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Is eucalyptol the cause of nocturnal events observed in Australia?

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Nocturnal nucleation events were observed from July 2005 to October 2006 in Tumbarumba in New South Wales, Australia. These events were observed on one third of the nights and they were often much more intense than normal daytime events. One of the main features found in this environment was the abundance of eucalyptol among the volatile organic compounds (VOC) emitted by the local Eucalypt forest. In contrast, in most other forest environments, such as Hyytiälä in southern Finland, eucalyptol is a minor component of VOC emissions. Therefore, the objective of this study was to evaluate the role of eucalyptol in the nocturnal nucleation events. For this purpose, a series of experiments and quantum mechanical calculations were performed. Both approaches showed that the role of eucalyptol in the nocturnal events can be ruled out.

Introduction

Aerosols are ubiquitous in the Earth's lower atmosphere. They affect human health, visibility, atmospheric chemistry and climate. Aerosols influence climate directly by scattering and absorbing radiation, and indirectly by acting as cloud condensation nuclei and affecting cloud properties. Gas-to-particle nucleation is an important source of new aerosol particles in the Earth's atmosphere (Kulmala *et al*. 2004a). This phenomenon has been the subject of intense studies in the last years, but the formation mechanism and the participating substances have not been resolved yet. A strong correlation has been observed between new-particle formation and sulfuric acid concentrations (Weber *et al*. 1996, Weber *et al*. 1997, Kulmala *et al*. 2000, Sihto *et al*. 2006, Riipinen *et al*. 2007). However, in many cases the observed rates of particle formation are much higher than the rates expected for binary homogeneous sulfuric acid-water nucleation. Different additional processes have been proposed to explain this difference, such as homogeneous ternary water-sulfuric acid-ammonia nucleation (Ball *et al*. 1999, Korhonen *et al*. 1999, Anttila *et al*. 2005) participation of organic molecules (Yu *et al*. 1999, Hoffmann *et al*. 1998) and ion induced nucleation (IIN) (Lovejoy *et al*. 2004, Yu and Turco 2000 and 2008, Boy *et al*. 2008). The contribution of IIN to the total number of particle formed is still under discussion. Examples are the studies by Yu and Turco (2008), Kulmala *et al*. (2007) and Boy *et al*. (2008) carried out at the same measuring site, the first one concluded that the contribution of IIN to new formed particle is close to 100% while the second and third studies concluded that the contribution of INN is less than 10%. This shows how uncertain our ability is to quantify the contribution of one process to the total amount of newly formed particles. On the other hand, the recently suggested activation theory (Kulmala *et al*. 2006) is able to explain atmospheric nucleation relatively well.

Organic volatile compounds (VOCs) have been suggested to contribute to the growth of nucleated clusters (O'Dowd *et al*. 2002, Kulmala *et al*. 2004b), although a recent work by Bonn *et al*. (2008) proposes that the VOCs can also be implied in the formation of the clusters from the very first steps.

Nucleation events are in most cases observed during daytime but in some locations they can occur also during the night. In Tumbarumba in New South Wales, Australia, these nocturnal events are very intense and frequently observed (32% of the nights in 2006; Suni *et al*. 2008). If we compare Tumbarumba with other sites where the nocturnal events have been observed but where they are much less intense and less frequent, like Hyytiälä in southern Finland (Junninen *et al*. 2008), one of the main differences turns out to be the composition of the forest. The forest in Tumbarumba is composed mainly of eucalypt trees and that in Hyytiälä of Scots pine. As a result, also the emitted VOCs are different. In Tumbarumba the most abundant monoterpene was eucalyptol (1,8-cineol), whereas in Hyytiälä carene, α- and β-pinene were emitted the most. Another clear difference between these two environments is the higher concentration of radon found in Tumbarumba.

The objective of this study was to evaluate the possible role of eucalyptol in nocturnal new particle formation. We designed a series of chamber experiments with the objective to reproduce the nocturnal events observed in Australia. Additionally, we used quantum chemical calculations to study the molecular mechanism behind the nocturnal nucleation events.

Material and methods

Experimental setup

We conducted the experiments in a 14-m^3 isolated room that was ventilated with an air flow of 40 liters per minute. The flow could optionally be piped through a small tank which contained a radon source to introduce up to 2000 Bq m^{-3} of radon in the room. The radon (^{222}Rn) concentration was continuously measured using a radon monitor Alphaguard P 30 (Genitron Instruments). Temperature and relative humidity conditions inside the room were monitored using Delta OHM DO 9847 logger with capacitive Mk-33 and Pt100 sensors.

We placed an Air Ion Spectrometer (AIS) inside the chamber to obtain the number size distribution of negative and positive air ions. The instrument is designed to make simultaneous ion distribution measurements of both polarities over a mobility range of 3.2–0.0013 cm^2 V^{-1} s^{-1}. The mobility distribution is divided to 27 logarithmically uniform bins which correspond to a Millikan diameter range of 0.8–40 nm. Mirme *et al*. (2007) give the details of this instrument and data inversion.

O_3 and SO_2 concentrations inside the room were measured with a Dasibi Model 1008-RS UV-absorption ozone photometer and a pulsed fluorescence SO_2 analyzer model 43C (Thermo Environmental Instruments, Inc.). A small piece of seal on the side of the chamber window was removed to allow closing the window and yet leading the inlet tubes (PTFE-Teflon) inside the chamber through the hole in the seal.

The concentration of volatile organic compounds (eucalyptol) was determined using Tenax-TA/carbopackB adsorbent tubes. We pumped air from the room through the Tenax tubes for 10 minutes with a constant flow of 100 ml per minute. The samples were analyzed afterwards in a laboratory using an automatic thermodesorption device connected to a gas chromatograph (HP-5890) and a mass spectrometer (HP-5972).

Theoretical method

Our calculations were performed using a systematic multi-step method recently developed by our group. This method is described elsewhere (Ortega *et al.* 2008), so only the relevant details are given here.

The multi-step method allows the study of clusters containing a large organic molecule and up to four sulfuric acid molecules using a reasonable amount of computing time. In this study, the initial guess geometries were chosen by using chemical intuition. These structures were pre-optimized at a low level of theory using SPARTAN program (http://wavefun.com). Then the more stable isomers among all initial guesses (usually between 3 and 4) were optimized with the SIESTA program (Soler *et al.* 2002), using the gradient-corrected BLYP functional (Miehlich *et al.* 1989) and the double-ζ polarized (DZP) functions. Vibrational harmonic frequencies were also calculated using SIESTA and were used to estimate the entropy and thermal contributions to the enthalpy and Gibbs free energy of the clusters.

To obtain a reliable energy, the optimized structures obtained from the SIESTA program were used to perform high-level, single-point energy calculations by using the TURBOMOLE program (Ahlrichs *et al.* 1989) with the Resolution of Identity-Coupled Cluster Single and Doubles method (RI-CC2) (Hättig *et al.* 2000) and the aug-cc-p$V(T+d)Z$ (Dunning *et al.* 2001) basis set, which is identical to aug-cc-pVTZ for hydrogen, oxygen and nitrogen atoms, and contains one extra set of d-orbitals for the sulfur atoms.

The calculated values for entropy and thermal contributions to the enthalpy and Gibbs free energy (ΔG) of the clusters were calculated assuming a pressure of 1013 hPa for the monomers. In order to obtain a realistic picture of the free energies in atmospheric conditions, we have to take into account the relative concentration of each molecular species in atmosphere. This was done via the law of mass action as showed in Ortega *et al.* (2008).

Results and discussion

Experimental results

We carried out different repetitive chamber experiments all leading to the same results, so only two examples are shown. In the first example we used only eucalyptol in the chamber, whereas in the second one we used eucalyptol and radon to simulate the high concentration of radon found in Tumbarumba.

Eucalyptol experiments

We carried out the first experiment on 7 April 2008. We used 1 ml of 99% pure eucalyptol (Sigma-Aldrich) in a glass container cooled with ice in order to decrease the vapor pressure of eucalyptol and keep the amount of eucalyptol introduced into the chamber as low as possible.

Before introducing the eucalyptol in the chamber, we took two Tenax tube samples to check the background concentration of organics in the chamber. The concentrations of all organic compounds measured were below 0.6 ng l^{-1}.

The eucalyptol was introduced in the chamber at 11:12. After four hours no event was observed (Fig. 1). Three Tenax tube samples were taken during that period (Table 1).

Within the first half hour we got a burst of eucalyptol, and after one hour its concentration dropped to around 10 ng l^{-1} (4×10^{10} cm^{-3}) at which level it appeared to remain. The highest concentration of eucalyptol found in Tumbarumba was 0.29 ng l^{-1} (1.13×10^{9} cm^{-3}) during the night, so the concentration in our experiments was around 30 times higher.

The conditions after the eucalyptol was introduced in the chamber were quite constant (Fig. 2), with the relative humidity between 27% and 31%, temperature between 26 and 29 °C, SO_2 concentration around 0.2 ppb (4.93×10^{9} cm^{-3}) and ozone concentration between 2 and 14 ppb (1.97×10^{11} cm^{-3}).

In Tumbarumba, ozone and SO_2 were only measured during an intensive campaign in November 2006 (T. Suni unpubl. data). At that time, the ozone concentration ranged from 10 to

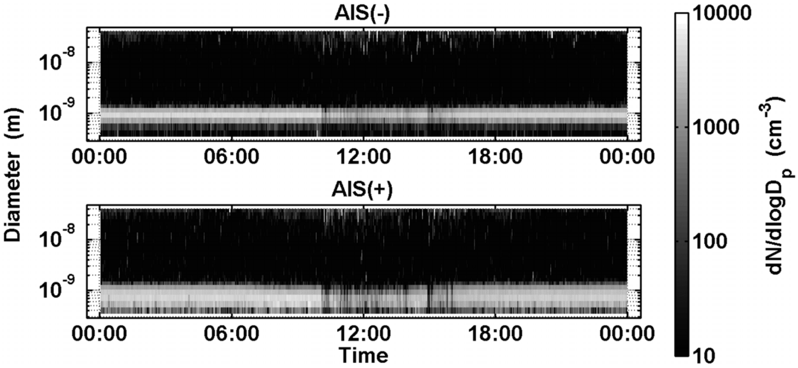

Fig. 1. Surface plot of air ion distribution measured on 7 April 2008 over size range of 0.34–40 nm in the Tammet diameter (Tammet *et al.* 1995)

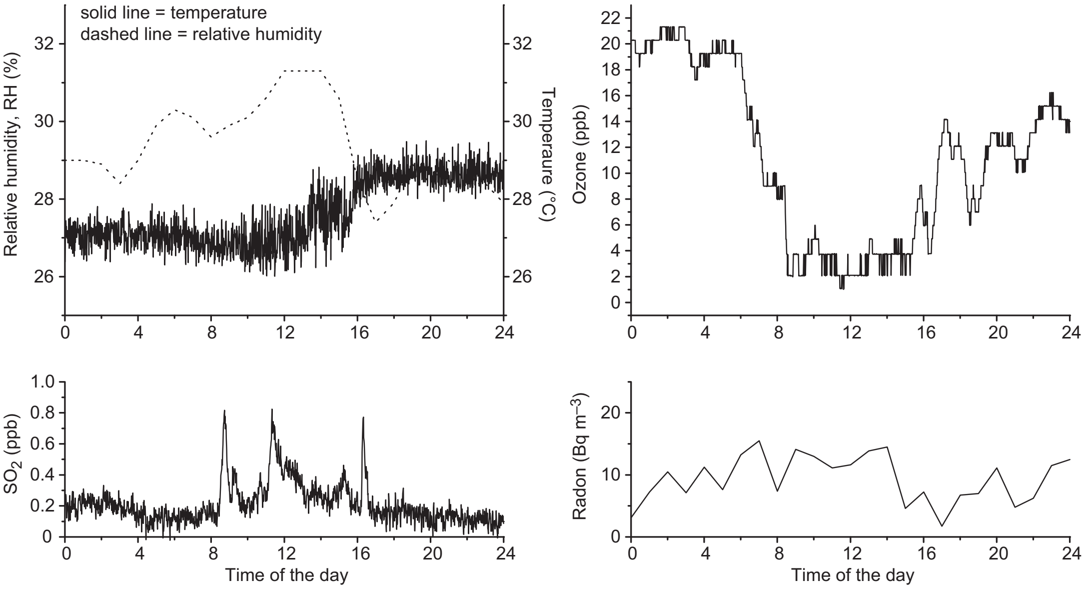

Fig. 2. Results of measurements on 7 April.

30 ppb even at night and the SO_2 concentration was around 0.2 ppb. These concentrations were similar to those in our experiment.

The lowest relative humidity found in the field during nocturnal events was 35%. The relative humidity in our experiment was slightly lower. Some recent studies on the role of humidity in nucleation events indicate that lower relative humidity in this range could favor the nucleation (Buzorius *et al.* 2001, Nilsson *et al.* 2001, Boy *et al.* 2002, Bonn *et al.* 2002, 2003, Hyvönen *et al.* 2005, Suni *et al.* 2008). So, the lower relative humidity in our laboratory experiment should lead to more, not less, frequent nucleation events than in the field.

The temperature during the experiment was 3 to 5 °C higher than the highest temperature found during the nocturnal events in Tumbarumba (23 °C). On the other hand, the concentration of eucalyptol in our experiments was 30 times higher than in the real atmosphere, so the

Table 1. Eucalyptol concentration during two hours after introducing it into the chamber.

Time	(ng l^{-1})	(cm^{-3})
11:50	47.48	1.85×10^{11}
12:50	10.87	4.24×10^{10}
13:50	9.33	3.64×10^{10}

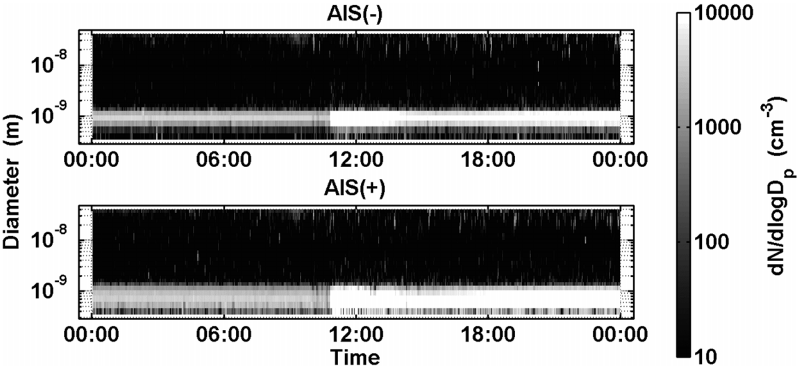

Fig. 3. Surface plot of air ion distribution measured on 8 April 2008 over size range of 0.34–40 nm in the Tammet diameter (Tammet *et al.* 1995)

negative effect caused by the higher temperature could have been compensated somewhat by the higher concentration of eucalyptol.

Radon experiment

To simulate the high concentration of radon observed in Tumbarumba (up to 100–200 Bq m^{-3} at night), we added radon in the chamber on 8 April (Fig. 3).

The air flow into the chamber via the tank containing the radon source was turned on and set up to 40 liters per minute at 10:46. One ml of eucalyptol was introduced into the chamber at the room temperature to obtain a higher concentration. At the start of the experiment, we observed a big burst of radon that had accumulated in the tank containing the radon source. The concentration reached a maximum of 2200 Bq m^{-3} and dropped then to around 500 Bq m^{-3} (Fig. 4). The eucalyptol concentrations was measured two times after the input of radon during five hours and the concentration was 20 and 25 ng l^{-1} (7.8×10^{10} and 9.7×10^{10} cm^{-3}).

The temperature increased to a maximum of 32 °C because the chamber door needed to be shut to keep radon inside the chamber, and the heat from the instruments warmed up the air quickly. As a result, also the relative humidity decreased to 25%. Ozone and SO_2 concentrations were around 8 ppb (1.97×10^{11} cm^{-3}) and from 0.1 to 0.2 ppb (4.93 to 9.86×10^{9} cm$^{-3)}$, respectively.

The presence of radon clearly increased the concentration of small ionic clusters. However, it was not able to induce any nucleation events even with a high concentration of eucalyptol.

These two experiments showed that eucalyptol was not able to create any particles, even in the presence of radon. To understand better the reasons behind these results, we performed some quantum mechanical calculations to study the molecular mechanism behind these results in detail.

The oxidation rates of eucalyptol (table 1 in Calogirou *et al.* 1998) show that the absence of a double bond makes its oxidation by NO_3 and ozone quite difficult. The only oxidant that reacts with eucalyptol at a similar rate as with monoterpenes is the OH radical. However, since we are dealing with nocturnal events, this path has no relevance for our study. Consequently, we limited our calculations to the eucalyptol molecule.

Quantum chemical calculations

The most stable configuration for each cluster composition was obtained using the SIESTA program with the BLYP functional and the DZP basis set (Fig. 5). The structures have been drawn using the MOLDEN 3.8 visualization package (Schaftenaar *et al.* 2000). The values of ΔG were obtained (with respect to formation from free molecules) at 298 K and with monomer pressures of 1013 hPa for clusters containing only sulfuric acid and clusters containing one molecule of eucalyptol (Table 2).

If we compare the formation energies for clusters containing the same number of sulfuric acid molecules (n), we see how adding one molecule of eucalyptol leads to a more negative

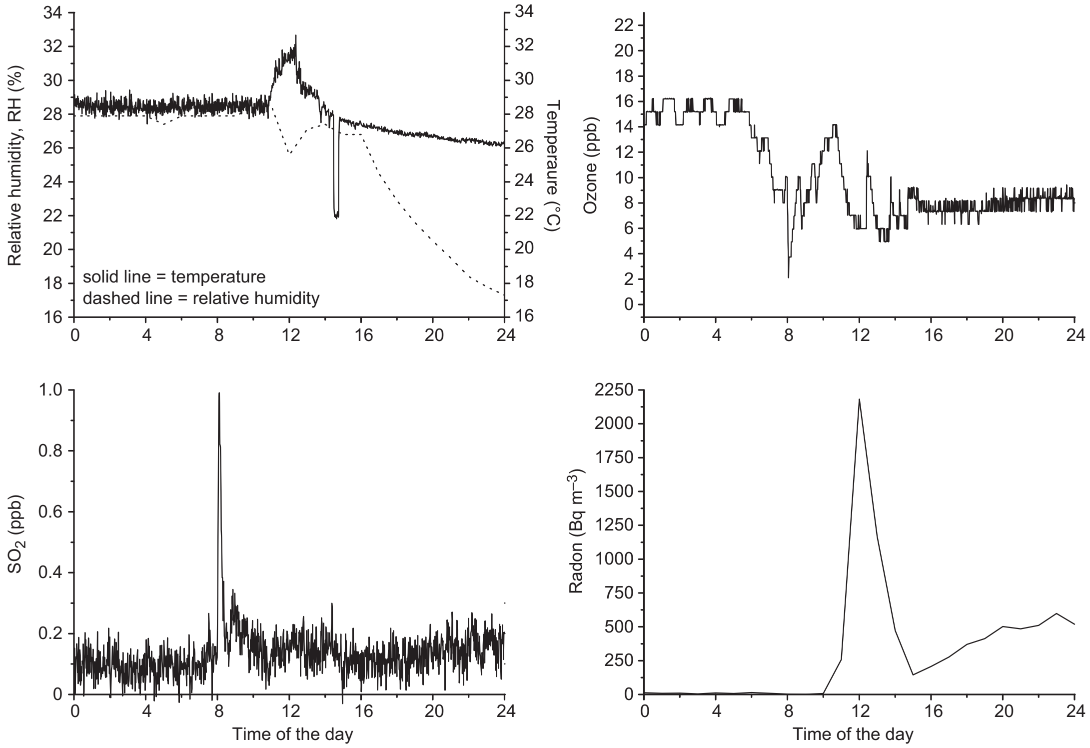

Fig. 4. Results of measurements on 8 April.

value of ΔG. The biggest difference was found for clusters containing three sulfuric acid molecules, for which the formation of clusters containing eucalyptol was around 7 kcal mol^{-1} more favorable. For largest clusters containing four sulfuric acid molecules, this difference dropped to the value of 2 kcal mol^{-1}.

To understand the thermochemistry further, we also calculated the reaction free energies for the addition of one sulfuric acid molecule to the different clusters (Table 3). The addition of a second molecule of sulfuric acid to a monosulfuric acid cluster was slightly less favorable when a molecule of eucalyptol was present in the cluster (less than 1 kcal mol^{-1}). For clusters with two molecules of sulfuric acid, this effect was opposite: adding a third molecule of sulfuric acid was easier (around 2.5 kcal mol^{-1}) for clusters containing eucalyptol. For the addition of a fourth molecule for sulfuric acid, the energies for both clusters were virtually the same (difference of 0.21 kcal mol^{-1}).

The free energies for complexation at standard conditions (Table 2) cannot be directly used to explain the nucleation-enhancing effect of eucalyptol. The free energy of cluster formation depends also on the relative atmospheric concentration of each molecular species in the atmosphere through the law of mass action (Ortega *et al*. 2008). So, the values of ΔG (Table 2) have to be corrected using atmospheric realistic concentrations. We chose a set of conditions to fit the conditions normally found in Tumbarumba

Table 2. Formation free energies at RI-CC2/Aug-cc-p*V*(*T* + *d*)*Z* level, temperature of 298 K and monomers pressure of 1013 hPa. The first column indicates the number of sulfuric acid molecules, the second column gives the free energy for a cluster consisting of sulfuric acid only, and the third column gives the free energy for a cluster with an additional eucalyptol molecule.

n	$(H_2SO_4)_n$ (kcal mol^{-1})	$C_{10}H_{18}O \times (H_2SO_4)_n$ (kcal mol^{-1})
1		–5.13
2	–6.18	–10.35
3	–9.58	–16.40
4	–12.78	–14.97

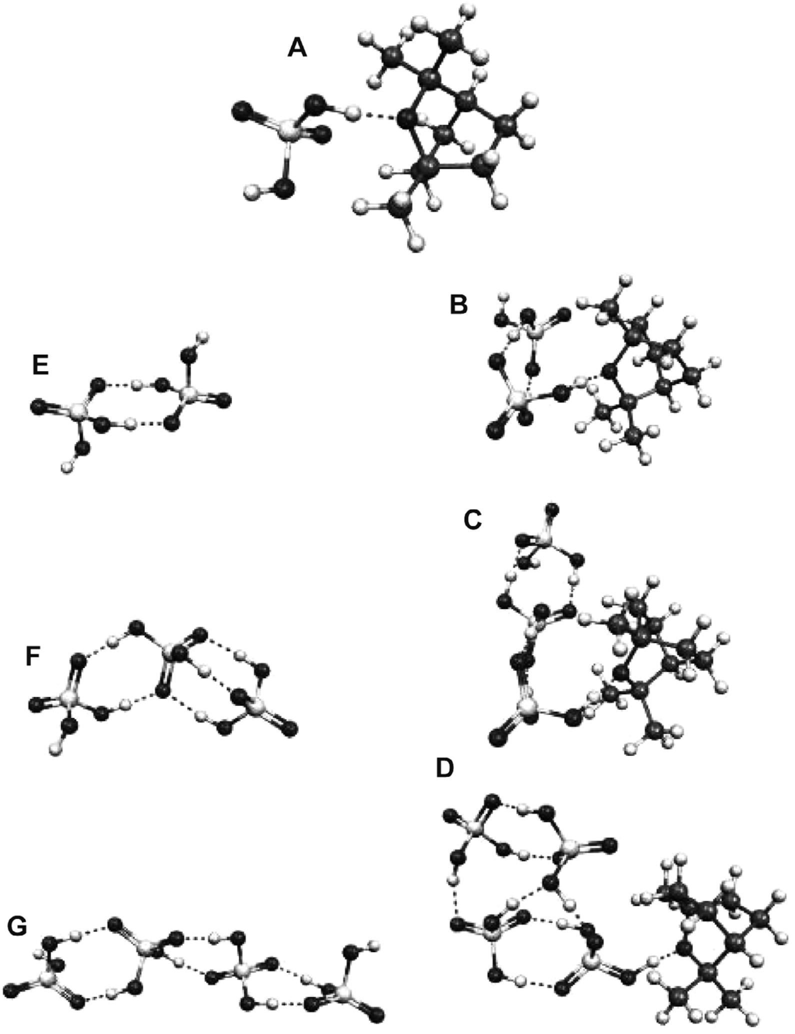

Fig. 5. Structures of the most stable cluster configurations obtained with the SIESTA model. **A**, **B**, **C** and **D** represent clusters with one molecule of eucalyptol and one to four molecules of sulfuric acid, respectively. **E**, **F** and **G** represent clusters containing from two to four sulfuric acid molecules, respectively. Black atoms correspond to oxygen, light grey to sulfur, dark grey to carbon and white to hydrogen.

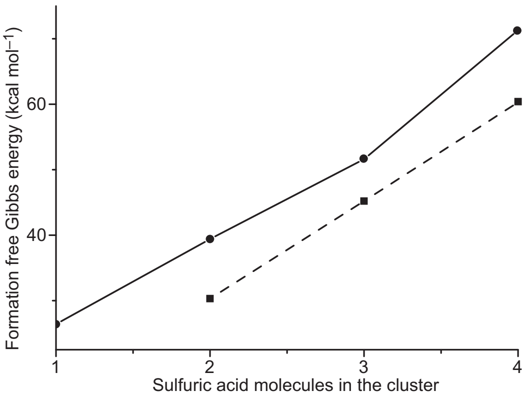

Fig. 6. Corrected values of ΔG *versus* number of sulfuric acid molecules in the cluster plots, dashed line corresponds to pure sulfuric acid clusters, and solid line corresponds to clusters containing one molecule of eucalyptol.

(Suni *et al*. 2008): 10^6 cm^{-3} of sulfuric acid calculated by a pseudo-steady state chemical box-model (Boy *et al*. 2005), 200 ppt (4.9×10^{10} cm^{-3}) of eucalyptol (corresponding roughly to the maximum concentration of eucalyptol found in Australia) and temperature of 298 K. These corrected values of ΔG (Table 4) can be presented as a function of the number of sulfuric acid molecules in the cluster (Fig. 6).

If we now take into account the corrected ΔG values obtained using the concentration of different species in the atmosphere (Table 4), the pure sulfuric acid clusters are more stable than clusters containing eucalyptol.

This difference is even more evident in the largest clusters we studied: the clusters contain-

Table 3. Formation free energy for addition of one sulfuric acid.

Reaction	ΔG (kcal mol^{-1})
$C_{10}H_{18}O + H_2SO_4 \rightarrow C_{10}H_{18}O \times H_2SO_4$	–5.13
$C_{10}H_{18}O \times H_2SO_4 + H_2SO_4 \rightarrow C_{10}H_{18}O \times (H_2SO_4)_2$	–5.22
$C_{10}H_{18}O \times (H_2SO_4)_2 + H_2SO_4 \rightarrow C_{10}H_{18}O \times (H_2SO_4)_3$	–6.04
$C_{10}H_{18}O \times (H_2SO_4)_3 + H_2SO_4 \rightarrow C_{10}H_{18}O \times (H_2SO_4)_4$	–3.41
$H_2SO_4 + H_2SO_4 \rightarrow (H_2SO_4)_2$	–6.18
$(H_2SO_4)_2 + H_2SO_4 \rightarrow (H_2SO_4)_3$	–3.40
$(H_2SO_4)_3 + H_2SO_4 \rightarrow (H_2SO_4)_4$	–3.20

ing four sulfuric acid molecules and one eucalyptol were less stable (11 kcal mol^{-1}) than those containing only sulfuric acid. The nucleation barrier was smaller for clusters containing only sulfuric acid than for clusters containing also eucalyptol (Fig. 6).

The results presented above are in a complete agreement with those obtained earlier in the experiments where we were not able to produce any events using eucalyptol. This observation is not surprising, considering that eucalyptol has only one oxygen atom available to interact with sulfuric acid molecules and that the position of the oxygen within the molecule makes this interaction even more difficult. A more oxidized molecule containing more functional groups, like a carboxylic acid, should be a better candidate for atmospheric nucleation than eucalyptol. Furthermore, the absence of a double bond in eucalyptol makes its oxidation by ozone impossible. Our conclusion is, therefore, that we have to look for the explanation of nocturnal events elsewhere, in other monoterpenes.

Conclusions

Eucalyptol is one of the most abundant organic compounds emitted from the eucalypt forest in Tumbarumba. The aim of this work was to study the role that eucalyptol could have in the nocturnal formation of new particles. We performed chamber experiments and quantum mechanic calculations to evaluate the importance of eucalyptol in this regard.

We were not able to induce any nucleation event using eucalyptol under conditions similar to those observed in Tumbarumba. Theoretical results indicated also that the eucalyptol cannot stabilize sulfuric acid clusters. Hence, both experimental and theoretical studies led to the same conclusion: the presence of eucalyptol does not enhance the nucleation of sulfuric acid clusters. According to our results, the participation of eucalyptol in nocturnal events can be ruled out.

Table 4. Formation free energies (kcal mol^{-1}) at the temperature of 298K, $[H_2SO_4] = 10^6$ cm^{-3} and $[C_{10}H_{18}O]$ = 200 ppt. The first column indicates the number of sulfuric acid molecules, the second column gives the free energy for a cluster consisting of sulfuric acid only and the third column gives the free energy for a cluster with an additional eucalyptol molecule.

n	$(H_2SO_4)_n$	$C_{10}H_{18}O \times (H_2SO_4)_n$
1		26.4
2	30.3	39.4
3	45.2	51.6
4	60.3	71.3

The explanation for the nocturnal events remains open. The most likely candidates for nocturnal events are VOCs containing one or more double bonds and having large enough oxidation rates. Therefore, further work in this direction is necessary: the work presented here should be repeated using different monoterpenes under dark conditions.

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