Application of Quantum Chemical and Statistical Mechanical Methods to Evaluate Local Environmental Impacts of Refrigerant Emissions

M. Flammia, S. Y. Lee, M. L. Cross-Killingsworth, N. Zimmer, D. D. Galvan and P. Blowers*

Department of Chemical and Environmental Engineering, University of Arizona, Tucson AZ, USA

*Author for correspondence e-mail: blowers@email.arizona.edu

Refrigerant emissions from cooling systems contribute to global warming due to their high radiative forcing values and their persistence in the troposphere. Due to their long lifetimes, they are well mixed globally. As they circulate in the atmosphere and degrade, they have the potential to have implications that affect local environments due to different predominant weather conditions. This work investigates both a new definition of global warming potential (GWP), while also investigating localized environmental implications of degradation species.

Global warming potential was created for comparing chemicals that may contribute to global climate change on a convenient basis. The generally accepted formal definition is:

$$GWP = \frac{\int_0^{TH} a_i[x_i(t)]dt}{GWP_{CO_2}}$$

where TH is an arbitrary time horizon, normally chosen to be 20, 100, or 500 years, a_i is the radiative forcing of a compound, i, defined as the energy absorbed per square meter of atmosphere per ppb of concentration of compound i, and $x_i(t)$ is the time dependent concentration time profile for chemical i. This definition inherently assumes that the parent compound i is the only species that will contribute to capturing energy and it is removed from the atmosphere by hydroxyl radical attack, the dominant removal mechanisms. However, larger compounds may fracture apart into daughter species that may form stable compounds which go on to have their own atmospheric lifetimes and radiative forcing values that may additionally contribute to global climate change. This would change the above equation to:

$$GWP_{total} = \sum_j \frac{\int_0^{TH} a_{i,j}\left[x_{i,j}(t)\right]dt}{GWP_{CO_2}}$$

where i is the parent species and j represents the various daughter species which may temporally form and dissipate. The expanded definition opens up the need for other data that may be experimentally inaccessible due to the difficulty of examining total degradation mechanisms and in identifying other removal mechanisms like dissolution into raindrops and then rain-out of species. This work applies quantum chemical calculations to evaluate several candidate species to highlight when it is important to use an expanded GWP definition to capture potential environmental liabilities of compounds. Where experimental data are unavailable, quantum chemical calculations are used to predict intermediate values for radiative forcing and kinetic degradation rate constants. The same information is used to examine localized rain-out impacts of daughter species.