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# Ozone, OH and $NO_3$ sink terms at a coniferous forest site in Central Germany: Role of biogenic VOCs

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Oxidation capacities of ecosystems are important to facilitate an ecosystem feedback on oxidation stress and in order to survive. We have conducted seasonal ambient measurements of a series of biogenic VOCs using a plant enclosure technique and determined the ambient levels of ozone, $NO_x$ as well as basic meteorological parameters at a managed spruce forest site in Central Germany (Mt. Kleiner Feldberg). The site is 810 m a.s.l. and faces distinct anthropogenic contributions from the Rhine-Main-area including the airport and major traffic routes in from the southeast. The opposite direction is moderately polluted and can be classified as Central German background condition. Since atmospheric chemistry and pollutants become very important especially for this site, which is the most polluted one in Germany with respect to ozone we approximated the sink terms for the atmospheric oxidation agents of interest at this site, i.e ozone, OH and $NO_3$ using the measurements and box model steady state calculations for intermediate species not measured directly between the first of April and the start of November 2011. BVOC measurements were obtained with PTR-MS every 36 s and averaged for 30 min intervals afterwards to facilitate the inclusion of the monitoring data of the Hessian Agency for the Environment and Geology (HLUG) in Wiesbaden, Germany: temperature, humidity, global radiation, ozone and $NO_x$. Analysis was performed with Matlab (Mathworks Inc.) and included the gas-phase chemistry set-up described by the Master Chemical Mechanism (MCM, v3, [1]). This resulted in the following outcome for sinks of oxidants:

*Ozone:* Significant contributions were found for mono- and sesquiterpenes as well as for $NO_x$. The individual contributions vary notably with the time of the day and the year and the emission strength of biogenic VOCs. Especially for the early season in April sesquiterpene reactions dominated the sink by up to 80% during nighttime, while $NO_x$ reactions dominated the sink terms during daytime. The contributions of monoterpene and isoprene reactions strengthened towards the summer period, while sesquiterpene reactions slowed down.

*Hydroxyl radical:* The picture becomes much more complex for OH. Besides the reaction with nitrogen dioxide, isoprene and monoterpenes were key destructing agents of OH with estimated contributions of about 50-60%, increasing towards the summertime. Contributions of their oxidation products to the total sink of OH are supposed to be less than 20% but showing more intense during summer and less towards cooler periods. Sesquiterpene OH-reactions only contributed to 10% with a maximum of about 20% at the early April.

*Nitrate radical:* $NO_3$ displayed a mixture of the sinks of OH and ozone. The dominant destruction takes place via $NO_x$-reactions (about 50%) and the remainder primarily via monoterpene (36±20%), sesquiterpene (11±8%) and isoprene (2±1%) OH-reactions.

From our observations at this particular site it is apparent that the spruce forest provides a quite efficient variety of pathways to compensate oxidation stress. This is essentially displayed in the variation of emission pattern of different compound classes with different reactivity for the three major oxidation agents. One needs to be aware of the fact that the sink is highly variable in space, too. Therefore we conclude: In order to understand and describe the oxidation tolerance of a certain ecosystem one needs to detect at least the reactive hydrocarbons.

[1] Jenkin, M.E., Shallcross, D. E., and Harvey, J. N.: Development and application of a possible mechanism for the generation of cis-pinic acid form the ozonolysis of $\alpha$- and $\beta$-pinene. *Atmos.Environ.*, **34**, 2837–2850, 2000.