



High Upward Fluxes of Formic Acid from a Boreal Forest Canopy

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Formic acid, HCOOH, is one of the most abundant carboxylic acids in the atmosphere. It affects cloud chemistry and acidity, and is a common product in the oxidative processing of volatile organic compounds (VOC), thus providing constraints on the importance of various pathways and precursors. Yet, significant uncertainties in the sources and sinks of atmospheric HCOOH remain. We present measurements of HCOOH mixing ratios and eddy fluxes over a boreal forest canopy in spring/summer. Boreal forests have been identified as a key region for much of the global production of HCOOH, as well as for our lack of understanding of the underlying processes. To our knowledge, these are the first direct measurements of HCOOH exchange above a boreal forest ecosystem. The measured HCOOH fluxes were bidirectional, but mostly upward during daytime, in contrast to studies made elsewhere that reported mostly downward fluxes. Episodes of downward flux were explained well by standard resistor models of dry deposition. The sum of net observed flux and modeled deposition yields an upward “gross flux” of HCOOH, which could not be quantitatively explained by literature estimates of direct vegetative/soil emissions nor by efficient chemical production from other VOC (e.g. monoterpenes). These observations suggest greatly underestimated HCOOH sources, by up to a factor of 10, of biogenic origin in the boreal forest. We implemented additional vegetative HCOOH sources into the GEOS-Chem chemical transport model to match our derived gross flux, and evaluated the updated model against air- and space-borne HCOOH observations. Model biases in the boundary layer were substantially reduced based on this revised treatment, suggesting that a significant fraction of the missing HCOOH source in boreal regions is located within or just above the forest canopy. Biases in the free troposphere remain unexplained.