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Seasonality of isoprene oxidation chemistry in the remote Amazon is mediated by anthropogenic pollution

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In the remote Amazon rainforest the atmosphere is dominated by isoprene, a volatile organic compound emitted by many plant species in response to increasing light and temperature. Isoprene is highly reactive and therefore mediates the oxidative capacity of the atmosphere and its oxidation products, formed through a cascade of reaction with OH, can condense to form secondary organic aerosols (SOA). These aerosols act as cloud condensation nuclei and thus emissions of isoprene have an influence on cloud formation, rainfall patterns, and ultimately, climate in the sub-continental region. Using direct observations over the course of 11 months, we show for the first time that isoprene emissions from the Amazon rainforest exhibit a natural seasonal cycle that can be explained entirely by the latest emission algorithms. However, by utilising the different deposition rates of the major isoprene oxidation products, of methyl vinyl ketone (MVK), methacrolein (MACR) and isoprene hydroxyhydroperoxides (ISOPOOH) we demonstrate that the fate of isoprene once released to the atmosphere is dictated by chemical reactions mediated by seasonal anthropogenic emissions of nitrogen oxides (NO_x). This NO_x pollution dramatically shifts the isoprene oxidation pathway away from its natural reaction with HO_2 under pristine conditions towards the NO pathway. This switch to the NO pathway suppresses the abundance of SOA precursors such as ISOPOOH during the dry season when regional biomass burning is at its peak, while increasing the yield of the second generation isoprene oxidation product formaldehyde, which has been used as a proxy for isoprene emissions in Earth Observation studies. Our work highlights that even the most remote regions of the Earth are influenced by mankind.