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5 AUTHORS, INCLUDING:

Robert L Waterland

Dupont

Stephen Oliver Andersen

Institue for Governance & Sustainable Dev…

Estimated 2017 Refrigerant Emissions of 2,3,3,3-tetrafluoropropene (HFC-1234yf) in the United States Resulting from Automobile Air Conditioning

STELLA PAPASAVVA,*,† DEBORAH J. LUECKEN,‡ ROBERT L. WATERLAND,§ KRISTEN N. TADDONIO,‖ AND STEPHEN O. ANDERSEN‖

Stella Papasavva Consulting, Royal Oak, Michigan 48073, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27709, E. I. du Pont de Nemours and Co., Inc. Wilmington, Delaware 19880, U.S. Environmental Protection Agency, Washington, DC 19805

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In response to recent regulations and concern over climate change, the global automotive community is evaluating alternatives to the current refrigerant used in automobile air conditioning units, 1,1,1,2-tetrafluoroethane, HFC-134a. One potential alternative is 2,3,3,3-tetrafluoropropene (HFC-1234yf, also known as HFO-1234yf). We have developed a spatially and temporally resolved inventory of likely future HFC refrigerant emissions from the U.S. vehicle fleet in 2017, considering regular, irregular, servicing, and end-of-life leakages. We estimate the annual leak rate emissions for each leakage category for a projected 2017 U.S. vehicle fleet by state, and spatially apportion these leaks to a 36 km square grid over the continental United States. This projected inventory is a necessary first step in analyzing for potential atmospheric and ecosystem effects, such as ozone and trifluoroacetic acid production, that might result from widespread replacement of HFC-134a with HFC-1234yf.

Introduction

Vehicle air conditioning is a significant and growing source of greenhouse gas (GHG) pollution. Current mobile air conditioning (MAC) systems use hydrofluorocarbon (HFC)-134a (1,1,1,2-tetrafluoroethane), which has a 100-yr global warming potential (GWP) of 1,430. MAC is the largest and most emissive sales market for HFC-134a. The use of MAC systems also consumes significant quantities of fuel as compared to similar driving conditions without operating the air conditioning. Current vehicle test procedures evaluate the differential fuel overconsumption due to MAC on conditions with windows closed. Recent life cycle GHG assessment studies (*1*) and previous work performed at the National Renewable Energy Laboratory (NREL) (*2*) have found that vehicle air conditioning accounts for up to 7% of motor vehicle fuel use in the U.S. and up to 20% in vehicles sold in climates that are hotter and more humid than average, such as those found in India and China (*1, 2*). However, turning off the air conditioner and rolling-down the windows also decreases fuel economy due to increased air drag but this scenario is not considered in these studies (*1, 2*).

In response to concern about climate change, policy-makers around the world are taking action to reduce GHG pollution from MACs. In 2002, the U.S. State of California passed Assembly Bill 1493, which requires the California Air Resources Board (CARB) to develop new regulations to reduce GHG emissions from new motor vehicles including MACs. In 2006, the European Commission issued Directive 2006/40/EC (commonly known as the F-Gas Directive) (*3*), which requires new types of air-conditioned cars sold in the EU to have a refrigerant with a GWP of 150 or less starting in 2011, and all new vehicles to have a refrigerant with a GWP of 150 or less by 2017. In 2009, President Obama announced new national fuel efficiency standards with the aim of reducing U.S. vehicle GHG emissions (*4*). When fully implemented, this policy will provide incentives to reduce both refrigerant and tailpipe GHG emissions.

International automotive manufacturers and their suppliers responded to this global regulatory activity by examining many alternative lower GWP refrigerants including carbon dioxide (CO_2, GWP = 1); hydrocarbons (GWP < 10); HFC-152a (1,1-difluoroethane, CH_3CHF_2, GWP = 122); and HFC-1234yf (2,3,3,3-tetrafluoropropene, $CH_2{=}CFCF_3$, GWP = 4). The automotive community is nearing a final decision to select HFC-1234yf (also known as HFO-1234yf) to replace HFC-134a, and the U.S. Environmental Protection Agency's Mobile Air Conditioning Climate Protection Partnership (USEPA MACCPP) is working to rapidly implement the transition from HFC-134a to HFC-1234yf worldwide.

The selection of HFC-1234yf was based on comprehensive studies performed by chemical suppliers, technical associations, environmental authorities, and industry−government partnerships. These reports included sophisticated life-cycle climate performance (LCCP) model studies which determined that HFC-1234yf systems will result in the lowest carbon footprint of all the proposed refrigerant alternatives (*1*) and comprehensive risk assessments that showed HFC-1234yf refrigerant poses the fewest overall safety risks compared to other refrigerant alternatives (*5*), taking into account its generally low overall human and environmental toxicity and mild flammability. Laboratory and smog chamber experiments have determined that HFC-1234yf has an estimated atmospheric lifetime of around 11 days with respect to hydroxyl radical reaction (*6*), decreasing to 6.6 days when all other reactions are also taken into account. HFC-1234yf has a zero stratospheric ozone-depletion potential and a 100-yr GWP of 4.4 (*7*).

While HFC-1234yf's relatively short atmospheric lifetime leads to a desirably low GWP, this also means that it has the potential to form ozone and other chemical species of concern in the troposphere. Ground-level ozone continues to be a serious problem in the United States and throughout the world (*8*), reaching levels in many places that can pose serious health effects. Concerns have also been raised about the potential effects of other chemical byproducts including trifluoroacetic acid and hydrofluoric acid. The tendency of HFC-1234yf to react faster than HFC-134a and hence closer to sources of emissions, increases the importance of understanding the distribution of emissions on smaller geographic scales than required for longer-lived refrigerants.

* Corresponding author e-mail: greengem09@gmail.com.
† Stella Papasavva Consulting.
‡ U.S. Environmental Protection Agency, Research Triangle Park, NC.
§ E. I. du Pont de Nemours and Co., Inc.
‖ U.S. Environmental Protection Agency, Washington, DC.

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The first step in understanding the implications of switching from the current system of HFC-134a to an alternative refrigerant is to develop a comprehensive understanding of the magnitude and distribution of emissions. In this paper, we develop two emissions scenarios for automotive refrigerants. These scenarios assume that the transition from HFC-134a to HFC-1234yf will begin in 2011 and that by 2017 air conditioning in all vehicles in the U.S will use the new refrigerant, which is an overestimate because cars produced before 2011 and still in operation will have HFC-134a systems. However, this assumption was necessary to fully assess the impact of a fleet of vehicles containing HFC-1234yf refrigerant. Due to the fact that the leak rates are the same for similar compounds, the emissions inventory developed in this paper can also be used to represent different types of automobile refrigerants, or even combinations of refrigerants (e.g., 50% of the fleet with HFC-134a and 50% with HFC-1234yf). This analysis tracks the emissions inventory of the fleet, considering direct leak emissions of the refrigerant during normal operation of the vehicle, accidents, service, and end-of-life. Emissions per vehicle are estimated using the life-cycle analysis GREEN-MAC-LCCP model (*9–11*) and applied for the entire fleet of each state in the US in the calendar year (CY) 2017, assuming that all vehicles use the new refrigerant.

The GREEN-MAC-LCCP model (*9*) was developed under the guidance of the Society of Automotive Engineers' International Interior Climate Control Committee (SAE's ICCC) and USEPA to disseminate a comprehensive and peer-reviewed life cycle analysis model for estimating the complete inventory of greenhouse gas emissions associated with MACs worldwide. Papasavva and Hill of General Motors (*9, 12*) established an international team of 50 world experts with representatives from industry, National Laboratories, Government and Non-Governmental Organizations, and academia to harmonize input data received and develop the model (*1, 9, 12*). These data included engineering, chemical, and physical data provided by original equipment manufacturers (OEMs) and suppliers, as well as state-of-the-art cabin comfort conditions using modeling results obtained at NREL (*13*).

GREEN-MAC-LCCP was released in 2006 and is recognized as the most transparent, flexible, and accurate life-cycle GHG model for MACs developed to date, and it became the industry standard, SAE J2766 (*10*). It has been endorsed by major industry organizations including SAE, all U.S. automobile manufacturers, the German Association of the Automotive Industry (VDA), and the Japanese Automobile Manufacturers Association (JAMA), and major chemical industrial suppliers of automotive refrigerants including DuPont, Honeywell, and INEOS Fluor. GREEN-MAC-LCCP is likely to become the global standard for measuring vehicle climate performance for MAC regulations and possibly for quantifying GHG emissions in carbon trading. The model is hosted on the USEPA Climate Protection Partnership Division Web site, http://www.epa.gov/cppd/mac.

In this paper, we present estimates of the emissions of HFC-1234yf across the continental U.S., using bottom-up estimation methods. We describe a way to account for uncertainty in the real-life emissions of refrigerants by defining low and high bounds of the emissions. This paper provides a spatially resolved emissions inventory, with reasonable uncertainty bounds, that can be used for future studies on how much and where emissions of new refrigerants could affect air quality.

Methods

Refrigerant Leak Rate Estimates using GREEN-MAC-LCCP. The direct refrigerant emissions are estimated for an average vehicle lifetime of 9 years in the U.S. By default, GREEN-MAC-LCCP contains leak rate data for 7 U.S. cities obtained using the standard methodology described in SAE J2766 (*10*). In this study we apply the same standard methodology to predict the refrigerant leak rates for all U.S. states.

We assume that car and truck refrigerant leak rates are identical and we consider four distinct Refrigerant Leak Categories as follows.

Regular Leaks. Permeation of the refrigerant from the hoses, connections, and compressor constitute regular leaks. These emissions are a function of ambient temperature conditions, with higher leaks occurring in warmer climates. We estimate regular leak emissions for each state in the U.S. by exponentially fitting, using eq 1, the best available experimentally obtained regular emissions data reported by Clodic et al. (*14*). In addition to the laboratory refrigerant leak data, which estimate a leak rate of 12.8 g/yr, the Clodic et al. study (*14*) also provides on-road refrigerant emissions from HFC-134a-based MAC systems from a fleet running in various European cities representative of cold and warmer temperatures, with an average ambient temperature of 13.1 °C, and an average leak rate of 14.8 g/yr. The temperature dependence of the regular leak emissions was obtained by fitting the laboratory measured leak rates (*14*) obtained at three ambient temperatures (30, 40, and 50 °C).

We have assumed that the refrigerant permeation of an HFC-1234yf system is the same as HFC-134a, based on laboratory test data (*15*). State-specific regular leak rates were estimated using eq 1. We computed each state's average annual temperature using weather data obtained from the U.S. Department of Energy's Energy Plus weather database (*16*), assuming the average monthly temperature of the state's highest population center to be representative of the whole state.

$$R_i = 2 \times 2.836796603 \exp (0.06393 T_i) \quad i = \text{any U.S. state} \tag{1}$$

where R_i is the predicted regular leak rate (g/yr) for each vehicle in state i, and T_i is the average annual temperature (°C) for the highest population center of state i.

Equation 1 incorporates a correction factor of 2 to adjust for the observed difference between laboratory and on-road regular leak rates. This correction adjustment takes into account the difference between the laboratory test environment and on-road conditions such as higher temperature in the engine compartment, vibrations, etc.

The adjusted regular leak rates obtained from eq 1 vary between 7 and 20 g/year/vehicle depending on temperature, and on average a U.S. vehicle is estimated to leak about 13.6 g of refrigerant per year. Although there are no extensive real world refrigerant emissions data in the U.S. with which to compare our predicted regular leak rates, the recent implementation of the SAE MAC System Refrigerant Emission Standard (*17*) SAE J2727, to brand new 2009 model year vehicles predicts regular leak rates in the U.S. on average 14.1 g/yr (*18*) which compares favorably with the value we obtained using eq 1.

These rates represent regular leak emissions from brand new vehicles without defects in their MAC systems. In real world conditions, as the vehicle ages, the hoses and fittings of the system leak more and the regular leak emissions will increase. The effect of aging on regular leak emissions is difficult to estimate because it depends on many factors, but based on advice from MAC experts, we have assumed a 10% increase in the regular leak rate for older systems.

Irregular Leaks. Vehicle accidents or having road debris, such as stones, hit air conditioning system components may cause irregular leaks. Such events, which can result in an "irregular" defect, would not include the normal wear and tear to which every component is physically prone, but some unusual instance such as a burst or corroded compressor, a burst dryer, perforations in the pipeline, or a crack in the evaporator. Schwarz (*19*) reported the three most commonly recorded causes of total refrigerant loss were accidents involving body damage (40%), minor collisions, stone impact, or internal emissive component defects (40–50%), and unknown causes where the vehicle was simply recharged (10–15%). We have taken irregular emission leak rates to be 17 g/year/vehicle (*10*).

Service Leaks. MAC servicing events, which in turn occur when the MAC system in the vehicle starts to lose its cooling performance (*15*), are the source of service leaks. In the U.S. MAC systems can be serviced by trained professionals or by the owner in a so-called do-it-yourself (DIY)-er service. GREEN-MAC-LCCP estimates that during one service these emissions are 40–70 g/vehicle/service, depending on the nature of the service. The less the system leaks, the less frequently the vehicle goes to service.

MAC service professionals are required by law to be trained and certified in proper refrigerant recovery and recycling procedures, and to use large, 30-lb refrigerant cylinders resulting in low residual unused refrigerant cylinder heels when containers are disposed. Professional servicers charge ~60 vehicles per cylinder resulting in heels at the end of cylinder use of ~2% or 5 g/vehicle/service (*20*). Although the average 2% heel assumed in this study is the best real world data we received from the industry, professional service can occasionally result in refrigerant heels as low as 1% or as high as 6%. We have estimated that professional servicing results in the lower service emission rate of 40 g/vehicle/service divided into 35 g/vehicle/service and 5 g/vehicle/service from cylinder heels.

DIYer services result in much higher refrigerant emissions mainly because DIYers do not have refrigerant detection or recovery and recycling equipment, and they typically use 12-ounce refrigerant cans which have significantly higher residual cylinder heels. DIYers very rarely fix leaks. Based on Tremoulet et al. (*21*), we estimate that, on average, a DIYer service produces refrigerant losses of 52 g/vehicle/service for the service itself and 108 g/vehicle/service as can heels, which is 160 g/vehicle/service on average and 4 times higher than a professional service.

End-of-Life Vehicle Leaks. The amount of refrigerant left in the system when a vehicle goes for scrapping and the amount of refrigerant recovered and recycled for further use determine end-of-life leaks. These emissions are difficult to estimate accurately but can be very substantial, in the range of 100–450 g/vehicle disposed, depending on how much refrigerant is recovered. End-of-life leaks are believed to be the largest source of emissions, and more accurate estimation is impossible without additional data from the industry. Field measurements of end-of-life emissions should be a priority for future work but will require a significant collaborative effort among vehicle scrap yards, the MAC community, and vehicle owners. Given these difficult circumstances we doubt that a better estimate of end-of-life emissions will be available in the medium-term future.

We note that the sum of the average annual regular and irregular emissions per vehicle, 30.6 g/y, represents 5.6% of the total refrigerant charge in the MAC system, assuming a typical sedan MAC with 550-g charge. As shown above, each service results in a further emission of 40–160 g of additional emission. On average in the U.S., a vehicle goes for a MAC service once during its 9-y lifetime, so vehicle servicing accounts for between 4.4 and 17.8 g/y of annual refrigerant emissions. Thus, the sum of regular, irregular, and service leaks represent an annual refrigerant loss rate of 35–48.4 g/yr or 6–8.8% of the original charge.

Total annual leak emissions for calendar year 2017 are estimated using the latest state vehicle registration data and assuming that all vehicles in the U.S. will be equipped with HFC-1234yf systems in 2017. Projected statewide vehicle registrations are estimated using the recursion eq 2

$$\text{Vehicle}_{i+1} = \text{Vehicle}_i + \text{Sales}_{i+1} - \text{Scrap}_i \tag{2}$$

where Vehicle_{i+1} and Vehicle_i are statewide registrations in CY $i + 1$ and i, respectively, Sales_{i+1} are statewide projected car and truck sales (*22*) in CY $i + 1$, and Scrap_i is the number of vehicles scrapped in CY i. Equation 2 is initiated with 2008 registration data and we have assumed a 5% average scrap rate for the U.S. (*23*).

We note that for all leak categories, we have assumed that cars and trucks leak identically. In reality, trucks likely leak more than cars, because they have larger refrigerant charges, and their MAC systems commonly have more connection joints. Unfortunately, there are no truck-specific data available to adjust the truck leak rates and, as a result, our assumption to consider equal regular leak rates for cars and trucks may underestimate total emissions. Future work should examine leak rates for trucks.

Due to the uncertainty in accurately estimating refrigerant leaks, we have constructed a *Low* and a *High Leak scenario* for 2017 refrigerant emissions. In the *Low Leak scenario*, regular leaks were estimated using eq 1, and the regular, irregular leakage for the entire fleet was obtained by multiplying the total vehicle registrations per state by the regular, irregular leaks per vehicle, shown in Table 1. Irregular leaks were assumed to be 17 g/vehicle. Given the complexity and large uncertainty in estimating irregular leak rates, it is quite unlikely that future work will significantly undermine our data assumption. In the *Low Leak scenario*, service leakage was calculated assuming only professional servicing takes place and that 10% of the entire fleet is serviced in 2017, and end-of-life vehicle leaks were estimated assuming 5% of the fleet is scrapped in 2017 and 100 g of refrigerant leaks from each scrapped vehicle. This estimate assumes 90% refrigerant recovery from 30–40% of the vehicle fleet, as observed in a U.S. survey performed by the MAC Society (*10, 20*).

In the *High Leak scenario,* regular leaks were estimated using eq 1 but the per vehicle leak rate was adjusted to reflect additional refrigerant leaks that might occur during the aging of the MAC system, assuming that these are 10% more than new systems. Irregular leaks are the same as those in the *Low Leak scenario*, but service and end-of-life leaks are treated differently. In the *High Leak scenario* we assumed that 15% of the entire fleet is serviced in 2017 with 25% of the services conducted by DIYers and 75% by professionals. Finally, in the *High Leak scenario* we assumed that 10% of the vehicle-fleet is scrapped in 2017 and that each vehicle releases 450 g of refrigerant, with no refrigerant recovery.

In the *Low Leak scenario* the total annual U.S. refrigerant leak from MACs is estimated to be 11.4 thousand metric tons (MT) per year, whereas the *High Leak scenario* predicts a value of 24.7 thousand MT per year. We compare our estimated U.S. leakage rates to current HFC-134a leak data obtained by two different methods. The fluorochemical industry estimates current annual U.S. sales of HFC-134a for MAC at ~30 thousand MT/yr (*24*). These annual sales must approximately equal the total annual MAC leak emission. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) program (*25*) collects worldwide HFC-134a production and sales data from nine of the largest global fluorochemical manufacturers. AFEAS also estimates annual HFC-134a emissions: in 2006 global emissions of HFC-134a for refrigeration were estimated as 117 thousand MT. Weighting this global refrigerant leakage emission by U.S. share of global gross domestic product (GDP) (*26*) equal to 25%, results in estimated 2007 U.S. emissions of 29 thousand MT per year which is quite consistent with the estimate given

TABLE 1. *Low* and *High Leak Scenario* Leak Rates Per Vehicle by State

state	low regular leakage rate (g-vehicle/yr)	high regular leakage rate (g-vehicle/yr)	irregular leakage rate (g-vehicle/yr)	low service leakage rate (g-vehicle)	high service leakage rate (g-vehicle)	low end-of-life leakage rate (g-vehicle)	high end-of-life leakage rate (g-vehicle)
Alabama	16.75	18.43	17.00	40.00	70.00	100.00	450.00
Alaska	6.83	7.51	17.00	40.00	70.00	100.00	450.00
Arizona	25.93	28.52	17.00	40.00	70.00	100.00	450.00
Arkansas	15.80	17.38	17.00	40.00	70.00	100.00	450.00
California	16.64	18.30	17.00	40.00	70.00	100.00	450.00
Colorado	11.32	12.46	17.00	40.00	70.00	100.00	450.00
Connecticut	10.98	12.08	17.00	40.00	70.00	100.00	450.00
Delaware	12.40	13.64	17.00	40.00	70.00	100.00	450.00
Dist. of Columbia	12.40	13.64	17.00	40.00	70.00	100.00	450.00
Florida	22.94	25.23	17.00	40.00	70.00	100.00	450.00
Georgia	16.41	18.05	17.00	40.00	70.00	100.00	450.00
Hawaii	27.87	30.66	17.00	40.00	70.00	100.00	450.00
Idaho	11.57	12.73	17.00	40.00	70.00	100.00	450.00
Illinois	10.70	11.77	17.00	40.00	70.00	100.00	450.00
Indiana	11.44	12.59	17.00	40.00	70.00	100.00	450.00
Iowa	10.87	11.96	17.00	40.00	70.00	100.00	450.00
Kansas	13.76	15.14	17.00	40.00	70.00	100.00	450.00
Kentucky	14.14	15.56	17.00	40.00	70.00	100.00	450.00
Louisiana	20.91	23.00	17.00	40.00	70.00	100.00	450.00
Maine	9.04	9.94	17.00	40.00	70.00	100.00	450.00
Maryland	13.15	14.47	17.00	40.00	70.00	100.00	450.00
Massachusetts	11.13	12.24	17.00	40.00	70.00	100.00	450.00
Michigan	10.27	11.29	17.00	40.00	70.00	100.00	450.00
Minnesota	9.26	10.19	17.00	40.00	70.00	100.00	450.00
Mississippi	17.58	19.34	17.00	40.00	70.00	100.00	450.00
Missouri	13.32	14.65	17.00	40.00	70.00	100.00	450.00
Montana	9.97	10.96	17.00	40.00	70.00	100.00	450.00
Nebraska	11.10	12.21	17.00	40.00	70.00	100.00	450.00
Nevada	20.09	22.10	17.00	40.00	70.00	100.00	450.00
New Hampshire	10.55	11.61	17.00	40.00	70.00	100.00	450.00
New Jersey	12.57	13.82	17.00	40.00	70.00	100.00	450.00
New Mexico	13.56	14.91	17.00	40.00	70.00	100.00	450.00
New York	12.56	13.81	17.00	40.00	70.00	100.00	450.00
North Carolina	15.73	17.30	17.00	40.00	70.00	100.00	450.00
North Dakota	7.90	8.69	17.00	40.00	70.00	100.00	450.00
Ohio	11.46	12.60	17.00	40.00	70.00	100.00	450.00
Oklahoma	15.32	16.85	17.00	40.00	70.00	100.00	450.00
Oregon	12.38	13.62	17.00	40.00	70.00	100.00	450.00
Pennsylvania	11.11	12.22	17.00	40.00	70.00	100.00	450.00
Rhode Island	11.42	12.56	17.00	40.00	70.00	100.00	450.00
South Carolina	18.44	20.28	17.00	40.00	70.00	100.00	450.00
South Dakota	9.33	10.26	17.00	40.00	70.00	100.00	450.00
Tennessee	16.80	18.48	17.00	40.00	70.00	100.00	450.00
Texas	20.80	22.88	17.00	40.00	70.00	100.00	450.00
Utah	12.06	13.27	17.00	40.00	70.00	100.00	450.00
Vermont	9.34	10.27	17.00	40.00	70.00	100.00	450.00
Virginia	14.44	15.89	17.00	40.00	70.00	100.00	450.00
Washington	11.62	12.78	17.00	40.00	70.00	100.00	450.00
West Virginia	12.74	14.01	17.00	40.00	70.00	100.00	450.00
Wisconsin	9.04	9.95	17.00	40.00	70.00	100.00	450.00
Wyoming	9.26	10.19	17.00	40.00	70.00	100.00	450.00
average	13.59	14.95					

by Powell (*24*). So. despite an approximately 12% increase in U.S. vehicle registrations from 2006 to 2017, we estimate total U.S. MAC refrigerant emissions will fall by between 60% (*Low Leak scenario*) and 15% (*High Leak scenario*).

The main reason of the decrease in total refrigerant emissions is the continuous improvement toward tighter MACs due to environmental regulations, cost reductions in purchasing materials by OEMs, and less refrigerant requirements in brand new MAC systems.

Although leak rates and future car volumes are uncertain, we believe that the *Low Leak scenario* predicts unrealistically low HFC-1234yf emissions in 2017 without further regulation restricting refrigerant emissions. The *High Leak scenario* for the U.S. fleet in 2017 is more in line with business-as-usual, and compares favorably with the current HFC-134a sales for MAC which represent the replenishing refrigerant requirements due to MAC leakage from service and repair. As a result the two scenarios provide a reasonable bracket of future HFC emissions from MAC systems. The type of refrigerant does not really matter in developing the emissions inventory because the leak rates of HFC-134a and HFC-1234yf are very similar. We assume a vehicle fleet in the U.S. equipped only with HFC-1234yf in 2017 to determine the potential environmental impacts of the new refrigerant (*27*), in particular the additional ozone and TFA production that may result when the new refrigerant is fully implemented.

Development of Spatially and Temporally Resolved Emission Fields for Air Quality Modeling. To use these annual, statewide emissions estimates in air quality modeling, it is necessary to resolve them to finer temporal and spatial scales. Depending on the type of model used, this may require anywhere from monthly and 800−1000 km allocation (for global models) to hourly and 1−50 km resolution (for urban-to-continental scale models). Considering the reactivity of HFC-1234yf, we have investigated ways to resolve these

TABLE 2. Total 2017 Direct and Indirect Leak Rates for Statewide Vehicle Fleet in the *Low* and *High Leak Scenarios*

state	low regular leakage rate (metric tons/yr)	high regular leakage rate (metric tons/yr)	irregular leakage rate (metric tons/yr)	low service leakage rate (metric tons/yr)	high service leakage rate (metric tons/yr)	low end-of-life leakage rate (metric tons/yr)	high end-of-life leakage rate (metric tons/yr)	low total leakage rate (metric tons/yr)	high total leakage rate (metric tons/yr)
Alabama	87	96	88	21	55	26	234	222	473
Alaska	5	6	13	3	8	4	34	25	61
Arizona	122	134	80	19	49	23	211	244	475
Arkansas	35	39	38	9	24	11	101	94	201
California	620	682	634	149	391	186	1,678	1,590	3,385
Colorado	65	72	98	23	60	29	259	215	489
Connecticut	38	41	58	14	36	17	154	127	290
Delaware	11.326	12	16	4	10	5	41	35	79
Dist. of Columbia	3	3	4	1	3	1	11	9	21
Florida	422	464	313	74	193	92	828	900	1,798
Georgia	153	168	158	37	98	47	419	395	843
Hawaii	32	35	19	5	12	6	51	61	117
Idaho	17	18	24	6	15	7	64	54	122
Illinois	119	131	189	44	117	55	499	407	935
Indiana	65	71	96	23	60	28	255	212	483
Iowa	41	45	64	15	39	19	169	139	318
Kansas	37	41	46	11	28	13	121	107	235
Kentucky	57	62	68	16	42	20	180	160	352
Louisiana	91	100	74	17	46	22	196	204	416
Maine	11	12	20	5	13	6	54	42	99
Maryland	66	73	86	20	53	25	227	197	439
Massachusetts	67	74	103	24	64	30	272	225	513
Michigan	94	103	156	37	96	46	412	332	768
Minnesota	49	54	90	21	56	26	238	186	437
Mississippi	39	43	38	9	24	11	101	98	206
Missouri	74	82	95	22	58	28	251	219	485
Montana	12	13	20	5	13	6	54	43	100
Nebraska	22	24	33	8	20	10	88	72	165
Nevada	31	34	26	6	16	8	69	71	145
New Hampshire	13	14	20	5	13	6	54	44	100
New Jersey	84	93	114	27	70	33	301	258	578
New Mexico	24	26	30	7	19	9	80	70	155
New York	159	175	216	51	133	63	571	489	1,094
North Carolina	111	123	120	28	74	35	319	295	636
North Dakota	6	7	14	3	8	4	36	27	65
Ohio	139	153	207	49	128	61	548	456	1,035
Oklahoma	55	61	61	14	38	18	162	149	321
Oregon	41	46	57	13	35	17	151	129	288
Pennsylvania	123	136	189	44	117	56	500	413	942
Rhode Island	10	11	15	4	10	5	41	34	77
South Carolina	72	79	66	16	41	19	175	172	360
South Dakota	9	10	16	4	10	5	43	34	78
Tennessee	96	106	97	23	60	29	257	245	520
Texas	410	451	335	79	207	99	887	922	1,880
Utah	30	33	43	10	26	13	113	96	215
Vermont	6	7	11	3	7	3	30	23	55
Virginia	108	118	127	30	78	37	336	302	659
Washington	74	82	109	26	67	32	288	240	545
West Virginia	21	23	28	6	17	8	73	63	140
Wisconsin	51	56	95	22	59	28	251	196	461
Wyoming	7	7	12	3	8	4	33	26	60
total	4,135	4,548	4,729	1,113	2,921	1,391	12,517	11,367	24,715

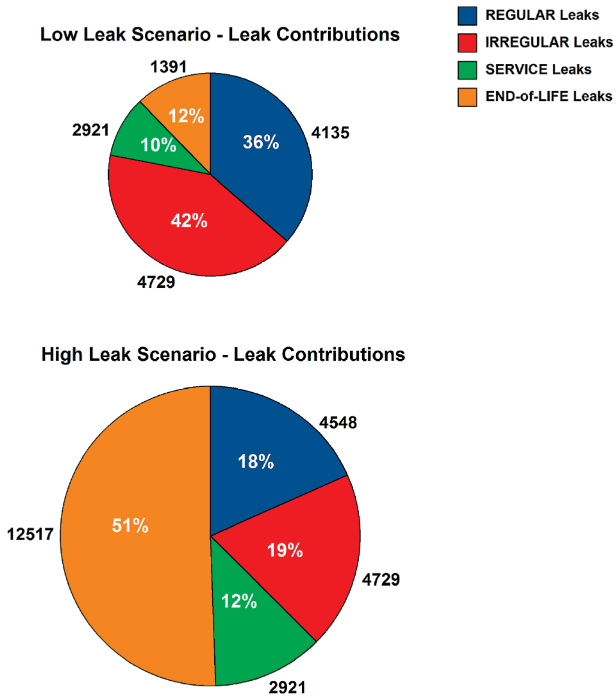

FIGURE 1. Contributions of individual leak rate categories to total 2017 MAC HFC-1234yf emissions in the *Low* (top) and *High* (bottom) *Leak Scenarios*. Leak rates in MT/yr and % of total emissions are shown outside and inside each slice, respectively. The relative area of the pie charts is proportional to the ratio of total emissions in the two scenarios.

emissions to hourly and 36-km modeling grid resolutions for use in regional air quality modeling simulations (*27*).

The *Low* and *High Leak scenarios* annual emissions were allocated to monthly emissions as follows. We first assumed that the regular, irregular, and servicing leaks occur mostly in the summer months when the air conditioning units are more likely to be used. As a first, conservative estimate, we have assigned the annual regular, irregular, and servicing leaks entirely and equally to the three months of June, July, and August. This is when the air conditioning units are more likely to be pressurized during usage, when servicing is most likely to occur, and when the higher temperatures and pressures will cause the greatest leak rates from small holes and tears. In contrast, we assumed that the end-of-life emissions occur throughout the year, and we have distributed these yearly emissions equally to each of the 12 months.

We then allocate the monthly and state-level emission estimates first spatially, and then to hourly emissions. We distributed the emissions among each state's counties based on population weighting from the 2000 Census data (*28*). This assumes that the fraction of total statewide residents that reside in each county remains constant. From the county-level emissions, we used the SMOKE emissions processing model (*29*) version 2.5 to allocate down to a 36-km resolution. Within SMOKE, we calculated factors to distribute the county-total emissions across the various 36-km grid cells that are wholly within or intersect the county. This is accomplished using a cross-referencing approach that assigns a spatial surrogate for on-road mobile nonlink sources based on the ratio of vehicle miles traveled (VMT) in a given grid cell to the total amount of VMT in the county. Allocation to smaller resolutions is based on census TIGER files of distribution of major roadways. Finally, HFC-1234yf emissions are given the same hourly temporal allocation as other mobile source emissions, based on national profiles of on-road activity data.

Results and Discussion

The computed 2017 statewide car and trucks registrations obtained from eq 2 are shown in Table S1 in the Supporting Information.

Table 1 presents the low and high leak rates for each vehicle and for each leak rate category. Table 2 presents leak rates for all vehicles by state and for the total 2017 U.S fleet for the *Low* and *High Leak scenarios*. Overall, the low emission estimate is approximately 46% of the high estimate.

Figure 1 shows the 2017 total U.S. HFC-1234yf emissions for the *Low Leak scenario* and Figure 1 presents the emissions of the *High Leak scenario*. Irregular leaks comprise 42% of all emissions in the *Low Leak scenario* with regular leaks accounting for a further 36%. Service and end-of life leaks are relatively modest. The breakdown of emissions is quite different in the *High Leak scenario*. Here 51% of total leaks are due to end-of-life losses and irregular leaks comprise 19% of the total. Regular leaks and service leaks together account for only 30% of total leaks.

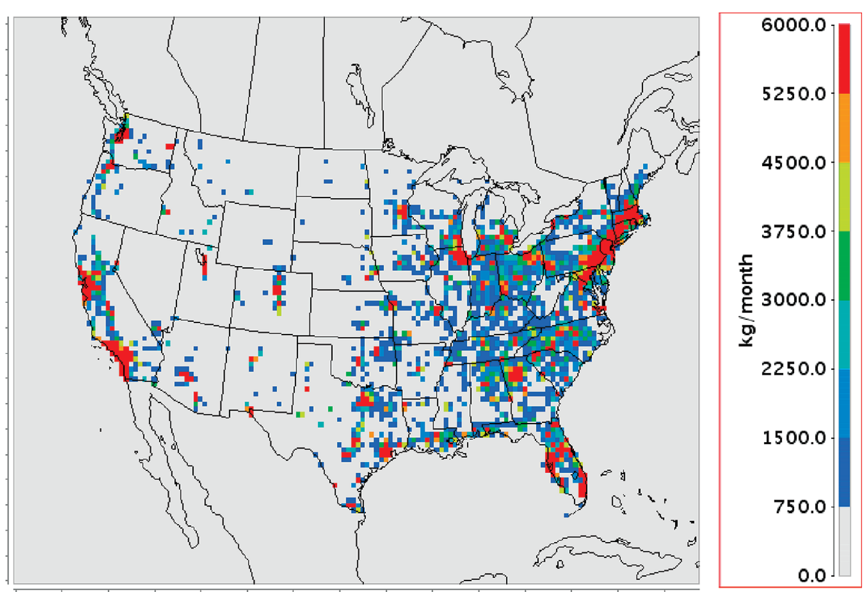

FIGURE 2. Estimated July monthly emissions of HFC-1234yf, in kg/month, for the *High Leak scenario*. Emissions are calculated for each 36 km × 36 km grid cell.

Figure 2 shows the resulting, spatially resolved distribution of emissions, summed over the month of July from the *High Leak scenario*. The spatial distribution of emissions in the *Low Leak scenario* is similar, although the magnitudes are lower. Because the state total emissions are allocated to 36-km grid cells based on the distribution of roadways and vehicle traffic, the highest emission rates correspond to urban areas with the highest population and traffic densities. In this summer month, the low scenario results in total emissions that are about 67% of the high emission rates, due to the large contribution of direct, indirect, and service emissions in the summer.

The amount of HFC-1234yf released is a small portion of the total volatile organic hydrocarbon (VOC) emissions into the atmosphere. The continental U.S. VOC emissions that result from HFC-1234yf average about 0.012% of total VOCs annually and 0.04% in the summer for the *Low Leak scenario*. Even in the *High Leak scenario*, HFC-1234yf is predicted to be less than about 0.027% of the total VOC inventory annually and 0.067% in the summer, which includes all VOC emissions from mobile, point, biogenic, and area sources. In addition, the major decay reaction of HFC-1234yf with OH is relatively slow, with a rate constant of 1.26×10^{-12} exp $(-35/T)$ cm^3 $molecule^{-1}$ sec^{-1} (*7*), resulting in an estimated lifetime with respect to OH decay of approximately 10−11 days.

A detailed study of the overall atmospheric reactivity of HFC-1234yf predicts an averaged maximum incremental reactivity of 0.267 g ozone/g VOC, similar to that of ethane (0.264 g ozone/g VOC) (*30*) and much less than the average reactivity of an urban mix of VOCs (3.502 g ozone/g VOC) (*31*). Each gram of HFC-1234yf that is released would therefore be predicted to produce only 8% of the ozone produced by an equivalent gram of "urban mix" VOC. Because of this, it is likely that the contribution of HFC-1234yf to total ozone formation will be even smaller than its relative contribution to the VOC inventory, but spatial and temporal inhomogeneities in emissions of HFC-1234yf and other reactive pollutants make it difficult to make definitive conclusions about the atmospheric implications.

Linking the HFC-1234yf emissions to the spatial and temporal allocations used in Mobile6 does not give an exact spatial distribution of the location of these emissions, but does serve as a first attempt to locate them approximately. We believe these assumptions will have little effect on the accuracy of the emissions distribution for two reasons. Because HFC-1234yf is moderately long-lived, it will disperse beyond the original emission sources, and the precise location of sources is not as important as the absolute magnitude of the emissions. In addition, at the 36 km grid resolution used in this allocation, precise location of sources is not necessary.

Because emissions of HFC-1234yf are expected to comprise a very small portion of the VOC inventory, it is likely that they will not contribute substantially to ozone formation, even in VOC-limited areas of the country, but more detailed modeling is required to determine the exact amount. The fate of reactive and fluorine-containing degradation products of HFC-1234yf is also of potential concern, given the widespread usage of MACs. We are currently pursuing detailed modeling studies using 3-D chemical-transport models to examine the magnitude and spatial distribution of degradation products across the U.S. (*27*), to investigate whether an increase in vehicle air conditioner fuel efficiency could offset air quality impacts from refrigerant VOC emissions.

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Supporting Information Available

Table 1 showing the current and projected vehicle registrations for each state. This material is available free of charge via the Internet at http://pubs.acs.org.

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