The emission of mono- and sesquiterpenes and their potentially different role in new aerosol particle formation

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Abstract
It is a well-known effect that plants emit volatile organic compounds (VOCs) as a stress response. Among these the reactive ones such as isoprene, mono- and sesquiterpenes are the most important defensive agents acting as plant communication and reducing the amount of ambient oxidants causing damage to the cells. Emissions of specific agents, i.e. isoprene, monoterpenes and sesquiterpenes are monitored since spring this year at Taunus Observatory using a plant cuvette enclosure technique to investigate a Central European spruce forest. Besides the gas-phase effects it has long been proposed that new particles are formed as a result of the oxidation of isoprenoids. In this presentation a novel explanation is given requiring mono- and sesquiterpenes besides ozone only. This explanation was tested in the different scales: (i) smog chamber using gases only, (ii) plant chambers using controlled conditions and (iii) field station using plant enclosure technique. The present hypothesis was capable explaining any of these. It initiates the first step of particle formation by ozone and sesquiterpenes, activates the products by organic radicals from monoterpenes and considers the further growth to be caused by partitioning of semi-volatile VOCs. Because of the need for large organic radicals the presence of isoprene acts suppressive on particle formation. This gets important when considering the potential changes in a future climate and biosphere-atmosphere feedback processes.

Methods

Field measurements were performed at Taunus Observatory (TO) at 810 m asl in a managed Central European forest consisting primarily of spruce trees. The site is on the ridge of Taunus Mountains and North of the Rhine-Main area with intensive traffic and airport. The nearest city is Bad Homburg in about 15 km to the East and Frankfurt about 25 km to the Southeast. The site faces the highest annual ozone mixing ratios of entire Germany as anthropogenic emissions meet biogenic emissions. Mixing ratio and emission measurements have been performed using a high-sensitivity proton-transfer mass-spectrometry and a dynamic cuvette enclosure technique. At ambient conditions the cuvette was mounted approximately 4 m above soil level around a healthy branch, ventilated and kept close for three minutes out of a 20 min cycle. Besides the PTR-MS measurements temperature, relative humidity and ozone were measured in and outside the cuvette. Other parameters were monitored in the vicinity of the spruce tree. Aerosol size distribution measurements were conducted at the hill top about 20 m in distance.

Smog chamber measurements

Smog chamber studies were performed at Frankfurt University using a flow reactor with a residence time between 145 and 330 s in a walk-in cold-chamber. Ozone was produced by a pen-ray at 184 nm and ethane or propene was added from a premixture stored in a stainless steel canister. The same applies for NO added in different amounts to test the role of radicals. Finally nopinone was provided to allow large radicals to form. Particles were detected using commercially available particle counters. Subsequently the experiments were simulated with an aerosol dynamics model (UHMA-KAS) and a match was achieved for the range between 26 ppt to 98 ppb of NO.

Plant chamber studies

Two plant chamber campaigns were conducted: (a) at Frankfurt University (June 2010) and (b) at MPI for chemical ecology (December 2010). Three different types of tobacco plants were used i.e. genetically modified and wild-type ones. The modification caused some of the tobacco plants to emit more sesquiterpenes than the wild–one. Concentration of terpenes were measured by PTR-MS and particle number concentrations were gained by condensation particle counter measurements.

Ambient measurements

A healthy spruce branch was enclosed by a glass cuvette of 15 L volume. It was ventilated by a fan to achieve continuous mixing and prevent gradients. Temperature and relative humidity were monitored with a HOBO ware sensor inside and outside the cuvette separately. Ozone was measured with a APOA 350E (Horiba). VOCs were sampled via a heated glass tube (60°C) of about 5 m length, a set-up, which has shown

the smallest loss for any of the compounds. Depending on the compound different sampling times between milliseconds and 20 s have been chosen. Aerosol size distribution measurements were made using a scanning mobility particle sizer (TSI 3936 with a long DMA and a TSI 3025A) between 9.8 and 422 nm in particle diameter. Data were sampled and averaged for 10 min intervals. Larger particles were collected by an aerosol particle sizer (TSI 3321).

Results

Emissions

So far emissions of isoprene, mono- and sesquiterpenes were recorded. Isoprene displayed a clear daily pattern and the well-established solar radiation effect. Monoterpenes were the reactive VOCs present in highest quantities and emission. A clear tendency of an elevated temperature dependency of them was found during the spring recovery, which subsequently decreased to the range published by Guenther et al. (1995). Sesquiterpenes behaved less rapidly. An elevated temperature dependency was found during the spring recovery as well. However a correlation with potential available field capacity (extractable soil humidity) was seen, indicating a notable role of water circulation and transpiration in trees. As the conditions became rather dry emissions declined.

Aerosols

Measured and simulated aerosol number concentration agreed within the uncertainty range. A clear effect of radicals, i.e. RO_2 and HO_2 became apparent. Tests with increased ozone levels on tobacco plants in Frankfurt displayed a rapid response of sesquiterpenes and enormous particle number concentrations formed instantaneously. Applying the hypothesis for nucleation led to agreement. Finally the ambient particle formation at Taunus Observatory showed in general nice agreement with the proposed nucleation mechanism and was capable in even explaining night time events.

Conclusions

Emissions of isoprene, mono- and sesquiterpenes have been monitored in a spruce forest for several months at different conditions. The emissions followed the expected pattern for isoprene and monoterpenes, although the temperature dependency was higher during the intensive growth period in spring. Sesquiterpene emissions were found substantial and could contribute to maybe 10% of the monoterpene emissions. Thus, they might at least contribute gently to filling the gap between known emissions and atmospheric carbon budgets (Goldstein and Galbally, 2007). A link to aerosol formation was apparent in our studies. An important role of both terpene groups, i.e. mono- and sesquiterpenes was found and particle formation at least tentatively explained. But much more future work and collaborative support is required in order to understand process of both production and emission of sesquiterpenes as well as particle formation.

References

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