Geophysical Research Abstracts
Vol. 18, EGU2016-10711, 2016
EGU General Assembly 2016

# High upward fluxes of formic acid from a boreal forest canopy

Siegfried Schobesberger (1), Felipe Lopez-Hilfiker (1), Emma D'Ambro (1), Ditte Taipale (2,3), Pekka Rantala (4), and Joel Thornton (1)

(1) Department of Atmospheric Sciences, University of Washington, United States, (2) Department of Plant Physiology, Estonian University of Life Sciences, Estonia, (3) Department of Forest Sciences, University of Helsinki, Finland, (4) Department of Physics, University of Helsinki, Finland

Formic acid (HCOOH) constitutes a large fraction of volatile organic compounds (VOC) in the atmosphere. It has important effects on acidity in precipitation and in atmospheric aqueous-phase chemistry (e.g., Keene et al., 1983; Jacob, 1986). It is also a common product in the oxidative processing of VOC, and thus observations provide potential constraints on the importance of various pathways and precursors (Millet et al., 2015). A key unresolved issue is that the atmospheric concentrations of HCOOH are often substantially higher, by factors of 2 to 6, than expected from present estimates of known HCOOH sources and sinks (e.g., Stavrakou et al., 2012; Yuan et al., 2015), a discrepancy that likely projects onto our understanding of the multiphase photochemistry of organic compounds, emissions inventories and deposition models.

Here, we present the results of concentration and eddy flux measurements, performed simultaneously for a wide range of organic compounds using a chemical ionization time-of-flight mass spectrometer, including HCOOH. The measurements took place over a boreal forest canopy from April to June 2014. 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 (Stavrakou et al., 2012). 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 bidirectional HCOOH fluxes which were mostly downward (e.g., Nguyen et al., 2015). Dry deposition rates calculated with a standard resistance model explained well the episodes of downward flux, and suggested that uptake was mainly onto the leaf cuticles. The sum of observed flux and modeled dry deposition yields an upward "excess flux" of HCOOH. Both literature estimates of direct soil and vegetative emissions of HCOOH, and unreasonably efficient chemical production from other VOC, such as monoterpenes, were unable to quantitatively explain this excess flux, suggesting that we are missing or underestimating one or more important sources of HCOOH. Our observations strongly suggest that the missing source is biogenic and both light- and temperature-dependent, similar to the existing parameterizations of emissions of many VOC. By scaling the local HCOOH source rate required for explaining our observations, we can compare with previous satellite and global modeling studies, which have postulated a large and widespread unknown source of HCOOH, and assess how large of a fraction of the missing HCOOH source identified by satellites is potentially located within or just above the forest canopy.

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