Chemical stability of levoglucosan in laboratory and ambient aerosol studies: An isotopic perspective

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Levoglucosan, used in receptor models as the specific tracer of particulate matter emissions from biomass burning, has long been considered being stable in the atmosphere. Lately, ambient and laboratory studies showed that the levoglucosan concentration strongly decays in aerosol particles exposed to OH radicals. Here, isotopic analyses can provide evidence for chemical processing since this causes changes in the relative abundance of heavy to light isotopes due to the kinetic isotope effect (KIE).

In this work, levoglucosan chemical stability was studied by exploring the isotopic fractionation of the reactant during the oxidation, in aqueous solutions and by exposing atmospherically relevant particles to gas-phase OH. In both cases, the samples, experiencing different extent of processing, were isotopically analyzed by using Thermal Desorption/Liquid Extraction - Two Dimensional Gas Chromatography - Isotope Ratio Mass Spectrometry. From the dependence of levoglucosan $\delta^{13}C$ and concentration on the reaction extent, the KIE of levoglucosan oxidation by OH in aerosol particles and aqueous solution was determined, showing values of 1.00235±0.00031 and 1.00185±0.00017, respectively. Both show good agreement within the uncertainty range.

The obtained laboratory kinetic data on the isotope effects of the levoglucosan degradation were employed to interpret ambient observations. Compound specific isotopic measurements of levoglucosan were carried out for ambient aerosol sampled during biomass burning episodes at different sites in Guangdong province, China. Further, the origin and pathways of the probed air masses were determined, basing on back trajectories calculated with the Lagrangian particle dispersion model FLEXPART from ECMWF meteorological data. The results combining laboratory KIE studies, observed $\delta^{13}C$ in field and back trajectory analyses show that the chemical loss of levoglucosan, typically employed as molecular tracers of biomass burning aerosol, can add up to 70% in air masses with a photochemical age of $3.2 \bullet 10^{11}$ molec s cm^{-3}.