the mean of n = 3 measurements.



Fig. 13. Relationship of temperature, elapsed time until the pyrolysis and flame phases and foliar hydration in *Cistus albidus* from the holm oak forest in Prades (Southern Catalonia). Each value is the mean of n = 3 measurements.

temperature and decrease of water availability projected for the next decades may produce an increase in flammability of these shrubland and forest species, especially in those that store volatile compounds. Flammability strictly depends on leaf water availability, as demonstrated with all species, but the present study also suggests some role of volatile terpene content and emission in flammability. For example, *G. alypum* plants containing more monoterpenes were more flammable, and were quicker to flame.

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## Table 4. Correlations between the temperature and elapsed time until each one of the three flammability phases, and total monoterpene content and emissions in the forest species

None of the correlations was significant at P < 0.05; n.d., not detected

|                            | Cistus albidus<br>Emissions | Content | Phillyrea latifolia<br>Emissions | <i>Quercus ilex</i><br>Emissions |
|----------------------------|-----------------------------|---------|----------------------------------|----------------------------------|
| Smoke temperature (°C)     | -0.01                       | 0.27    | -0.21                            | 0.18                             |
| Smoke elapsed time (s)     | 0.26                        | 0.06    | -0.11                            | 0.33                             |
| Pyrolysis temperature (°C) | 0.27                        | -0.25   | -0.44                            | -0.13                            |
| Pyrolysis elapsed time (s) | 0.53                        | -0.35   | -0.12                            | -0.23                            |
| Flame temperature (°C)     | n.d.                        | n.d.    | -0.42                            | -0.16                            |
| Flame elapsed time (s)     | n.d.                        | n.d.    | -0.12                            | -0.36                            |

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