We can summarize the possible causes of ozone destruction within clouds. At pH > 5 ozone is destroyed via reaction (2), $O_3 + O_2^-$; this situation probably occurs during cloud formation where CCN determines the chemical composition (high calcium ion concentration). In the case of a SO_2-rich environment, high S(IV) concentrations build up due to effective scavenging of SO_2, and additional ozone destruction occurs with sulfate formation via reaction (1); Fig. 3 supports this hypothesis. Our experimental results for clouds where ozone is destroyed (class I in Table 1) show a cloud-water composition high in calcium ions and sulfate. Nitrate is also enriched in these clouds. Class II clouds, characterized as maritime or remote, do not show a capacity to destroy ozone, however, this does not mean that ozone was not destroyed within these clouds, but that the destruction capacity was nil when they were observed over the Brocken, and the interstitial ozone was similar to that outside the cloud.

Another possible explanation for the ozone decrease with passing clouds, however, could be a different ozone content due to changing vertical and horizontal transport processes. We cannot totally exclude local vertical transports, but this is typically observed during the formation of orographic clouds (cap clouds). Most cloud events with ozone depletion, however, have been characterized as nonorographic clouds within large-scale air motion. In our opinion, the most probable explanation of the ozone depletion is the simultaneous occurrence of two effects: (a) chemical processes within the cloud on its pathway, as suggested by the different chemical compositions of cloud-water classes I and II, and (b) changing mesoscale transport advecting air with a different ozone content.

Based on the experimental results, we conclude that clouds deplete and destroy ozone and that this removal capacity increases with pollution; the results support the different ozone removal pathways suggested by models. Our preliminary data show that an understanding of tropospheric ozone balance would be incomplete without consideration of chemical processes within clouds. We are continuing these investigations; our data from 1993 show a similar behavior between ozone and clouds. Thus, a more detailed analysis should be possible using sufficiently analyzed events and back-trajectory calculations.

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Light-dependent Emission of Monoterpenes by Holm Oak (*Quercus ilex* L.)

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Monoterpenes and isoprene constitute the most significant fraction of natural volatile organic compounds released by many terrestrial plants into the atmosphere. Because of their abundance and chemical activity, they can play important roles in tropospheric chemistry, in particular in relation to ozone, hydroxyl radical and carbon monoxide budgets and aerosol and acid formation [1]. In global and regional emission inventories it has been estimated that the emission rates of these compounds show an order of magnitude comparable to the emission of methane [2]. The inventories are based on emission algorithms which have been developed from results of growth-chamber studies and describe the emission rates as a function of temperature and light. Concerning the isoprene emissions of trees, it has now been well established that both temperature and light quickly effect the quantity emitted, and a lot of research work has been done to clarify the underlying mechanisms (e.g. [3]). In contrast, most investigations on monoterpene emissions, mainly performed on coniferous trees, report a dominant influence of temperature; other factors, such as light, humidity, and CO_2 mixing ratio, have no or little effect on emission rates (e.g. [4]). Therefore, physiological processes are assumed to play a very small role in determining the short-term variation of monoterpene emission rates, and, in consequence, the monoterpenes diffusing from the plant organs should derive from a standing and large monoterpene pool whose size and composition may only alter over a time scale of weeks or months. The resin ducts of conifer needles provide such a permanent emission source where the monoterpene contents seem to be relatively stable during the period between full needle maturation and abscission [5].

There are only a few investigations emphasizing that light and related physiolog-

ical processes may also influence monoterpene emissions on a shorter time scale of minutes and hours. Temperature-normalized emission rates from pine and spruce species were found to be significantly lower during the night than during the day [6]. Other investigations carried out on spruce, using a climate-controlled micro-cuvette, showed that α-pinene emission increases with increasing illumination and, during a 24-h fumigation with $^{13}CO_2$-containing air, a substantial portion of ^{13}C-labeled α-pinene can be identified in the emissions [7]. In view of these findings it was suggested that a proportion of the emitted monoterpenes must have been synthesized recently, originating in a small and light-dependent pool located in the mesophyll.

In this context, our observations on monoterpene emissions from Holm oak (*Quercus ilex*) are of some interest. Our investigations form part of a project on biogenic emissions in the Mediterranean area (BEMA), which chiefly aims at quantifying the emission rates of selected trace gases from vegetation in the Mediterranean basin. A first plant emissions screening revealed that the evergreen oak species *Q. ilex* emits large amounts of monoterpenes but only small amounts of isoprene. α-Pinene, β-pinene, and sabinene account for about 80% of the total non-methane hydrocarbons emitted by Holm oak, which agrees fairly well with data from other investigations [8]. In addition, our results showed that the monoterpenes are not accumulated inside leaf or bark and that the high emission rates are influenced by light as well as temperature [9]. Following these surprising observations, we performed some further greenhouse and field experiments designed to clarify the influence of light. Emissions were measured with the help of closed dynamic Teflon cuvettes suitable for investigating the mass balance of gas exchange. Volatile organics were trapped from cuvette air in adsorption tubes and analyzed by gas-chromatographic methods. The greenhouse experiments were conducted on 7-year-old potted Holm oak saplings in a temperature- and humidity-controlled 30-l cuvette system. This device was used to independently determine the influence of temperature and light on emission rates and to monitor the process of emission during a dark-light-dark transition. The influence of temperature and light is shown in Fig. 1. At constant light

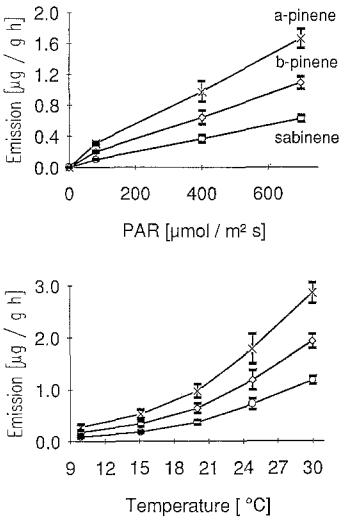

Fig. 1. Influence of temperature (lower graph) and light (upper graph) on monoterpene emission rates from Holm oak (*Quercus ilex* L.). Emission rates ($\mu g\,h^{-1}\,g^{-1}$ LDW) are shown as means plus standard deviation of three or four replicate measurements from the same plant. Temperature dependence was determined at a light level of approx. 400 $\mu mol\,m^{-2}\,s^{-1}$ PAR by increasing the temperature from 10 to 30 °C in 5-degree increments. The influence of light was studied at a temperature of 20 °C by measuring at four different light levels (approx. 0, 80, 400, and 700 $\mu mol\,m^{-2}\,s^{-1}$ PAR) provided by two 1000-W high-pressure sodium lamps and two 400-W metal halide lamps. Relative humidity was maintained between 65% and 75% throughout all measurements

exposure of 400 $\mu mol\,m^{-2}\,s^{-1}$ PAR (photosynthetically active radiation), the monoterpene emissions from Holm oak increase exponentially within the range of temperature treatments (Fig. 1, lower graph). The slopes ($\Delta \ln E/\Delta t$) of the resulting log-linear relationships between emission rates and temperature ($n = 16$) are 0.12 for α-pinene ($r^2 = 0.92$), 0.12 for β-pinene ($r^2 = 0.92$), and 0.13 for sabinene ($r^2 = 0.94$). In the literature, similar functions have been found for a large number of monoterpene-emitting plants, where the reported slopes range from 0.06 to 0.13 [4].

The function describing the relationship between light and emission rates (Fig. 1, upper graph) is more difficult to deduce from the results of only four various light treatments, but the dependence on light is apparent, since emission rates increase significantly with increasing light intensity. Particularly interesting are the extremely low values in the dark, indicating a predominant role of light in controlling emission. Dark emissions ranged between 0.0005 and 0.003 $\mu g\,h^{-1}\,g^{-1}$ LDW (leaf dry weight) but often fell beyond the detection limit. No influence of temperature on emissions in the dark could be found (data not shown).

Dark-to-light and light-to-dark transitions of the plant had a distinct effect on emission rates, as shown in Fig. 2. Emission increase or decrease can already be recognized from the first measurement following the transition. The response to darkness seems to be somewhat faster than to illumination, as is the case with CO_2 assimilation. However, a better sampling frequency is needed to describe in more detail the dynamic response of monoterpene emissions to changes in light exposure. The field measurements were carried out by means of two partly temperature-controlled 100-l branch cuvettes installed on the top of two 30-year-old Holm oaks in a plantation of a nature preserve about 15 km south of Rome. The diurnal emission courses of

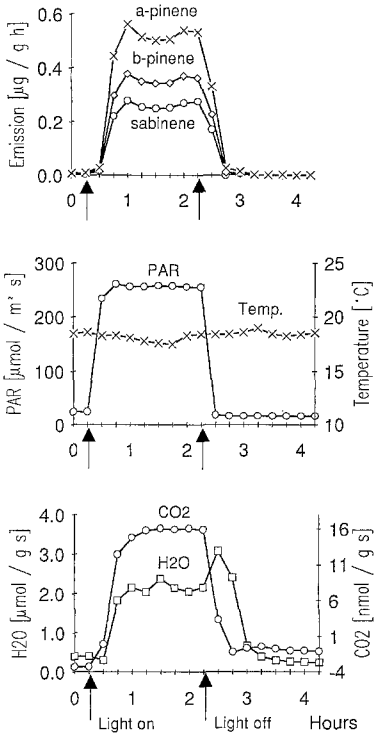

Fig. 2. Emission response ($\mu g\,h^{-1}\,g^{-1}$ LDW) of a dark-adapted Holm oak sapling to a 2-h light exposure at 18±0.5 °C. The emission rates (above) were obtained from successive 15-min measurements. Temperature and PAR data (middle) and transpiration and CO_2-assimilation data (below) are mean values averaged over the same 15-min period

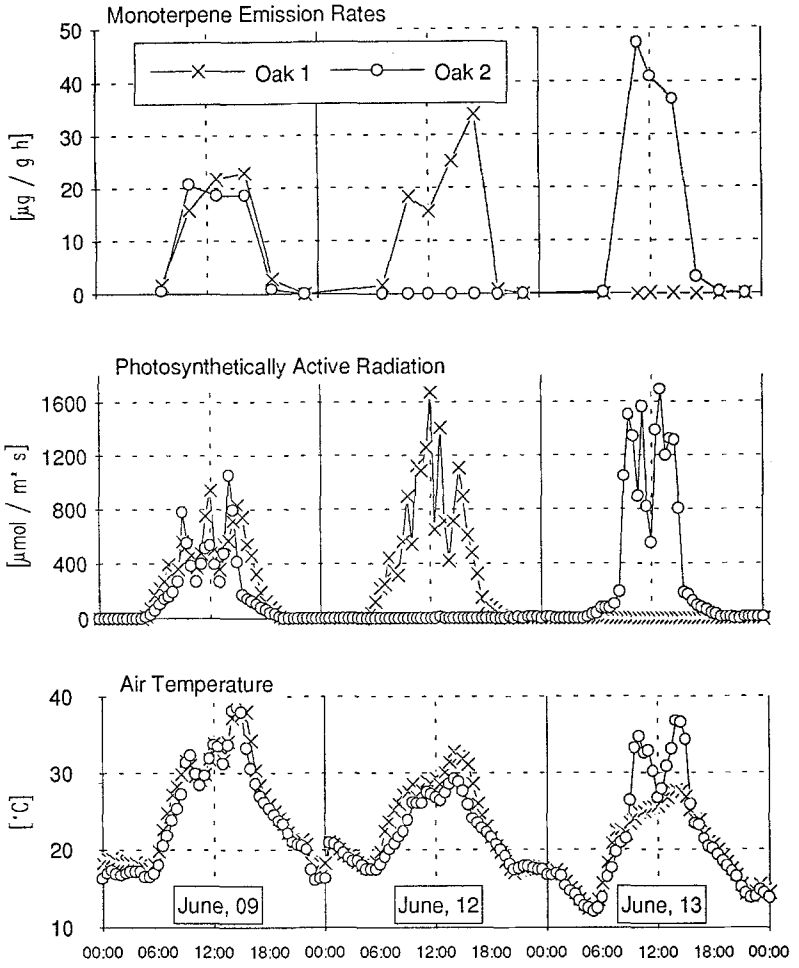

Fig. 3. Diurnal courses and effect of cuvette darkening on monoterpene emission (sum of α-pinene, β-pinene, and sabinene) from Holm oak under field conditions. The emission rates ($\mu g\, h^{-1}\, g^{-1}$ LDW) of two branches were simultaneously measured five or six times during sunlight hours and once in the night for 3 days in June. On day 1, both cuvettes were kept under normal conditions to characterize the natural emission course at the test site. On day 2, cuvette Oak 2 was artificially darkened for 24 h by wrapping with tin-foil the night before, and on day 3, cuvette Oak 1 was darkened in the same way. During all days the weather was sunny and very warm with occasional clouds in the hours around noon

both branches were measured for 2 days under natural light conditions and for 1 day under artificial darkness. The emission rates, plus temperature and radiation data of all 3 days are shown in Fig. 3. Under natural light conditions, the monoterpene emission rates of Holm oak varied by three orders of magnitude during the course of the day, with maxima of $20-40\, \mu g\, h^{-1}\, g^{-1}$ LDW between 10 a.m. and 4 p.m. and minima of $0.01-0.04\, \mu g\, h^{-1}\, g^{-1}$ LDW in the night. The emission rates from the artificially darkened branches were only slightly higher than the nighttime values, despite of temperature levels nearly as high as in the sun-exposed cuvettes. Comparing emission rates and temperature data for both cuvettes over all 3 days shows that daytime emissions are reduced by approx. two orders of magnitude due to artificial dark exposure, independently of temperature. On the contrary, the emission rates in the night following the artificial darkening have not been affected.

To summarize, both field and greenhouse measurements point to the following conclusion: Monoterpene emissions from Holm oak are predominantly controlled by a light-dependent mechanism. The monoterpene pool or emission source exhausts rapidly in the dark and recovers in the light. For this reason, as well as for the lack of monoterpene storage, the high emission rates should be linked to a ongoing, highly active monoterpene metabolism. As already suggested from previous studies on coniferous trees, it seems that this ongoing metabolism includes monoterpene biosynthesis located in the leaf mesophyll, which is limited by metabolites originating in photosynthetic processes [7]. In contrast to conifers or aromatic shrubs, where a possible light-dependent emission would probably be veiled by storage-derived emissions, the unequivocal situation with *Quercus ilex* could help us to demonstrate a possibly ubiquitous aspect of monoterpene emissions from plants. In consequence, emission inventories for monoterpenes with algorithms based only on temperature may fail in providing the realistic figures needed to understand, for example, the contribution of biogenic emissions to ozone formation in the Mediterranean basin.

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Natural Reproduction of Recolonizing Atlantic Salmon, *Salmo salar*, in the Rhenanian Drainage System (Nordrhein-Westfalen, Germany)

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This contribution provides the first evidence, by means of genetic taxon markers, of natural reproduction of pure-bred Atlantic salmon (*Salmo salar* L.) in three affluents of the Rhine, the rivers Sieg, Bröl, and Agger, in 1994. This finding documents the success of the considerable efforts invested by various institutions to permit recovery of the Atlantic salmon in the Rhenanian drainage system after its extermination from this historic stronghold in Central Europe, where the species used to be common enough to serve as major fishing target [2].

After a period of extinction of more than three decades (pollution, river obstruction, overexploitation) [5, 10], a single mature Atlantic salmon was caught in the Rhenanian affluent Sieg, close to its confluence with the Rhine, in November 1990 [11]. Others followed, confirming the efficiency of various governmental and private salmon conservation and anti-pollution measures [5], but only in November 1993 could spawning of large salmonids be observed in the rivers Sieg, Bröl, and Agger within Nordrhein-Westfalen [6]. In February and March 1994, one, two or three yolk-sac larvae were sampled from 10-cm-deep gravel beds in the rivers Sieg, Bröl, and Agger, respectively (Fig. 1). Since unambiguous species diagnosis of salmon and sea trout is difficult on the basis of their phenotypes, particularly if only larvae are available [1, 14], and since previous electrophoretic work had demonstrated the presence of hybrids between Atlantic salmon and sea trout (*Salmo trutta*) in artificially reared salmonid fry originally bred for restocking the Rhine river system [9], allozyme genotyping of these yolk-sac larvae was performed. The taxon-specific banding patterns of glucose phosphate isomerase, phosphoglucomutase [1, 13, 14], and esterase (substrate methyl umbelliferyl acetate) [8, 9] revealed that pure-bred Atlantic salmon naturally reproduced in Nordrhein-Westfalen in 1994. Resolution of these taxon markers has been confirmed in a population-genetic screening of 36 allozyme loci in 27 Atlantic salmon, 120 sea trout from the Rhine or Elbe drainage systems, and 12 F1 hybrids between these two salmonid species [8] which had been artifically produced and reared to document taxon specificity of electrophoretic protein markers. In order to exclude the possibility that young larvae at the yolk-sac stage of ontogenetic development display deviations from the allozyme patterns familiar from our population-genetic survey of Central European salmonids [7, 8], yolk-sac larvae of Atlantic salmon (origin: eggs of wild-caught salmon from Ireland), and of trout (origin: breeding

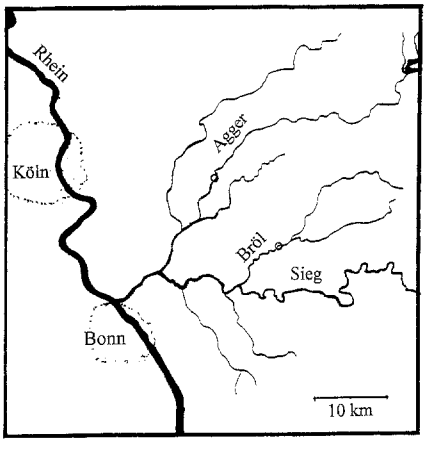

Fig. 1. Map, indicating the tributaries Sieg, Bröl, and Agger of the river Rhine; ○ places where the gravel beds of *Salmo salar* were found

