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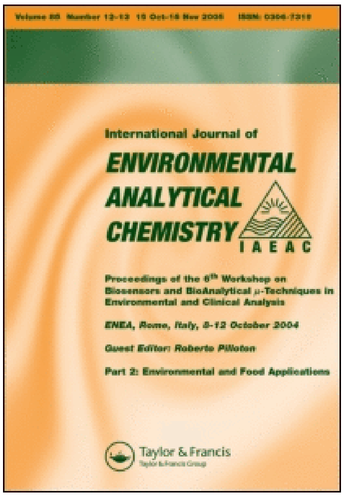

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MEASUREMENTS OF BIOGENIC HYDROCARBONS AND THEIR ATMOSPHERIC DEGRADATION IN FORESTS

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An analytical procedure for the sampling and quantitative determination of biogenic hydrocarbons in the atmosphere is presented. The method is based on the adsorptive preconcentration of the hydrocarbons using Tenax TA/Carbopack B filled sampling tubes followed by thermodesorption of the trapped compounds and gas chromatographic analysis. To avoid losses of the biogenic alkenes as a consequence of their reaction with ozone on the adsorbents during the sampling step, an ozone scrubber is used in front of the adsorption tubes. Diurnal variations of the monoterpene- and ozone-concentrations are determined at different heights in and above a forest stand (coniferous and deciduous trees) in the Vosges (Col du Donon, 760 m a.s.l.) in order to elucidate the importance of terpene-oxidation reactions on the formation of peroxidic products in forest air.

KEY WORDS: Biogenic hydrocarbons, atmospheric chemistry, forest decline, air sampling, thermodesorption, GC-MS.

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INTRODUCTION

Natural sources, like deciduous and coniferous forests, are responsible for the release of substantial amounts of reactive hydrocarbons to the atmosphere. Estimations on the global emission of these compounds, dominantly isoprene and monoterpenes, have shown that the vegetation surpass anthropogenic activities as a source for non-methane-hydrocarbons (NMHC's).[1] Besides the influence of natural NMHC's on the global and regional budgets of photochemical oxidants, carbon monoxide, hydrogen and possibly organic aerosols, biogenic hydrocarbons are suspected to be involved in the mechanism by which ozone damages plants.[2,3]

Due to their unsaturated character natural NMHC's react readily with ozone[4], but also with other oxidising tropospheric species like OH- and NO_3-radicals.[5,6] Consequently, the products of these reaction are formed close to the leaves and needles of the plants. Recent laboratory investigations have shown the formation of considerable amounts of hydrogen peroxide[7] and organic peroxides[8,9] as a consequence of the terpene-ozone reaction (Figure 1), compounds whose phytotoxic properties are well documented.[10] The observation of

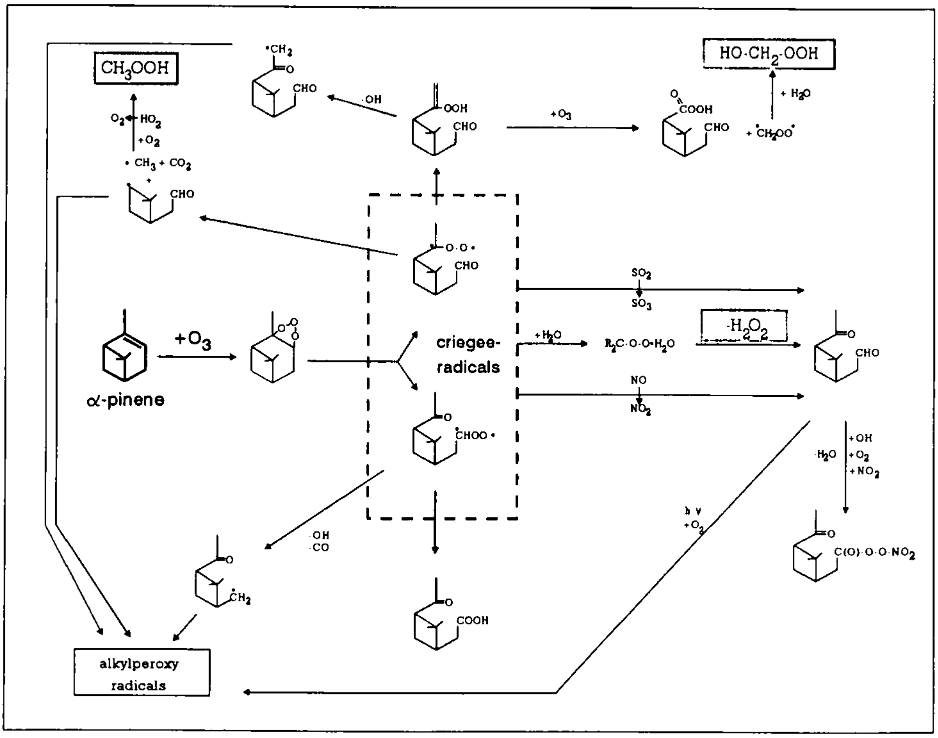

Figure 1 Gas-phase ozonolysis of α-pinene - Formation of possible products.

elevated H_2O_2-concentrations inside forests in comparison to those measured outside[11] supports the presumption of a link between the terpene-ozone reaction and tree injury. This is why we focused our investigations on the development of a reliable sampling and determination technique for the detection of isoprene and monoterpenes in order to carry out field measurements of terpenes and terpene degradation in forests.

EXPERIMENTAL

Sampling and determination of atmospheric biogenic hydrocarbons

Special effort has been made to determine the losses of trapped species during sampling by their reaction on the adsorbent with ozone. The results have shown that ozone scrubbing prior to the preconcentration step is necessary, otherwise a underestimation of the more reactive terpenes (e.g. α-pinene, limonene) is unavoidable.[12,13]

Therefore, a technique based on the adsorptive preconcentration on two adsorbents (Tenax TA/Carbopack B), combined with an ozone scrubber (using a MnO_2-coated copper-screen) in front of the sampling tubes has been chosen for the measurement of biogenic

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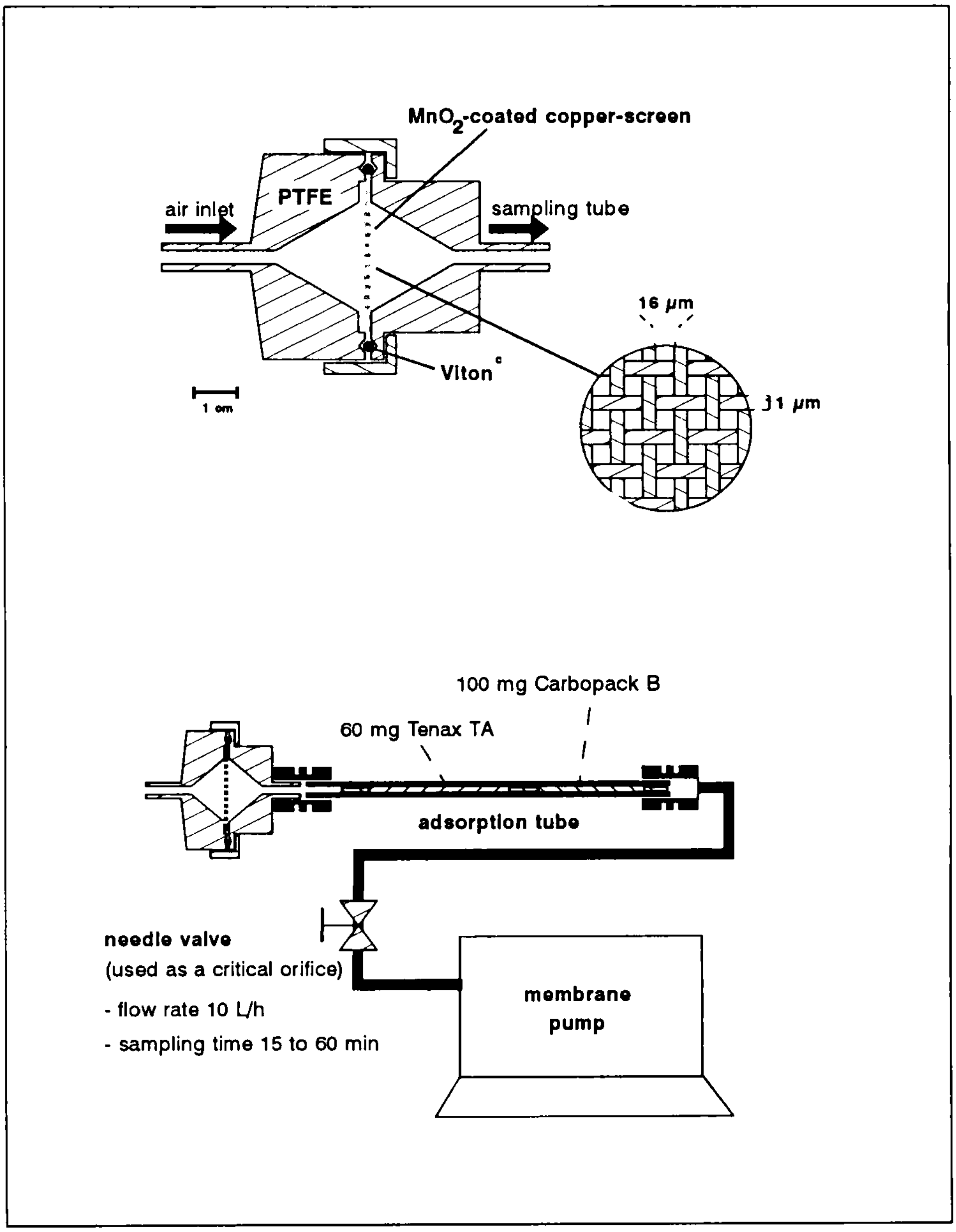

Figure 2 Sampling device.

hydrocarbons (Figure 2). The complexity of the composition of ambient air requires the use of a HRGC-separation (50m DB-5, 0.32 mm i.d.) coupled with a mass spectrometric detector (ion trap). The thermally desorbed components are concentrated automatically in a cryotrap and afterwards injected into the capillary column by computer-controlled heating of the trap.

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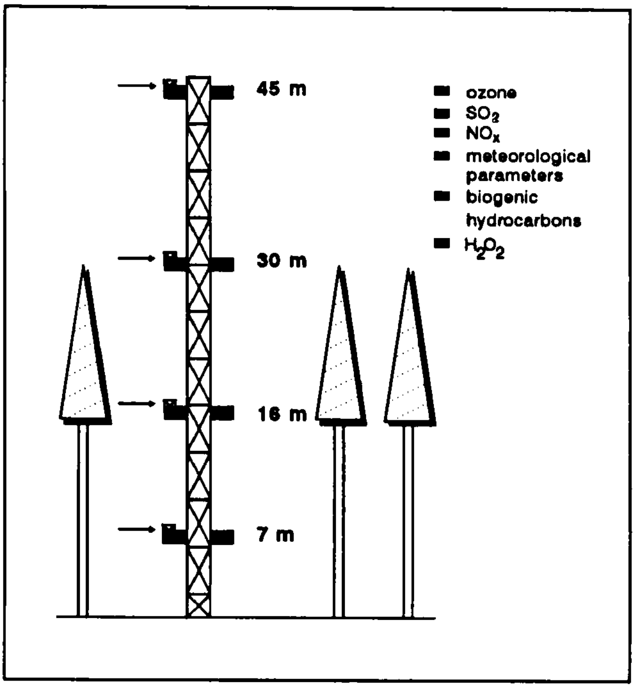

Figure 3 Air pollution monitoring station 'Col du Donon' (Vosges, France).

The eluted substances were monitored by their typical fragment ions (e.g. isoprene m/z 67–68, monoterpenes m/z 93) and identified by comparison of their full scan mass spectra and retention times with reference compounds.

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RESULTS AND DISCUSSION

Several measurement campaigns were carried out at an air pollution monitoring station in the Vosges (Col du Donon, 760 m a.s.l.) to investigate isoprene and monoterpene concentrations as well as their degradation in and above forests. At this location, meteorological parameters as well as the concentrations of some trace gases (O_3,SO_2, NO_2 and NO) are constantly monitored at 4 heights along a 46 m tall tower within a mixed deciduous/coniferous forest (Figure 3). Subsequently some results of these field studies are represented.

Typical species in forest air are isoprene, α-pinene, β-pinene, camphene, d-3-carene, myrcene, d-limonene, tricyclene and 1,8-cineole.

The concentrations of the individual terpenes depend on the season, temperature and time of day and range from a few ppt(V/V) in winter up to several ppb(V/V) (for the most abundant monoterpene α-pinene) during the warmer months.

The isoprene concentrations showed a distinct diurnal variation with high values during the day and a negligible nocturnal mixing ratios. Therefore, the isoprene release from the plants seems to be influenced dominantly by the actual light intensity.

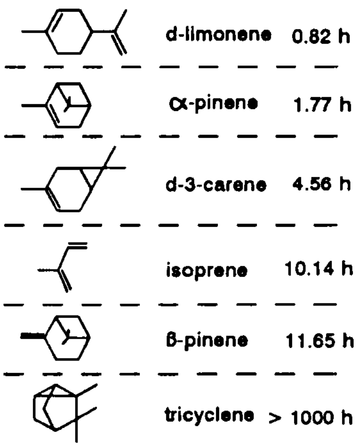

Figure 4 Atmospheric lifetimes of some biogenic HC's[4] ($[O_3]=60$ ppb(V/V)).

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The same behavior was observed for two monoterpenes, sabinene and thujene, both C_{10}-hydrocarbons with a thujan-skeleton. Evidently the emission characteristics of these substances differed in comparison to other monoterpenes, most probably caused by a different route of their biosynthesis in the plants. The possibility of an exclusive light-dependent emission of some monoterpenes from plants should be taken into account for the evaluation of emission scenarios.

Frequently a distinct negative correlation between the mixing ratios of reactive monoterpenes (e.g. α-pinene) and ozone has been observed. In order to exclude the possibility that this diurnal variation is controlled only by the stability and thickness of the boundary layer, the relation of different reactive monoterpenes in forest air was determined. For this reason the amounts of tricyclene, α-pinene and β-pinene were measured. Tricyclene is a saturated monoterpene and therefore a negligible fraction of this HC is influenced by the reaction with ozone. Figure 4 gives the structures and atmospheric lifetimes[4], regarding their reaction with O_3($[O_3]=60$ ppb(V/V)), of the most important biogenic hydrocarbons.

The observation of low values of the [α-pinene]/[tricyclene]-ratio during elevated ozone episodes and high values when the ozone concentration is low, strongly indicates the influences of chemical reactions on the concentrations of the more reactive terpenes (Figure 5A). In contrast, the concentrations of the less reactive monoterpenes (e.g. β-pinene) are affected in a lesser extent by the reaction with ozone (Figure 5B), an observation that correlates well with their atmospheric reactivity.

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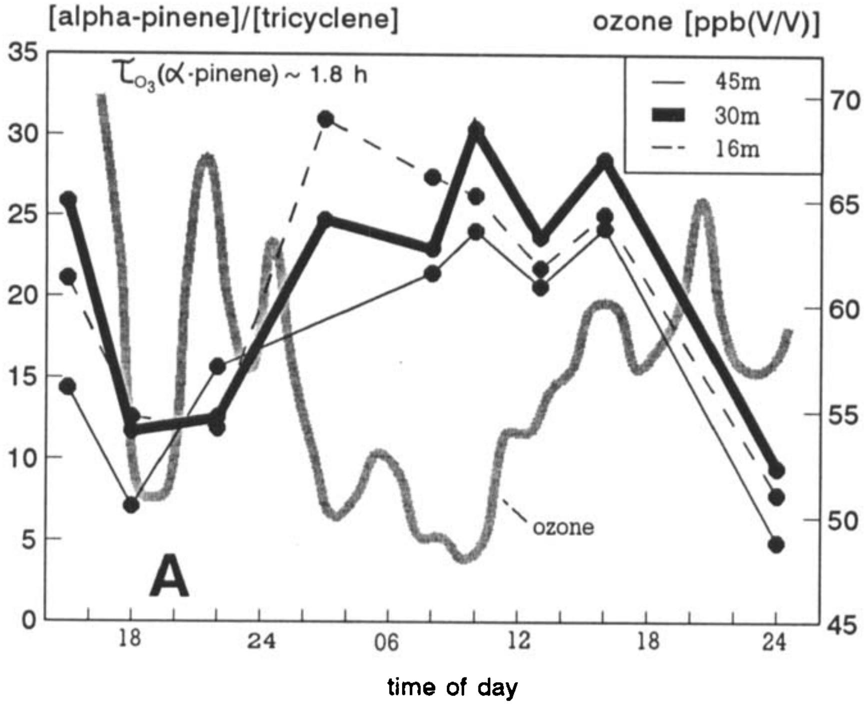
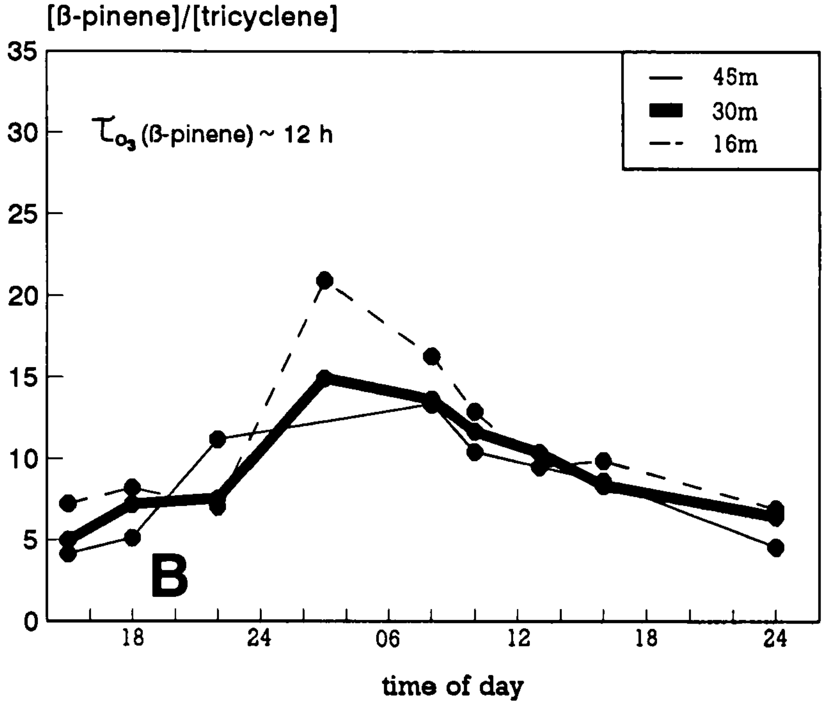


Col du Donon, 17.-18.10.1990



Col du Donon, 17.-18.10.1990

Figure 5 Atmospheric degradation of different reactive monoterpenes in and above a forest.

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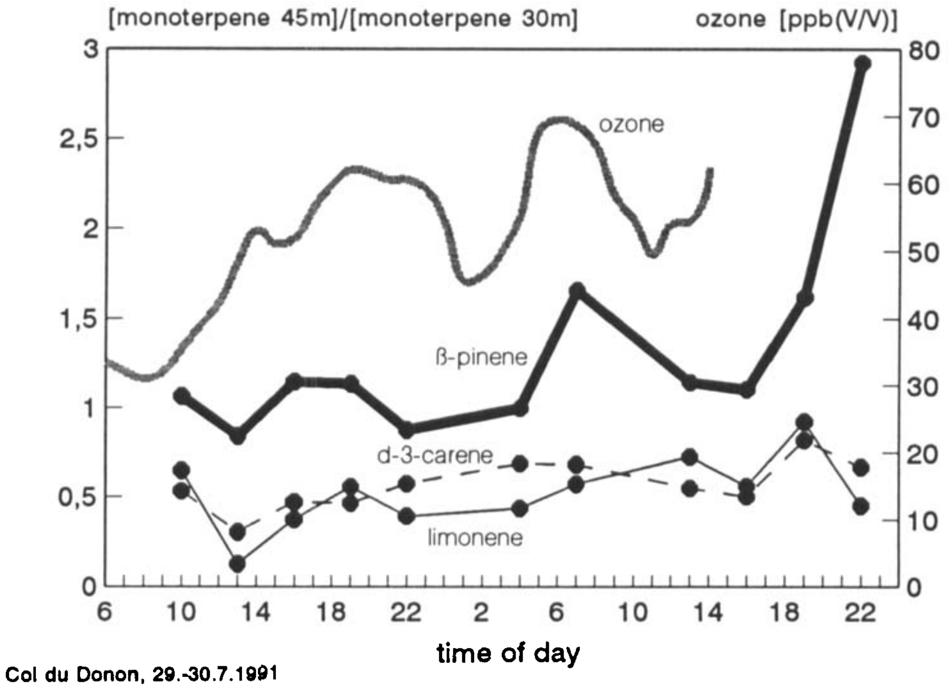

Figure 6 Comparison of the monoterpene concentrations in and above a forest canopy.

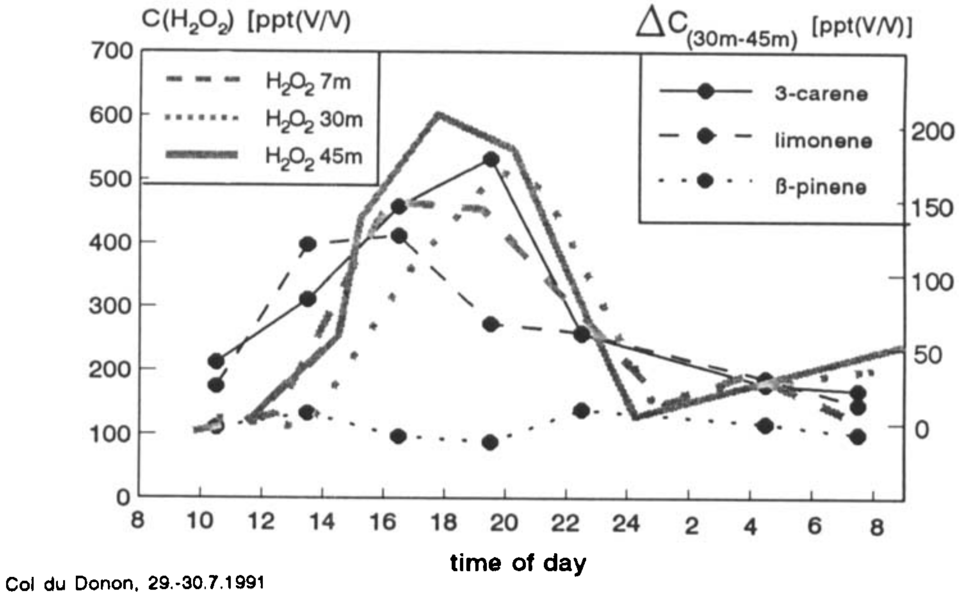

Figure 7 Monoterpene degradation and H_2O_2-concentration in and above a forest stand.

Similar results were obtained by measuring the concentration gradients of biogenic HC's in different heights in and above the forest. Depending on the reactivity of the individual monoterpenes with ozone, the mixing ratios of the compounds above the forest canopy were diminshed to a different extent. Figure 6 shows the concentrations of several monoterpenes above the canopy (45m) compared with their concentrations directly in the crowns of the trees (30m). It is obvious that the amounts of the more reactive natural NMHC's (e.g. d-limonene, d-3-carene) were decreased considerably during their vertical transport above the forest, whereas the concentrations of monoterpenes with small rate constants (β-pinene) remained almost constant. We assume that the concentration differences between 30m and above the canopy (45m) reflect the terpene fraction which has reacted with ozone. Accordingly, products like peroxides should be formed within the forest. Figure 7 shows the amount of degradated monoterpenes (MT) (calculated as the difference between the MT-concentrations in 30 and 45m) as well as the hydrogen peroxide concentrations in 3 different heights at the same location. The obvious correlation between H_2O_2-concentrations and natural NMHC's degradation confirms that peroxide production in forests is initiated by ozonolysis of biogenic alkenes.

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CONCLUSIONS

The results clearly indicate the importance of chemical reactions on the concentrations of the more reactive monoterpenes.

The simultaneous observation of elevated H_2O_2-concentrations and biogenic hydrocarbon degradation supports the presumption that ozonolysis-reactions are a source of peroxidic products in forests. Accordingly, the formation of phytotoxic compounds close to the needles or leaves of the trees as a consequence of the ozone/alkene-reaction could be involved in the mechanism by which ozone damages plants.

Acknowledgement

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