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Rapid formation of isoprene photo-oxidation products observed in Amazonia

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Abstract. Isoprene represents the single most important reactive hydrocarbon for atmospheric chemistry in the tropical atmosphere. It plays a central role in global and regional atmospheric chemistry and possible climate feedbacks. Photo-oxidation of primary hydrocarbons (e.g. isoprene) leads to the formation of oxygenated VOCs (OVOCs). The evolution of these intermediates affects the oxidative capacity of the atmosphere (by reacting with OH) and can contribute to secondary aerosol formation, a poorly understood process. An accurate and quantitative understanding of VOC oxidation processes is needed for model simulations of regional air quality and global climate. Based on field measurements conducted during the Amazonian Aerosol Characterization Experiment (AMAZE-08) we show that the production of certain OVOCs (e.g. hydroxyacetone) from isoprene photo-oxidation in the lower atmosphere is significantly underpredicted by standard chemistry schemes. Recently reported fast secondary production could explain 50% of the observed discrepancy with the remaining part possibly produced via a novel primary production channel, which has been proposed theoretically. The observations of OVOCs are also used to test a recently proposed HO_x recycling mechanism via degradation of isoprene peroxy radicals. If generalized our observations suggest that prompt photochemical formation of OVOCs and other uncertainties in VOC oxidation schemes could result in uncertainties of modelled OH reactivity, potentially explaining a fraction of the missing OH sink over forests which has previously been largely attributed to a missing source of primary biogenic VOCs.

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