

## Atmospheric lifetimes of neoteric short-lived HFCs against oxidation by the hydroxyl radical, and the resulting dry and wet deposition of trifluoroacetic acid in a WRF/Chem simulation

**J. Kazil**<sup>1,2,\*</sup>, S. McKeen<sup>1,2</sup>, S.-W. Kim<sup>1,2</sup>, R. Ahmadov<sup>1,2</sup>, G. Grell<sup>3</sup>,  
R. K. Talukdar<sup>1,2</sup>, A. R. Ravishankara<sup>2</sup>

<sup>1</sup> Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA

<sup>2</sup> Chemical Sciences Division, NOAA Earth System Research Laboratory, Boulder, CO, USA

<sup>3</sup> Global Systems Division, NOAA Earth System Research Laboratory, Boulder, CO, USA

\* Corresponding author: Jan.Kazil@noaa.gov

HFC-134a (1,1,1,2-tetrafluoroethane) is the prevalent refrigerant in automobile air conditioning units (MACs). With an atmospheric lifetime of ~14 years and a global warming potential (GWP) of 1370 on a 100-year time horizon, HFC-134a does not meet current and expected requirements for MAC refrigerants in many parts of the world. One of the simplest way to achieve lower GWP is to use chemicals with shorter atmospheric lifetimes. Two potential substitutes for HFC-134a have been put forth by industry: 2,3,3,3-tetrafluoropropene (TFP) and 1,2,3,3,3-pentafluoropropene (PFP). The WRF/Chem model was used to calculate atmospheric lifetimes of TFP and PFP against oxidation by the hydroxyl radical OH based on rate coefficients from laboratory experiments. The formation of trifluoroacetic acid (TFA) from TFP and PFP oxidation products was simulated in the model, and the dry and wet deposition of TFA over the contiguous USA during the May-September 2006 period that would result from replacing HFC-134a in MACs with a 1:1 molar ratio mixture of TFP and PFP was determined. We calculated the atmospheric lifetimes from this simulation to be ~5 and ~4 days for TFP and PFP, respectively. These lifetimes are approximately 50% shorter than previous estimates, which used a mean atmospheric OH concentration of  $10^6 \text{ cm}^{-3}$ . The shorter lifetimes obtained in the WRF/Chem simulation arise from a higher mean OH concentration of  $1.5 \times 10^6 \text{ cm}^{-3}$ , and from spatial variability of OH concentrations, which are elevated in population centers, where TFP and PFP are preferentially emitted. Deposition of TFA was calculated to be highest in the eastern USA because of numerous large sources and high precipitation in the region. West of the Continental Divide, TFA deposition was significantly lower, and was attributable to emissions from California. Rainwater concentrations of TFA, averaged over the five-month simulation period remained, at all locations, below  $0.1 \text{ mg L}^{-1}$ ; this threshold value is considered safe for the aquatic ecosystem. On shorter timescales, TFA rainwater concentrations can reach significantly higher values at locations with very low rainfall rates and low TFA deposition, mainly in California and Nevada. While the TFA rainwater concentrations expected from a replacement of HFC-134a with the shorter-lived TFP and PFP appear environmentally safe at most locations, TFA rainwater concentrations do not predict TFA concentrations in bodies of water, where accumulation may occur. The role of high TFA rainwater concentrations at locations with very low rainfall rates, and wash down of dry deposited TFA require further investigation.