Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement

7 AUTHORS, INCLUDING:

Robert L Waterland
Dupont
32 PUBLICATIONS **645** CITATIONS

William Hutzell
United States Environmental Protection A…
35 PUBLICATIONS **319** CITATIONS

Stephen Oliver Andersen
Institue for Governance & Sustainable Dev…
36 PUBLICATIONS **525** CITATIONS

Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), A Potential Greenhouse Gas Replacement

DEBORAH J. LUECKEN,*,†
ROBERT L. WATERLAND,‡
STELLA PAPASAVVA,§
KRISTEN N. TADDONIO,‖
WILLIAM T. HUTZELL,† JOHN P. RUGH,⊥
AND STEPHEN O. ANDERSEN‖

U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27709; E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19880; Stella Papasavva Consulting, Royal Oak, Michigan 48073; U.S. Environmental Protection Agency, Washington, D.C. 19805; and U.S. Department of Energy National Renewable Energy Laboratory, Golden, Colorado 80401

We use a regional-scale, three-dimensional atmospheric model to evaluate U.S. air quality effects that would result from replacing HFC-134a in automobile air conditioners in the U.S. with HFO-1234yf. Although HFO-1234yf produces tropospheric ozone, the incremental amount is small, averaging less than 0.01% of total ozone formed during the simulation. We show that this production of ozone could be compensated for by a modest improvement in air conditioner efficiency. Atmospheric decomposition of HFO-1234yf produces trifluoroacetic acid (TFA), which is subject to wet and dry deposition. Deposition and concentrations of TFA are spatially variable due to HFO-1234yf's short atmospheric lifetime, with more localized peaks and less global transport when compared to HFC-134a. Over the 2.5 month simulation, deposition of TFA in the continental U.S. from mobile air conditioners averages 0.24 kg km^{-2}, substantially higher than previous estimates from all sources of current hydrofluorocarbons. Automobile air conditioning HFO-1234yf emissions are predicted to produce concentrations of TFA in Eastern U.S. rainfall at least double the values currently observed from all sources, natural and man-made. Our model predicts peak concentrations in rainfall of 1264 ng L^{-1}, a level that is 80× lower than the lowest level considered safe for the most sensitive aquatic organisms.

Introduction

Hydrofluorocarbons (HFCs) were introduced as ozone-friendly alternatives to chlorofluorocarbons because they do not participate in chlorine or bromine catalytic cycles that deplete stratospheric ozone (*1*). However, most HFCs are potent greenhouse gases and their atmospheric concentrations are increasing rapidly; estimated 2050 global emissions are equivalent to 9–19% of projected global CO$_2$ emissions in business-as-usual scenarios (*2*). HFC-134a (1,1,1,2-tetrafluoroethane) in particular, is widely used for refrigeration, air conditioning, and thermal insulating foam, but its largest and most emissive application is for mobile automobile air conditioners (MACs), used in more than 80% of passenger cars and commercial vehicles worldwide (*2*).

International concern about the contribution of HFCs to global climate change has led to regulations on their use and release. The 1997 Kyoto Protocol (*3*) established binding targets for reduction of greenhouse gas emissions by participating industrialized nations, and in 2006 the European Parliament banned the sale of new cars with air conditioning systems using fluorochemical ("F-Gas") refrigerants having 100-yr global warming potentials (GWPs) above 150 (*4*). This Directive precludes the use of HFC-134a (100-year GWP = 1430) in new vehicle types starting in 2011 and all new automobiles starting in 2017.

Refrigerant manufacturers have proposed several alternatives to HFC-134a for MAC applications. On the basis of currently available toxicity, flammability, life-cycle climate performance, and engineering data, a promising replacement is the hydrofluoro-olefin HFO-1234yf (2,3,3,3-tetrafluoropropene) (*5*). The double bond in HFO-1234yf increases its atmospheric reactivity relative to HFC-134a, resulting in an overall atmospheric lifetime of ∼6 days and a low 100-year GWP of 4 (*6*). Because HFO-1234yf reacts faster than HFC-134a, this study examines inter alia whether HFO-1234yf will contribute to local tropospheric ozone formation. Ozone is a serious problem in the U.S (*7*). and in other countries where regional concentrations can reach levels that pose threats to human and ecosystem health.

Atmospheric degradation of HFCs can also produce trifluoroacetic acid (CF$_3$COOH, TFA) via hydrolysis of trifluoroacetyl fluoride (CF$_3$COF, TFF). HFC-134a produces TFA at a slow rate and a low yield of ∼21%. In contrast, HFO-1234yf reacts much faster and produces TFF in ∼100% yield (*8*). The combination of these two factors suggests TFA deposition will be enhanced if HFO-1234yf is used instead of HFC-134a, if emission rates are the same.

TFA is a mildly phytotoxic (*9*) strong organic acid (*10*) with no known degradation mechanism in water. TFA is persistent and highly soluble in water, so it will preferentially partition to aquatic media. It has been detected in ionic form in precipitation (*11–15*), streams and lakes (*16–19*), and the marine environment (*20–22*). Measured concentrations of TFA in deep ocean waters are constant (∼150 ng L^{-1}) implying a massive unknown natural source of TFA (*22*). Risk assessments indicate that deposition of TFA derived from decomposition of current-use HFCs does not pose a risk to aquatic ecosystems, although TFA may accumulate to higher concentrations in specific environments, such as seasonal pools (*9, 23*). The potentially higher deposition rates from use of HFO-1234yf suggests a re-examination of these issues.

The goal of this work is to address the question: While substitution of HFC-134a with HFO-1234yf will benefit the environment by decreasing global climate forcing, might it also degrade air quality by increasing tropospheric ozone or causing other multipollutant problems?

Two earlier modeling simulations of fluorocarbon compounds (*24, 25*) examined global distributions using chemical transport models with midlatitude grids of ∼800 × 1000 km

* Corresponding author email: luecken.deborah@epa.gov.
† U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.
‡ E. I. du Pont de Nemours and Co., Inc.
§ Stella Papasavva Consulting.
‖ U.S. Environmental Protection Agency, Washington, D.C.
⊥ U.S. Department of Energy National Renewable Energy Laboratory.

resolution, parameterized chemistry and climatological meteorology. However, the relatively fast reaction of HFO-1234yf necessitates a more finely resolved model. In this study, we use 36-km grids within a regional-scale photochemical model to examine potential air quality effects of HFO-1234yf in MACs in the U.S. In particular, we focus on the spatial and temporal extent of ozone formation and TFA deposition. This is the first time that a fully 3-D air quality model with explicit photochemistry, hourly transport, resolved emissions, and subgrid cloud parameterization has been used to analyze effects of HFCs. We include hourly description of clouds and the role of aqueous chemistry in transforming HFC degradation products. To quantify atmospheric impacts of HFO-1234yf, we incorporate kinetic and thermodynamic data for HFO-1234yf, and use an emission inventory we have recently described (26). Future MACs will likely be more leak-tight and energy efficient, driven by technological, economic and regulatory concerns, so we investigate how potential increases in MAC efficiency might offset air quality impacts from refrigerant emissions.
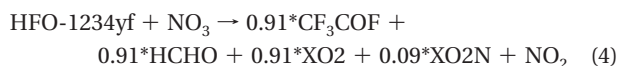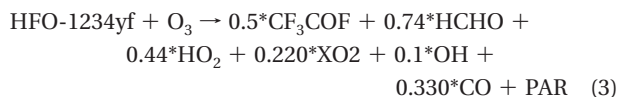
Methods

Air Quality Model Formulation. We used the Community Multiscale Air Quality Model, CMAQ v.4.7 (27) and perform simulations on a continental-scale domain with 36-km horizontal grid resolution and 24 vertical layers. Chemical boundary conditions for VOCs and inorganic species were derived from the GEOS-CHEM global model. Cloud and aerosol processes were included and meteorological fields were obtained from the Pennsylvania State University/NCAR MM5 model, v. 3.6.1 (http://box.mmm.ucar.edu/mm5). We performed simulations for June, July, and August of 2005, reserving the first two weeks in June to allow concentrations of radicals and TFF to stabilize. Our model results are presented for the last two weeks in June, and all of July and August.

Because HFO-1234yf is not currently in widespread use, there are no measurements or global modeling studies with which to initialize concentrations or characterize crossboundary transport, so we set boundary conditions and initial conditions to zero. Initial analyses showed that this should not adversely impact concentrations at the eastern or western boundaries, due to the short lifetime of HFO-1234yf, which can vary from 2 days to 11 days, depending on conditions, and the rapid solubility of TFA. Neglecting transport from the southern and northern boundaries may slightly impact areas close to the boundaries of the U.S.

The CMAQ cloud module includes parameterizations for subgrid convective precipitating and nonprecipitating clouds, and gridscale resolved clouds, diagnosed at each hour and grid cell. When clouds are present, gas and aerosol-phase pollutant concentrations in the CMAQ model are affected by convective mixing, wet scavenging, aqueous chemistry, and removal by wet deposition. Subgrid-scale cloud effects are simulated by diagnosing the fraction of grid covered by cloud, performing aqueous chemistry, transport and deposition on this fraction, and mixing into the entire grid, on a weighted basis, at each time step.

Representation of Gas and Aqueous Chemistry of HFCs and Their Products. We represent chemical degradation of HFO-1234yf and production of ozone and TFA by extending the base CB05 chemical mechanism with chlorine (28) to include reactions of HFO-1234yf and its products:

$$HFO\text{-}1234yf + OH \rightarrow CF_3COF + HCHO + HO_2 + XO2 \tag{1}$$

$$HFO\text{-}1234yf + Cl \rightarrow 0.92^*CF_3COF + 0.56^*FMCL + 2.0^*XO2 + CO \tag{2}$$

$$HFO\text{-}1234yf + O_3 \rightarrow 0.5^*CF_3COF + 0.74^*HCHO + 0.44^*HO_2 + 0.220^*XO2 + 0.1^*OH + 0.330^*CO + PAR \tag{3}$$

$$HFO\text{-}1234yf + NO_3 \rightarrow 0.91^*CF_3COF + 0.91^*HCHO + 0.91^*XO2 + 0.09^*XO2N + NO_2 \tag{4}$$

The dominant degradation pathway of HFO-1234yf is reaction with hydroxyl radical (OH) with a rate constant of $1.26 \times 10^{-12}\exp(-35/T)$ cm^3 molecule^{-1} sec^{-1} (6), where addition at either end of the double bond produces TFF, formaldehyde, hydroperoxy radical (HO$_2$), and oxidation of NO to NO$_2$. In reactions 1−4, XO2 and XO2N are CB05 model operators representing NO to NO$_2$ conversion and NO to organic nitrate conversion over multiple steps, and PAR represents single-bonded carbon (28). We represent reaction of HFO-1234yf with atomic chlorine using a rate of 7.03×10^{-11} cm^3 molecule^{-1} sec^{-1} (29), with 56% addition to the terminal carbon and 44% to the central carbon. Reaction 2 produces TFF, with two NO to NO$_2$ conversions and formyl chloride (FMCL) (8). Reaction 3 is a minor pathway with a rate constant 2.77×10^{-21} cm^3 molecule^{-1} sec^{-1} (29). Products of this reaction were estimated from reaction of ozone with propene, assigning all aldehydes of 2 or more carbons to TFF, and adding PAR to balance carbon. HFO-1234yf is expected to react with nitrate radical (NO$_3$), however no measurements were available, so we include an upper limit rate constant, 3.0×10^{-15} cm^3 molecule^{-1} sec^{-1}, based on other perfluorocarbons (6). We estimate products of this reaction by similarity to the NO$_3$ + propene reaction, assuming 9% nitrate formation and 91% alkoxy formation in reaction with NO.

In the gas phase, the only major reaction of TFA is with OH:

$$TFA + OH \rightarrow XO2 + COF_2 \tag{5}$$
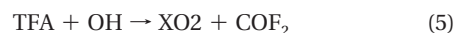
with rate constant of 9.35×10^{-14} cm^3 molecule^{-1} sec^{-1} (8). We assume no nitrate formation and 100% formation of peroxy radical operator XO2. Formation of organic nitrate from reactions of NO and peroxy radicals was not needed to fit recent smog chamber studies (30).

TFF is unreactive in the gas phase, but hydrolyzes to TFA in water (31):

$$CF_3COF(g) \leftrightarrow CF_3COF(aq) \tag{6}$$

$$CF_3COF(aq) + H_2O \rightarrow CF_3COOH(aq) + HF(aq) \tag{7}$$

This is the only route for production of TFA in our modeling. We use a Henry's Law constant of 3 M atm^{-1} and hydrolysis rate of 150 s^{-1} from George et al. (31), which converts most TFF into TFA when cloudwater is present. De Bruyn et al. (32) report lower hydrolysis values, ~10−25% of those used here, so our results provide an upper limit to TFA production. We explicitly account for partitioning of TFF and TFA into cloudwater and formation of TFA from TFF in grid cells and times when cloudwater is present by integrating over the time used to resolve clouds in CMAQ (300 s) with a 0.25 s time step for aqueous cloud chemistry. There are no data for effect of pH on hydrolysis of TFF or dehydration of TFA; we assume that hydrolysis occurs irreversibly.

TFA partitions into the gas phase when cloudwater evaporates and is highly soluble in cloudwater. We use $K_H = 5780^*\exp(-4120^*(1/298.15−1/T))$ M atm^{-1}, and $\Delta H = -34.2$ kJ mole^{-1} (33), and remove aqueous TFA by both wet scavenging and deposition. We remove TFA via dry deposition by similarity to nitric acid (34).

Representation of General Emissions. Nonrefrigerant emissions for the June−August Base Case period were extracted from the 2005 National Emission Inventory for point and area sources, the BEIS model for biogenic emissions

(http://www.epa.gov/asmdnerl/biogen.html), the Mobile Source Model (http://www.epa.gov/OTAQ/m6.htm) for on-road and off-road emissions, and allocated spatially and temporally to grid cells using the SMOKE emissions processor (http://www.smoke-model.org/index.cfm).

Refrigerant Emission Inventory. The refrigerant emission inventory for HFO-1234yf was developed using the GREEN-MAC-LCCP life cycle analysis model, which takes into consideration direct and indirect emissions associated with the manufacturing, operation, shipping, and end-of-life of MACs (*5*), described in detail elsewhere (*26*). We consider refrigerant emissions from normal operation, vehicle accidents, servicing, and end-of-life vehicle scrapping. We assume that all vehicles in the US are equipped with HFO-1234yf systems in 2017. This overestimates HFO-1234yf emissions since we do not account for the fraction of the 2017 fleet manufactured before 2011 and equipped with HFC-134a systems, but it gives us a better estimate of future-year emissions. Due to uncertainty in accurately estimating refrigerant leaks, we consider a Low and High leak Scenario for the number and mix of vehicles in calendar year 2017, when the switch will take place. Emissions in the Low Scenario are roughly 67% of the High Scenario for the three summer months simulated here. State-level emissions are allocated to county-level based on population weighting and further allocated to 36-km grids covering the continental U.S using the SMOKE model, and based on vehicle miles traveled (VMT), roadway distribution, and profiles of on-road activity data. No emissions inventory was available from Mexico and Canadian mobile sources, so this analysis considers only the effect of U.S. emissions on concentrations in the U.S.

Emissions Resulting from Improvements in MAC Operating Efficiency. Every refrigerant transition requires redesign and reoptimization of components and controls, and application of regulatory standards. Studies have shown that current MAC system efficiency can be improved by more than 30% (*5*). While HFO-1234yf is approximately 5% less efficient than HFC-134a based on chemical and physical properties alone (*35*), engineering innovations are expected to result in at least a 10% improvement in coefficient of performance (COP) (*36*) in response to increased fuel prices, climate concerns, and fuel efficiency and greenhouse gas standards (*37*). To study effects of MAC improvements that might occur with transition to HFO-1234yf, we performed an additional simulation incorporating the effect of a 10% increase in COP over existing systems. We assume equivalent incremental engine efficiency for both systems for relating work to fuel usage, and a linear relationship between fuel use and exhaust emissions. Tailpipe emissions from operation of an optimized MAC based on HFO-1234yf are derived based on tailpipe emissions in a current system with HFC-134a:

$$\frac{COP_{HFC-134a}}{COP_{HFO-1234yf}} = \frac{COP_{HFC-134a}}{1.1 \times COP_{HFC-134a}} = \frac{Emiss\_AC_{HFO-1234yf}}{Emiss\_AC_{HFC-134a}} = 0.909 \quad (8)$$

where Emiss_AC are tailpipe emissions from air conditioning alone and both systems remove an equivalent amount of heat. We modified the mobile source portion of the inventory by multiplying only the air conditioning-related fraction of emissions by 0.909, recombining it with the other mobile emissions, and spatially and temporally reallocating to 36-km grids.

Scenarios Studied. We simulated four emissions scenarios:

(1) Base Case Scenario. Using 2005 emissions, this scenario provides a baseline of ozone concentrations and radicals from current sources of organic and inorganic emissions. TFA is not calculated because HFC-134a, the current refrigerant, has a very low reactivity;
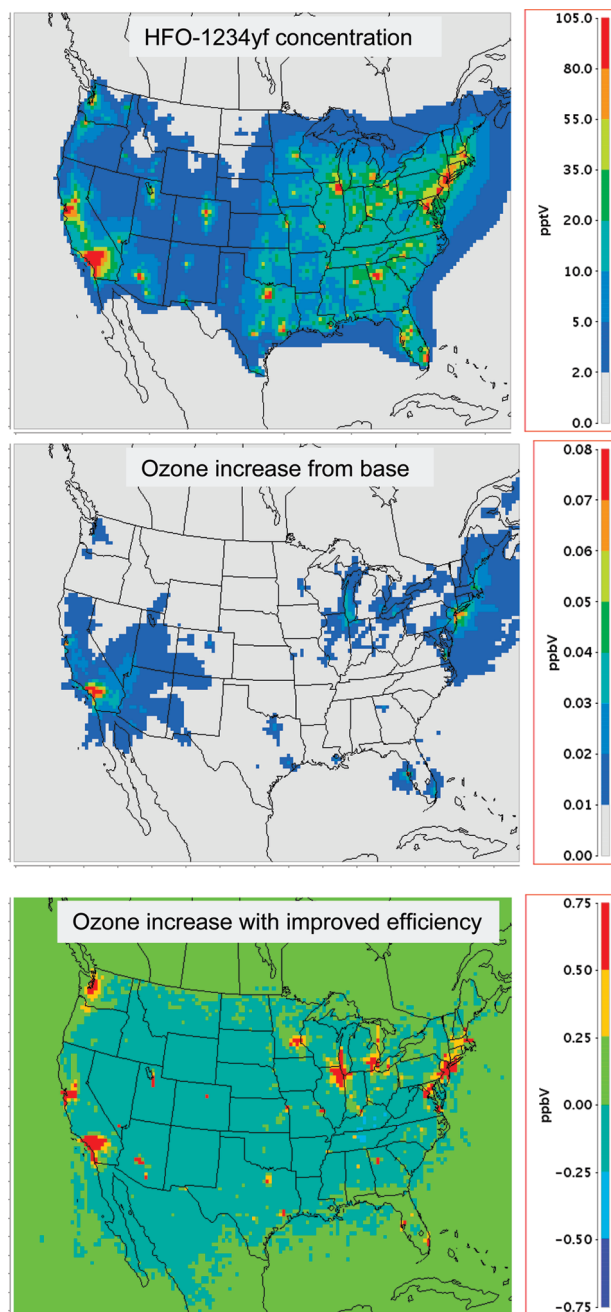

FIGURE 1. Model results for the High Scenario: average concentration of HFO-1234yf, pptV (top); maximum increase in an 8-h average ozone concentration that could occur with substitution of HFC134a with HFO-1234yf, ppbV (middle); and maximum change in 8-h ozone concentration when combined with 10% increase in MAC efficiency, ppbV (bottom). All values are calculated from 16 June through 31 August, 2005.

(2) Low Scenario. Using the lower estimate of HFO-1234yf emissions added to Base Case emissions;

(3) High Scenario. Using the upper estimate of HFO-1234yf emissions added to Base Case emissions; and

(4) High Scenario with COP Improvement. Using emissions from the High Scenario combined with reduced mobile source emissions assuming a 10% increase in COP.

Results and Discussion

Figure 1 (top) shows average predicted summer concentrations of HFO-1234yf in the High Scenario. The Low Scenario predicts concentrations that range from 65% (in the north)

to 70% (in the south) of these (Figure S-1, Supporting Information). The concentration distributions reflect the spatial distribution of emissions of HFO-1234yf which have been previously reported (26), with high concentrations in areas of high automobile density. Although there are grids with average concentrations on the order of 100−300 ppt, mean HFO-1234yf concentrations over the U.S. are 5.0 ppt (Low Scenario) and 7.4 ppt (High).

Ozone concentrations in the Base Case Scenario, without HFO-1234yf emissions, are shown in Figure S-2, Supporting Information. The CMAQ model has been used extensively for predicting ozone, and previous evaluations have shown it reasonably reproduces both the magnitude and temporal behavior of ozone (38). While CMAQ with a 36-km resolution cannot predict every observed value, comparison of Base Case predictions against point observations at 1189 ozone monitoring sites is good (Figure S-2, Supporting Information), with mean bias values of 7.6 (July) and 5.8 ppb (August), and mean absolute gross errors of 11 ppb (July) and 10 ppb (August).

Changes in ozone resulting from HFO-1234yf emissions in the High Scenario are shown in Figure 1 (middle), defined as (High−Base Case Scenario). This figure shows the maximum difference in daily maximum 8-h concentrations at each grid cell over the 2.5 month period. This was calculated by (1) computing maximum 8-h ozone concentration for each day for both scenarios; (2) subtracting the Base Case value from the High Scenario value for each day; and (3) selecting the maximum difference over the entire episode. From a regulatory standpoint, the maximum 8-h average during a day is of most concern, therefore this maximum difference identifies the largest possible increase in ozone that might occur with the substitution of HFC-134a by HFO-1234yf. Figure 1 (middle) shows that HFO-1234yf does produce ozone, but the incremental amount above the Base Case is small when compared to overall ozone, averaging <0.01% of the total ozone formed during the Base Case. The Low Scenario produces ozone similar to the High Scenario, with a difference less than 0.04 ppb, despite the large difference in emissions between the Low and High Scenarios (Figure S-1, Supporting Information). Increases in ozone between the Base Case and High Scenarios are much smaller than decreases in ozone that could be realized by even modest fuel efficiency improvements from improved MAC operation. Figure 1 (bottom) shows maximum differences in ozone predictions from the Base Case when HFO-1234yf emissions are implemented along with a 10% COP improvement (High Scenario with COP improvement). In this scenario, ozone decreases in most of the U.S., although in some areas of the domain, such as Los Angeles, the decrease in NO_x emissions resulting from increased fuel efficiency causes ozone to increase slightly.

Figure 2 shows predicted dry, wet, and total deposition of TFA from the High Scenario during the 2.5 month period. Dry deposition comprises 10−75% of the total, depending on location and with a different spatial pattern than wet. Production of TFA depends on the presence of cloudwater, so the highest deposition occurs in areas with high cloudwater during the simulation period (Figure S-3, Supporting Information). Average TFA deposition is 0.16 kg km^{-2} in the Low Scenario and 0.24 kg km^{-2} in the High Scenario. Average precipitation concentrations of TFA in the High Scenario range from 100 to 1000 ng L^{-1} (Figure S-4, Supporting Information). The largest concentrations occur in areas with small precipitation but large emissions, such as southern California. Deposition of TFA from the Low Scenario is 67−68% of the High Scenario—roughly linear with emissions difference between scenarios.

The 3 months modeled in this study provide a baseline for estimating production and deposition of TFA under
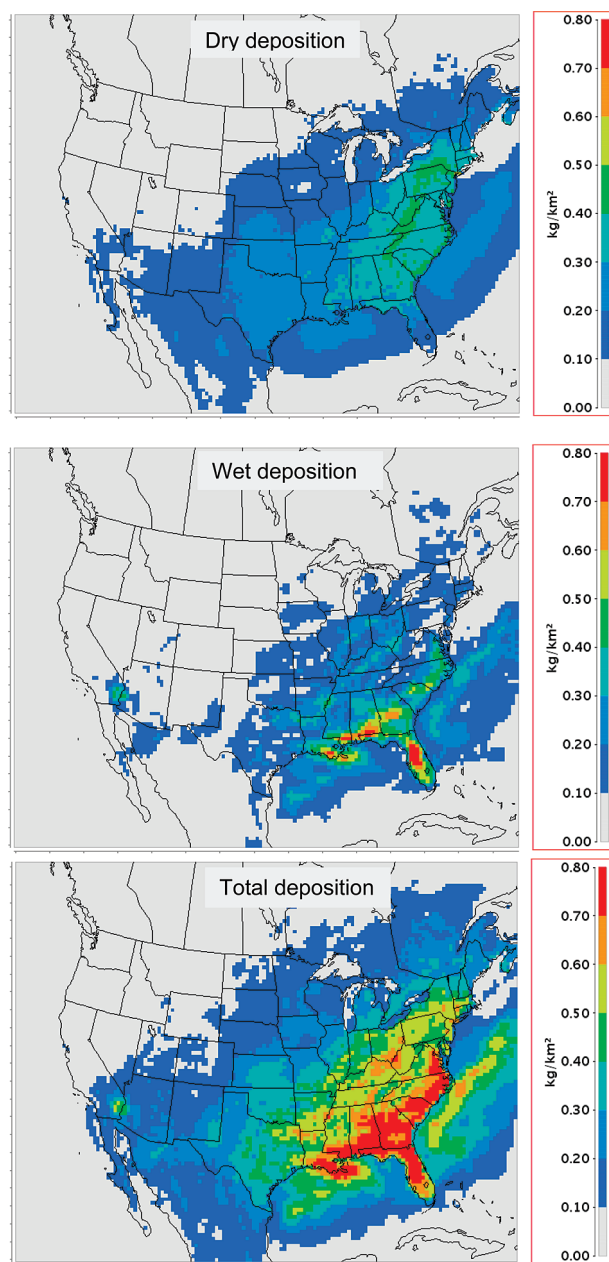

FIGURE 2. Predicted total deposition of TFA in the High Scenario, due to dry deposition (top); wet deposition (middle); and total deposition (bottom), in units of kg km^{-2}. Values are summed for the period of 16 June through 31 August, 2005.

longer-term simulations. The temporal allocation of emissions of HFO-1234yf is highly uncertain—we allocate a large portion of annual emissions into the three month scenario to ensure that we conservatively account for effects of HFO-1234yf on ozone. Although we have not simulated an entire year, the 2.5 months presented here include ~52% of annual emissions with the majority of MAC leaks occurring during the summer (26) when MACs are more likely to be pressurized and serviced. If deposition of TFA varies approximately linearly with emission rate, then we estimate that full year emissions from MACs would result in about twice as much deposition as reported here. Production and deposition of TFA depends on the presence of liquid water in the atmosphere and radical concentrations, both of which vary seasonally, so the pattern and magnitude of deposition may change seasonally. For example, western Washington State, which receives higher precipitation outside of the summer

months, would be expected to have more than twice as much deposition of TFA on an annual basis than presented here.

We neglect potential production of TFA in liquid water on atmospheric aerosols, because of lack of laboratory data on partitioning and reactions in aerosols and the high uncertainty in characterizing nonideal solutions on aerosols. Partitioning into aerosols is highly sensitive to aerosol composition, including dissolved solutes and their effect on activity coefficients of H+, TFA anion, and TFA. For typical summer temperatures and the acidic aerosols seen in the U.S., liquid partitioning would be small. In contrast, there is nearly complete removal of TFF and TFA when clouds are present, the processes we do represent. A recent, detailed study of larger perfluorocarboxylic acids similarly concluded the partitioning to terrestrial aerosols is negligible compared to cloud and precipitation (39). Similarly, we do not produce TFA in fogwater, due to potentially large deviation from nonideality. While production and deposition of TFA from aerosols and fog would be much smaller than through cloudwater, both routes could provide additional formation of TFA, increasing deposition in some areas.

Comparison with Previous Modeling Estimates. A previous simulation of formation and deposition of TFA from current HFCs, including HFC-134a (25) used a coarse grid, chemical transport model applied over global scales. That study predicted total deposition ranging from $0-1.5$ kg km^{-2} with hot spots in Western Europe and Eastern U.S. reaching $2.0-2.5$ kg km^{-2}. Over 20 years of simulation, that averages out to about 0.075 kg km^{-2} yr^{-1}, with hot spots of 0.125 kg km^{-2} yr^{-1}. In contrast, we report much higher deposition rates from modeling HFO-1234yf. If the annual deposition is twice the summer deposition that we report here, then our annual deposition fluxes are 1.4 kg km^{-2} across much of the Southeast, with hot spots of 2.34 kg km^{-2}; approximately $18\times$ larger than those previously modeled for HFC-134a. The earlier study (25) also predicted different spatial patterns, with most TFA deposition occurring in the tropics and over oceans, where maximum rainfall occurs. We predict more localized high deposition for HFO-1234yf simulations, over land, and closer to major urban areas. Most of the differences between the earlier HFC-134a study and this HFO-1234yf study can be attributed to the different parent compound: HFO-1234yf reacts with OH radical about $240\times$ faster than HFC-134a, and the yield of TFF from HFO-1234yf is $5\times$ higher. In addition, there are large differences in treatment of aqueous chemistry, cloud formation, water content, and precipitation rate between the two models. The contribution of dry deposition to total deposition of TFA in our study is also higher than the average 20% previously reported (25), due to the role of tropical moisture on total deposition.

Comparison with Experimental Measurements. The most recent North American TFA monitoring data are those of Scott et al. (13), who reported TFA concentrations in precipitation and total wet deposition TFA fluxes in nine locations in the U.S. and Canada from 1998 to 2004 (Table S-1, Supporting Information). Annual mean concentrations of TFA in precipitation vary considerably from year to year, but tend to be significantly higher in urban and near-urban U.S. locations, with means of $51-209$ ng L^{-1}. With HFO-1234yf, our model predicts summertime mean precipitation concentrations of TFA ≈ 500 ng L^{-1} in most of the eastern US and considerably higher concentrations (>1000 ng L^{-1}) downwind of the Los Angeles basin (Figure S-4, Supporting Information). The concentration of TFA in precipitation derived solely from MAC HFO-1234yf emissions is more than double the values currently observed from all sources, natural and man-made. In urban and near-urban U.S. locations, total annual wet deposition fluxes of TFA were measured in the range of $34-132$ g km^{-2} year^{-1} (13), while our model simulations predict a 2.5-month wet deposition flux of ~ 200

g km^{-2} in most of the eastern U.S. and up to 750 g km^{-2} in the southeastern U.S. Again, the model gives MAC-derived wet deposition fluxes of TFA more than double those currently observed from <u>all</u> sources, natural and man-made.

Aquatic toxicity studies of the sodium salt of TFA identified the most sensitive aquatic species studied as an algae (*Selenastrum capricornutum*) with a NOEC (No Observed Effect Concentration) of 120 000 ng L^{-1}, corresponding to 100 000 ng L^{-1} TFA (40). A recent report concluded that TFA concentrations approaching 1 000 000 ng L^{-1} may be toxic to some aquatic life forms (41). Our model predicts peak concentrations in rainfall of 1264 ng L^{-1}, a level that is $80-800\times$ less than the safe level for aquatic organisms. Although our predicted values are substantially lower than the NOEC, concentration effects from accumulation and evaporation in pools, and in landlocked lakes with high background TFA, should be studied further.

Our analysis quantifies production and deposition of TFA only from MAC sources of HFO-1234yf in the continental U.S. Use of HFO-1234yf in other applications and other countries will result in additional TFA production, so total deposition will likely be larger than predicted here.

Transport of HFO-1234yf from the eastern and western boundaries of the domain, however, will likely be small. The lifetime of HFO-1234yf ranges from 2 days to 6 days in the summer, depending on the concentrations of radicals and other oxidants, so significant decay will occur during transport across the ocean. HFO-1234yf emissions within the U.S. disperse rapidly and react moderately quickly in the summer, decreasing to less than 2% of coastline conditions within 700 km (Supporting Information, Figure S-5), which is 6% of the distance across the Pacific Ocean. In addition, TFA is highly soluble in rainwater and essentially all TFA that is transported or produced over the oceans would be removed before reaching our domain boundaries. While it is possible that Eastern and Western boundaries could contribute to HFO-1234yf in the U.S., the contribution will certainly be small. Transport across the Northern and Southern boundaries however, could contribute to results in the Southwestern and Northern U.S.

Although inclusion of boundary conditions would not change the conclusions of this study, characterization of appropriate boundary concentrations should be a priority of future studies for completeness. This will require a large and coordinated effort to characterize the global mobile source fleet, including fleet ages, driving patterns, and vehicle types.

Future studies should incorporate possible HFO-1234yf emissions from other refrigerant applications when reliable future use information becomes available. Additional sources of TFA would also include production from previously emitted HFC-134a, which will remain in the atmosphere long after it is emitted, as well as other industrial fluorocarbon emissions.

While we have attempted to quantify the potential upper limit of production of ozone and TFA from use of HFO-1234yf, the significance of MAC-derived TFA deposition and potential toxicity to ecosystems is still an open question. It is possible that locally high concentrations may be of concern, and additional research and analysis should be performed to examine possible adverse effects, given the potential widespread, global use of alternate refrigerants.

Supporting Information Available

Additional plots of model output and listing of global measurements of TFA are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) World Meteorological Organization. *Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report No. 50*; Geneva, Switzerland, 2007.

(2) Velders, G. J. M.; Fahey, D. W.; Daniel, J. S.; McFarland, M.; Andersen, S. O. The large contribution of projected HFC emissions to future climate forcing. *Proc. Natl. Acad. Sci.* **2009**, *106*, 10949–10954.

(3) United Nations. *Kyoto Protocol to the United Nations Framework Convention on Climate Change*; New York, NY, 1997.

(4) The European Parliament and the Council of the European Union. Directive 2006/40/EC relating to emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC. *Off. J. Europ. Union* 2006, *161*, 12−18.

(5) Papasavva, S. T.; Andersen, S. O. The life-cycle climate performance metric for mobile air conditioning environmental superiority that levels the playing field and facilitates technology choice. *Environ. Prog. Sustain. Ener. J.* 2009. submitted.

(6) Papadimitriou, V. C.; Talukdar, R. K.; Portmann, R. W.; Ravishankara, A. R.; Burkholder, J. B. $CF_3CF=CH_2$ and $(Z)-CF_3CF=CHF$: temperature dependent OH rate coefficients and global warming potentials. *Phys. Chem. Chem. Phys.* **2008**, *10*, 808–820.

(7) *U.S. Environmental Protection Agency*. National Air Quality, Status and trends through 2007;EPA-454/R-08−006: Research Triangle Park, NC, 2009.

(8) Hurley, M. D.; Wallington, T. J.; Javadi, M. S.; Nielsen, O. J. Atmospheric chemistry of $CF_3CF=CH_2$: Products and mechanisms of Cl atom and OH radical initiated oxidation. *Chem. Phys. Lett.* **2008**, *450*, 263–267.

(9) Boutonnet, J. C.; Bingham, P.; Calamari, D.; de Rooij, C.; Franklin, J.; Kawano, T.; Libre, J.-M.; McCulloch, A.; Malinverno, G.; Odom, J. M.; et al. Environmental risk assessment of trifluoroacetic acid. *Human Ecol. Risk Assess.: Int. J.* **1999**, *5* (1), 59–124.

(10) Henne, A. L.; Fox, C. J. Ionization constants of fluorinated acids. *J. Am. Chem. Soc.* **1951**, *73* (5), 2323–2325.

(11) Scott, B. F.; Spencer, C.; Martin, J. W.; Barra, R.; Bootsma, H. A.; Jones, K. C.; Johnston, A. E.; Muir, D. C. G. Comparison of haloacetic acids in the environment of the Northern and Southern hemispheres. *Environ. Sci. Technol.* **2005**, *39* (22), 8664–8670.

(12) Rompp, A.; Klemm, O.; Fricke, W.; Frank, H. Haloacetates in fog and rain. *Environ. Sci. Technol.* **2001**, *35* (7), 1294–1298.

(13) Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. Poly and perfluorinated carboxylates in North American precipitation. *Environ. Sci. Technol.* **2006**, *40* (23), 7167–7174.

(14) Berg, M.; Muller, S. R.; Muhlemann, J.; Wiedmer, A.; Schwarzenbach, R. P. Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ. Sci. Technol.* **2000**, *34* (13), 2675–2683.

(15) von Sydow, L. M.; Grimvall, A. B.; Boren, H. B.; Laniewski, K.; Nielsen, A. T. Natural background levels of trifluoroacetate in rain and snow. *Environ. Sci. Technol.* **2000**, *34* (15), 3115–3118.

(16) Cahill, T. M.; Seiber, J. N. Regional distribution of trifluoroacetate in surface waters downwind of urban areas in Northern California, U.S.A. *Environ. Sci. Technol.* **2000**, *34* (14), 2909–2912.

(17) Scott, B. F.; MacTavish, D.; Spencer, C.; Strachan, W. M. J.; Muir, D. C. G. Haloacetic acids in Canadian lake waters and precipitation. *Environ. Sci. Technol.* **2000**, *34* (20), 4266–4272.

(18) Scott, B. F.; Spencer, C.; Marvin, C. H.; MacTavish, D. C.; Muir, D. C. G. Distribution of haloacetic acids in the water columns of the Laurentian Great Lakes and Lake Malawi. *Environ. Sci. Technol.* **2002**, *36* (9), 1893–1898.

(19) Wujcik, C. E.; Cahill, T. M.; Seiber, J. N. Determination of trifluoroacetic acid in 1996−1997 precipitation and surface waters in California and Nevada. *Environ. Sci. Technol.* **1999**, *33* (10), 1747–1751.

(20) Scott, B. F.; Macdonald, R. W.; Kannan, K.; Fisk, A.; Witter, A.; Yamashita, N.; Durham, L.; Spencer, C.; Muir, D. C. G. Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. *Environ. Sci. Technol.* **2005**, *39* (17), 6555–6560.

(21) Jordan, A.; Frank, H. Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs. *Environ. Sci. Technol.* **1999**, *33* (4), 522–527.

(22) Frank, H.; Christoph, E. H.; Holm-Hansen, O.; Bullister, J. L. Trifluoroacetate in ocean waters. *Environ. Sci. Technol.* **2002**, *36* (1), 12–15.

(23) Hanson, M. L.; Solomon, K. R. Haloacetic acids in the aquatic environment. Part II: ecological risk assessment. *Environ. Pollut.* **2004**, *130*, 385–401.

(24) Kanakidou, M.; Dentener, F. J.; Crutzen, P. J. A global three-dimensional study of the fate of HCFCs and HFC-134a in the troposphere. *J. Geophys. Res.* **1995**, *100* (D9), 18781–18801.

(25) Kotamarthi, V. R.; Rodriguez, J. M.; Ko, M. K. W.; Tromp, T. K.; Sze, N. D.; Prather, M. J. Trifluoroacetic acid from degradation of HCFCs and HFCs: A three-dimensional modeling study. *J. Geophys. Res.* **1998**, *103* (D5), 5747–5758.

(26) Papasavva, S. T.; Luecken, D. J.; Taddonio, K. N.; Waterland, R. L.; Andersen, S. O. Estimated 2017 refrigerant emissions of 2,3,3,3-tetrafluoropropene (HFC-1234yf) in the United States resulting from automobile air conditioning. *Environ. Sci. Technol.* 2009. in press.

(27) Byun, D.; Schere, K. L. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Appl. Mech. Rev.* **2006**, *59* (2), 51–77.

(28) Yarwood, G.; Rao, S.; Yocke, M.; Whitten, G. Z. *Updates to the Carbon Bond Mechanism: CB05. Final Report to the US EPA, RT-0400675*; Yocke and Company: Novato, CA, 2005. Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.

(29) Nielsen, O. J.; Javadi, M. S.; Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Singh, R. Atmospheric chemistry of $CF_3CF=CH_2$: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O_3. *Chem. Phys. Lett.* **2007**, *439*, 18–22.

(30) Carter, W. P. L. *Investigation of atmospheric ozone impacts of 2,3,3,3-tetrafluoropropene*. Final report to Honeywell International, June 9, 2009. Available at http://www.cert.ucr.edu/~carter/pubs/YFrept.pdf.

(31) George, C.; Saison, J. Y.; Ponche, J. L.; Mirabel, Ph. Kinetics of mass transfer of carbonyl fluoride, trifluoroacetyl fluoride, and trifluoroacetyl chloride at the air/water interface. *J. Phys. Chem.* **1994**, *98* (42), 10857–10862.

(32) de Bruyn, W. J.; Shorter, J. A.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Uptake of haloacetyl and carbonyl halides by water surfaces. *Environ. Sci. Technol.* **1995**, *29* (5), 1179–1185.

(33) Kutsuna, S.; Hori, H. Experimental determination of Henry's law constants of trifluoroacetic acid at 278−298 K. *Atmos. Environ.* **2008**, *42*, 1399–1412.

(34) Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. *J. Phys. Chem. A* **2004**, *108* (4), 615–620.

(35) Spatz, M., Minor, B. HFO-1234yf low GWP refrigerant: A global sustainable solution for mobile air conditioning. *SAE Alternate Refrigerant Systems Symposiums* **2008**, http://www2.dupont.com/Refrigerants/en_US/assets/downloads/SmartAutoAC/MAC_SAE08_HFO_1234yf.pdf.

(36) OEM Group. Update: 1234yf as a replacement for R134a. MAC Summit 2008, Scottsdale, AZ, June 27, 2008. Available at http://epa.gov/cppd/mac/HFO1234YF%20EXPERT%20CONSENSUS-%20GROUP.ppt.

(37) White House Press Office, President Obama announces national fuel efficiency policy. May 19, 2009. Available at http://www.whitehouse.gov/the_press_office/President-Obama-Announces-National-Fuel-Efficiency-Policy/.

(38) Appel, K. W.; Gilliland, A. B.; Sarwar, G.; Gilliam, R. C. Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance. Part I-ozone. *Atmos. Environ.* **2007**, *41*, 9603–9615.

(39) Arp, H. P. H.; Goss, K.-U. Gas/particle partitioning behavior of perflurorcarboxylic acids with terrestrial aerosols. *Environ. Sci. Technol.* **2009**, *43*, 8542–8547.

(40) Berends, A. G.; Boutonnet, J. C.; De Rooij, C. G.; Thompson, R. S. Toxicity of trifluoroacetate to aquatic organisms. *Environ. Toxicol. Chem.* **1999**, *18* (5), 1053–1059.

(41) IPCC/TEAP. *Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*; Cambridge University Press: New York, NY, 2005.

ES902481F