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High-Global Warming Potential F-gas Emissions in California: Comparison of Ambient-Based versus Inventory-Based Emission Estimates, and Implications of Refined Estimates

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Supporting Information

ABSTRACT: To provide information for greenhouse gas reduction policies, the California Air Resources Board (CARB) inventories annual emissions of high-global-warming potential (GWP) fluorinated gases, the fastest growing sector of greenhouse gas (GHG) emissions globally. Baseline 2008 F-gas emissions estimates for selected chlorofluorocarbons (CFC-12), hydrochlorofluorocarbons (HCFC-22), and hydrofluorocarbons (HFC-134a) made with an inventory-based methodology were compared to emissions estimates made by ambient-based measurements. Significant discrepancies were found, with the inventory-based emissions methodology resulting in a systematic 42% underestimation of CFC-12 emissions from older refrigeration equipment and older vehicles, and a systematic 114% overestimation of emissions for HFC-134a, a refrigerant substitute for phased-out CFCs. Initial, inventory-based estimates for all F-gas emissions had assumed that equipment is no longer in service once it reaches its average lifetime of use. Revised emission estimates using improved models for equipment age at end-of-life, inventories, and leak rates specific to California resulted in F-gas emissions estimates in closer agreement to ambient-based measurements. The discrepancies between inventory-based estimates and ambient-based measurements were reduced from −42% to −6% for CFC-12, and from +114% to +9% for HFC-134a.

1.0. INTRODUCTION

The fastest rising sector of greenhouse gas (GHG) emissions globally are from the high-global-warming potential (GWP) substitutes to ozone-depleting substances (ODS), primarily hydrofluorocarbons (HFCs),[1,2] which have 100-year GWPs up to thousands of times greater than carbon dioxide.[3] HFCs are synthetic gases used in refrigeration, air conditioning, insulating foams, solvents, aerosol products, and fire protection. In 2012, HFC emissions were estimated to contribute to approximately 1 to 2% of all global GHG emissions in carbon dioxide (CO_2)-equivalents (using 100-year GWP values).[1] By 2050, without reduction measures in place, HFC emissions are likely to contribute between 9 and 19% of all global GHG emissions (on a CO_2-equivalent basis).[2] Additionally, ODS including chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are also important high-GWP compounds that continue to contribute significantly to GHG emissions, although their use is being phased out as part of the Montreal Protocol.[4,5]

The California Global Warming Solutions Act of 2006, Assembly Bill 32 (AB 32) requires California to reduce greenhouse gas (GHG) annual emissions to 1990 levels by 2020, a reduction of 16% below estimated business-as-usual

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emissions in 2020 without AB 32 regulations in place.[6] Additional GHG emission reductions are required by California Executive Order S-3-05 which sets a long-term goal of 80% reduction of GHG emissions in California between 1990 and 2050.[7] The California Air Resources Board (CARB), tasked with implementing AB 32 to reduce GHG emissions, recognizes HFCs and other high-GWP ODS substitutes as the fastest-growing GHG sector. CARB also continues to monitor ODS emissions and develop measures to reduce their emissions.

A necessary first step in managing and reducing emissions of high-GWP GHGs was for CARB to develop a state-specific inventory of emissions from high-GWP fluorinated gases (commonly referred to as "F-gases") that include the following 32 F-gases estimated to comprise more than 99% of all F-gas emissions (by mass and by CO_2-equivalents) in California:

- **CFCs**: CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 ($C_2F_3Cl_3$), CFC-114 ($C_2F_4Cl_2$), and CFC-115 (C_2F_5Cl)
- **HCFCs**: HCFC-22 ($CHClF_2$), HCFC-123 ($C_2HF_3Cl_2$), HCFC-124 (C_2HF_4Cl), HCFC-141b ($C_2H_3FCl_2$), HCFC-142b ($C_2H_3F_2Cl$), and HCFC-225ca/cb (50−50 blend of $C_3HF_5Cl_2$ isomers)
- **HFCs**: HFC-23 (CHF_3), HFC-32 (CH_2F_2), HFC-43−10mee ($C_5H_2F_{10}$), HFC-125 (C_2HF_5), HFC-134a ($C_2H_2F_4$), HFC-143a ($C_2H_3F_3$), HFC-152a ($C_2H_4F_2$), HFC-227ea (C_3HF_7), HFC-236fa ($C_3H_2F_6$), HFC-245fa ($C_3H_3F_5$), and HFC-365mfc ($C_4H_5F_5$)
- **Perfluorocarbons (PFCs) and perfluoropolyethers (PFPEs)**: PFC-14 (CF_4), PFC-116 (C_2F_6), PFC-218 (C_3F_8), PFC-318 (C_4F_8), and PFC/PFPEs (used as a proxy for a diverse collection of PFCs and PFPEs employed for solvent applications)
- **Brominated fluorocarbon fire suppressants (Halons)**: Halon 1211 (CF_2ClBr), and Halon 1301 (CF_3Br)
- **Miscellaneous F-gases**: Sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), and sulfuryl fluoride (SO_2F_2)

F-gas emission estimates in California are based upon a bottom-up inventory methodology developed by CARB staff.

2.0. INITIAL METHODOLOGY AND RESULTS

The initial methodology used to estimate high-GWP F-gas emissions in California were not based on data or emission factors that were regional or state-specific, but were simply scaled-down from U.S. EPA national estimates.[8]

2.1. Initial Methodology Using Scaled National Estimates. F-gas emission estimates for California were first derived in 2007 from population proportion scaling of the results of the national Vintaging Model developed by the U.S. EPA.[8,9] The Vintaging Model was developed as a tool for estimating the annual chemical emissions from industrial sectors that have historically used ozone-depleting substances (ODSs) in their products, or use ODS substitutes, including HFCs. The model name refers to the fact that it tracks the use and emissions of annual "vintages" of equipment that enter service in a given production year. The Vintaging Model is a "bottom-up" model that utilizes information regarding the annual market size, growth, amount of the chemical required by each unit of equipment, chemical substitute history, amount of F-gas used during equipment lifetime, and emission losses at end-of-life.[9]

Emission sectors reported in the Vintaging Model include commercial refrigeration, domestic refrigeration, industrial process refrigeration, mobile air conditioning, stationary air-conditioning (AC) large commercial, stationary AC small commercial, stationary AC residential, transport refrigeration, metered dose inhaler (MDI) aerosol propellants, non-MDI aerosol propellants, solvents, fire suppressants, and insulating foam.

To preserve confidential industry data, emissions of specific compounds are not reported, but are instead aggregated by group as CFC, HCFC, HFC, or Halons, and reported as CO_2-equivalent GHG emissions (using 100-year GWPs). Therefore, the Vintaging Model could not be used in isolation to estimate emissions of specific compounds such as CFC-12, HCFC-22, and HFC-134a from specific emission sectors. It should be noted that the U.S. EPA "Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990−2011" does show the GHG emissions for the following specific fluorinated compounds: HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-236fa, and CF_4 (PFC-14).[10] Although the specific emission estimates are an improvement over aggregated HFC and PFC emission estimates shown in the Vintaging Model, the available data were still not sufficient to estimate the emissions of specific compounds from specific emission sectors.

2.2. Initial Methodology—Applying State-Specific Data. Inventory estimates of F-gas emissions have historically used records of reported production and sales, and applied estimated emission factors that describe the delays between manufacture and emissions to the atmosphere based on the various uses.[11−13] However, this approach is no longer valid for ODS such as CFCs and HCFCs that have ceased production. The banks of existing ODS in equipment and materials now determine current emissions. The emissions from banks of ODS are often difficult to estimate due to incomplete data on the types and numbers of equipment that continue to use ODS refrigerant, or the amount of products and materials still in use or landfilled that contain ODS. Further complicating emission estimates of ODS are unreported amounts of stockpiling, recycling, black market smuggling across borders, and possible illicit production.[14]

Since 2007, CARB has steadily refined the initial F-gas emission estimates by replacing scaled-down Vintaging Model estimates with California state-specific emission estimates as additional state-specific data became available. CARB used the U.S. EPA Vintaging Model as a starting point, and further disaggregated the 14 emission sectors into the following 30 subsectors, as shown in Table 1.

For each emission subsector, an emissions estimates methodology was developed, using accepted methodologies for ODS substitutes emissions as recommended by the IPCC guidelines for estimating GHG emissions.[15] The emissions estimates methodology is comprehensively described in the Supporting Information for this paper, and summarized below.

For commercial stationary refrigeration and air-conditioning (AC) subsectors, we analyzed more than 30 000 refrigeration and AC equipment refrigerant usage records from 2002−2010 as reported to the South Coast Air Quality Management District (SCAQMD) in compliance with Rule 1415, "Reduction of Refrigerant Emissions from Stationary Refrigeration and Air Conditioning Systems".[16,17] The refrigerant usage records were used to determine types of systems used, average charge sizes (capacity of refrigerant), annual leak rates, and types of refrigerant used. For residential refrigeration and AC, CARB-sponsored original research was reported by Mathis et al., 2011.[18]

Table 1. F-Gas Emission Sectors and Subsectors Used To Determine California High-GWP Emissions

emission sector of F-gas	subsector description
aerosol propellants (MDI)	metered dose inhalers (MDI)
aerosol propellants (non-MDI)	consumer product and commercial/industrial aerosols
commercial refrigeration and AC large (>22.7 kg [50 lbs] systems)	centralized system ≥907.2 kg (2 000 lbs)
	centralized system 90.7 to <907.2 kg (200 to <2 000 lbs.)
	centrifugal chiller ≥907.2 kg (2 000 lbs)
	centrifugal chiller 90.7 to <907.2 kg (200 to <2 000 lbs)
	chiller packaged 90.7 to <907.2 kg (200 to <2 000 lbs)
	cold storage ≥907.2 kg (2 000 lbs)
	cold storage 90.7 to <907.2 kg (200 to <2 000 lbs)
	process cooling ≥907.2 kg (2 000 lbs)
	refrigerated condensing units 22.7 to ≤90.7 kg (50 to ≤200 lbs)
	unitary AC 22.7 to ≤90.7 kg (50 to ≤200 lbs)
commercial refrigeration and AC small (≤22.7 kg [50 lbs] systems)	refrigerated condensing units ≤22.7 kg (50 lbs)
	unitary AC ≤22.7 kg (50 lbs)
fire suppressant	fire suppressant
fluorinated pesticides	sulfuryl fluoride fumigant
foam insulating	foam (appliance building refrigeration equipment transport marine buoyancy)
industrial	industrial solvents
	semiconductor manufacturing
	sulfur hexafluoride uses
medical	medical sterilants
mobile and transport	light duty (LD) vehicle AC
	heavy duty (HD) vehicle (non-bus) AC
	bus AC
	off-road heavy duty vehicle
	transport refrigerated units (TRUs) including rail cars
	refrigerated shipping containers
	ships (marine vessels)
residential	residential refrigerator-freezers
	residential AC

Mobile vehicle AC emissions and transport emissions were estimated by CARB by developing a methodology to determine the number of units, charge sizes, annual refrigerant loss rates, and end-of-life refrigerant losses. The methodology relies on vehicle data and emissions using the CARB EMissions FACtor model (EMFAC), and the OFFROAD model. Significant new research was also conducted by the authors to develop an emissions methodology to determine emissions from the remaining F-gas emissions sectors. Details are provided in the Supporting Information.

For each emissions subsector, an emissions profile was developed, which includes types and number of units [equipment or material], average lifetime of equipment/material, types and distribution of F-gases used in sector, average F-gas charge per unit, average annual leak or loss rate, and average loss rate of F-gases at equipment/material end-of-life. Annual emissions from each of the emission subsectors were calculated using the following basic formula:

$$\begin{aligned}\text{emissions} = {} & [\text{number of units (equipment in use)} \\ & \times \text{average F-gas charge/unit} \times \text{average annual} \\ & \text{leak or loss rate}] \\ & + [\text{number of units reaching EOL} \\ & \times \text{average F-gas charge/unit} \\ & \times \text{average loss rate at EOL}]\end{aligned}$$

where EOL denotes end-of-life.

Emissions by mass were then proportionally distributed to specific F-gas compounds by the actual equipment/material distribution for each F-gas. Several emission sectors that do not use banked amounts of F-gases in equipment are considered 100% emissive, with emissions equal to usage for the following sectors: MDIs, consumer product and commercial/industrial aerosol propellant, medical sterilants, industrial solvents, semiconductor manufacturing, sulfuryl fluoride, and sulfur hexafluoride in all uses except electric switchgear.[15]

An important outcome of conducting a state or regional-specific F-gas emissions inventory (rather than relying on scaled-down national estimates) was highlighted by the discovery of a regional anomaly of relatively high GHG emissions in California from sulfuryl fluoride (SO_2F_2), a non-ODS pesticide fumigant substitute for methyl bromide. Sulfuryl sulfide has an estimated 100-year GWP value of 4780.[19−21] Although not included in the U.S. EPA GHG inventory, and regarded by the European Commission as contributing "a negligible share of global greenhouse gases", between 50 to 60% of the entire global usage of sulfuryl fluoride takes place in California, with estimated emissions of 960 metric tonnes (4.6 $MMTCO_2E$) in 2008, or 9% of all F-gas emissions in California (51.0 $MMTCO_2E$) by GHG CO_2-equivalents (for comparison, all non-F-gas GHG emissions in CA in 2008 were 471.4 $MMTCO_2E$).[22−24]

2.2.1. Selecting F-Gases for Comparison of Inventory-Based Emissions Estimates with Ambient-Based Emissions Estimates. After inventory-based F-gas emission estimates had been completed for emissions year 2008, as part of a quality assurance/quality control check, the emissions estimates were compared to ambient-based emission estimates from air samples collected at Mount Wilson in Los Angeles County, California. Bottom-up inventory-based emissions for 2008 in California at a state-wide level were scaled to the population proportion of the Los Angeles County Air Basin.

For comparison, we began with bottom-up inventory emission estimates of representative F-gases from the three main groups studied (CFCs, HCFCs, and HFCs), selecting the F-gases with the estimated highest emissions (by mass or by GHG CO_2-equivalents) for each group: CFC-12 for CFCs, HCFC-22 for HCFCs, and HFC-134a for HFCs. Using the inventory-based emissions estimates from the first refinement of the emissions model, the three selected F-gases (CFC-12, HCFC-22, and HFC-134a) were estimated to represent approximately 70% of F-gas emissions by mass, and 65% of F-gas emissions by GHG CO_2-equivalents. An additional rationale for our selection is that each F-gas represented one of the three "generations of refrigerants", with each generation displaying slightly different emission patterns. The CFCs (first generation) were phased out of production by the end of 1995, and much of their emissions would be expected at equipment EOL. HCFCs (second generation) would not begin phase-

down in new equipment until 2010 for HCFC-22 (the most common HCFC used), and would represent a class of F-gases used continuously for several decades, with a balance of emissions from annual use and EOL. HFCs (third generation), developed as substitutes to ODSs, were not in common use until after 1995, and as a newer class of refrigerants, we expect emissions from active use to be greater than EOL emissions.

2.2.2. Ambient-Based Emissions Estimates Methodology. An air quality monitoring station adjacent to the Mount Wilson Observatory in Los Angeles County was installed in April 2007 to study GHG emissions in the Los Angeles (LA) urban area. Mt. Wilson is a prominent peak located in northern LA County. The monitoring station is south-facing, overlooking the LA metropolitan area and is an ideal site to collect air samples from the LA urban plume due to the strong and rapid upslope flow of well-mixed air from the urban lowland during daylight hours,[25] with reversed subsidence flow replacing the urban air with air from the lower free troposphere at night. Air samples were collected using hourly canister sampling for comprehensive organic gases and carbon monoxide (CO) during four intensive sampling periods: April 28th to May sixth, 2007; September 8th to 16th, 2007; November 10th to 18th, 2007; and February 9th to 17th, 2008.[26] Canister samples were quantified with a gas chromatography system (GCs) calibrated immediately before organic gases analysis. Three HP 6890s form the core of the analytical system. Electron-capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), and a quadrupole mass spectrometer (MS, for unambiguous compound identification and selected ion monitoring) were employed. We sampled for a suite of 54 hydrocarbons, halocarbons, and alkyl nitrates by cryogenic preconcentration and split injection into a multicolumn/detector GC system, which is described in detail by Gorham et al., 2010.[27] Absolute accuracy is estimated to vary from 2% to 10%. The limit of detection is less than 0.1 parts per trillion by volume (pptv) for the halocarbons of interest and the precision is 1% to 5%. The whole air samples were also analyzed for CO using a separate GC system that employed a packed column separation followed by catalytic conversion of CO to methane and subsequent detection by FID. The limit of detection for CO is 1 part per billion by volume (ppbv), with an accuracy of 5% and 4 ppbv precision.

Atmospheric measurements of the ratio of the selected F-gas (CFC, HCFC, or HFC) to carbon monoxide (CO) (CFC:CO, HCFC:CO, or HFC:CO) are combined with measured CO emission rates. The selected F-gas emissions were estimated by scaling from estimates of CO emissions using the enhancement ratio of concentrations above background.

F-gas emission studies in California show that several F-gases and carbon monoxide exhibit good collocation, which indicates that F-gases are correlated with urban CO emissions from human activities, and tend to be well-mixed in urban areas in the atmosphere before reaching the sampling site.[28−30] For example, Barletta et al., 2013, notes, "Considering that most HCFC and HFC emissions are released from refrigeration and stationary and mobile air conditioning systems, HCFC and HFC emissions will be collocated with CO emissions related to residential and commercial activities and to transportation. In the SoCAB [Southern California Air Basin], transportation dominates CO emissions (light-duty trucks and passenger vehicles emit about 43% of CO in the SoCAB) ... as a result, CO and halocarbon emissions are relatively well collocated as indicated by the regression analysis."[30]

The relationship between the interested halocarbons and CO mixing ratios measured between 11 am and 6 pm at the Mount Wilson monitoring station during the four discrete seasonal campaigns shows a good linear correlation, indicating that these gases are well mixed before reaching the Mount Wilson site and source contributions of these compounds are reasonably consistent. The accuracy of the "top-down" approach utilized for Mount Wilson ambient air measurements relies both on the quality of the CARB CO inventory, which has been developed over decades using extensive monitoring programs with validation from ambient ratio studies, tunnel studies, fuel-based inventories, and remote sensing techniques;[31−34] and on the validity of the assumption that the approximately constant CFC-12, HCFC-22, and HFC-134a to CO ratios observed at Mount Wilson is representative of the total emission of the LA County area. Additional details on the ambient air measurements are provided in the Supporting Information.

2.3. Initial Results. Large discrepancies were apparent when emission estimates were compared between the results of the ambient-based and inventory-based estimates, as shown in Figure 1.

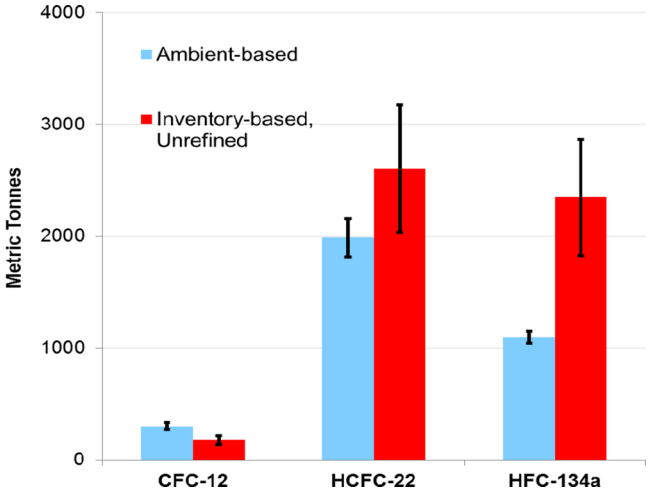

Figure 1. Los Angeles County, California; selected F-gas emissions estimates in metric tonnes (MT) for 2008, ambient-based vs inventory-based.

Ambient-based air measurement emission estimates shown in blue are compared to the initial, unrefined inventory-based emission estimates shown in red. CFC-12 ambient-based emissions estimates were 303 ± 33 MT vs 177 ± 39 MT for inventory-based estimates. HCFC-22 ambient-based emissions estimates were 1987 ± 173 MT vs 2602 ± 472 MT for inventory-based estimates. HFC-134a ambient-based emissions estimates were 1097 ± 52 MT vs 2345 ± 516 MT for inventory-based estimates. (A description of the uncertainty analysis is included in the Supporting Information.)

The initial inventory-based emission estimates were less than ambient-based emission estimates for CFC-12 by −42%; greater than ambient-based emission estimates for HCFC-22 by 31%, and also greater for HFC-134a by 114%.

Uncertainty levels for inventory-based emission estimates were relatively higher at plus or minus 14 to 25%, compared to the uncertainty levels of ambient-based measurements, which ranged from plus or minus 5 to 11%. Therefore, it was assumed that the ambient-based emission estimates were likely to be more accurate than bottom-up inventory-based emission

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estimates that often rely on incomplete data and best estimates of F-gas usage and equipment numbers.[14] The discrepancy in emission results served as a catalyst for CARB staff to develop a more refined methodology for inventory-based emissions estimates. To determine the cause of the discrepancies from the inventory-based methodology, we first had to analyze the underlying assumptions and factors used to estimate F-gas emissions.

3.0. REFINED METHODOLOGY

Analysis of initial results: In the initial inventory-based estimates, emissions of CFC-12 were apparently underestimated, and emissions of HFC-134a were apparently overestimated. A preliminary explanation for the discrepancy was that an overestimation was made of the magnitude and rate at which HFC-134a had replaced CFC-12. It was known that by 1996, HFC-134a had made a complete replacement of CFC-12 for new vehicles in the mobile vehicle AC sector, and also for new appliances in the residential refrigerator-freezer sector.[4] The emissions methodology refinement began with these two sectors because it was known that their F-gas emissions of CFC-12 and HFC-134a were inversely related, that is, emissions had to be either CFC-12 or HFC-134a (except for a small amount of HCFC-22 emissions from bus AC systems).

The causes of the apparent 31% overestimate of HCFC-22 emissions were analyzed further to ascertain which, if any, emissions methodology factors or assumptions were contributing to a discrepancy with ambient air estimates. Unlike HFC-134a, HCFC-22 was not a replacement for CFC-12, but had been in use in parallel with CFC-12 for many years, which indicated that the discrepancy of the HCFC-22 emissions would not be related to a phase-out of CFCs. Additionally, for all 30 emissions sectors and 32 F-gases investigated, all emission factors and assumptions used to estimate inventory-based emissions were compared to previously published usage, emission factors, and assumptions, and emission assessments of ODS and ODS substitutes, including U.S. EPA studies,[8−10,35−38] IPCC reports,[15,39] United Nations Environment Programme (UNEP) Reports,[40−44] and technical associations and consultant reports.[45−51]

3.1. Equipment Age at End-of-Life Oversimplification Skews Emission Estimates. After all the assumptions and emissions input factors for each of the 30 emission subsectors and all F-gases had been compared to previous research and emissions inventory reports, several factors were selected for additional improvement/refinement, which included updating assumed refrigerant leak rates during lifetime of the equipment and at the end of equipment useful life (EOL), speciating all refrigerants used in a given equipment production year (rather than grouping similar refrigerant classes together), and conducting additional research on the number of commercial facilities in California with stationary refrigeration systems. However, the assessment indicated that the strongest possibility for improving emission estimates could be through additional refinement of the assumptions regarding age of refrigeration and AC equipment at EOL. An overly simplistic approach had been employed that assumed that all equipment from a given production year (or vintage) is in use until average lifetime is reached, at which time all of the equipment retires and none is used past its average lifetime.

The 0 to 100% retirement (within one year) assumption does not adequately represent an expected normal distribution curve of equipment retirement, with some of the equipment retiring before or after the age of average lifetime; and would not adequately estimate EOL emissions for equipment using recently introduced F-gases, or those that have been phased-out of production and are no longer used in newer equipment.

For example, for residential appliances with an average lifetime of 14 years, it had been assumed that all CFC-containing refrigerator-freezers manufactured before 1996 would reach EOL before 2009. Beginning in disposal year 2009, no CFC-containing appliances would be within the mix of appliances reaching EOL.[18] Similarly, on the basis of U.S. EPA Vintaging Model outputs, it was assumed that all mobile AC emissions by 2010 would be HFC-134a, with no emissions of CFC-12.[8] However, additional information on appliance recycling and auto dismantling indicated that appliances and vehicles containing CFC-12 were in fact, still being recycled as of 2010.[35,52,53] The existing simplistic application of age of equipment at end-of-life resulted in a systematic, compounding effect of under-estimating emissions of F-gases from older equipment, while overestimating emissions of F-gases from newer equipment. The net results were to significantly underestimate CFC emissions, and significantly overestimate HFC emissions.

A less simplistic methodology was needed to develop more accurate equipment age distributions at end-of-life. Studies available on equipment and appliance retirement age (EOL) indicate a normal distribution curve represents actual appliance and equipment retirement ages.[54−57] Using retirement age data and regression curves, it is shown that appliances begin to retire almost immediately after their year of manufacture, with the longest tail-end of equipment functioning until 200% the age of the average lifetime of the equipment.

We applied the normal distribution of functional life and retirement age, or "survival curve" to the emission equations for all refrigeration and AC equipment. Data are lacking on the retirement ages of very large commercial refrigeration and AC equipment, therefore, it was assumed that commercial equipment follows a similar functional life and retirement age curve ("survival curve") as smaller equipment. See Figure 2 for a comparison of equipment survival curves.

Figure 2 shows survival curves that include the original, unrefined "curve" used, shown as a dashed green line, where all equipment is in use until average lifetime is reached, at which

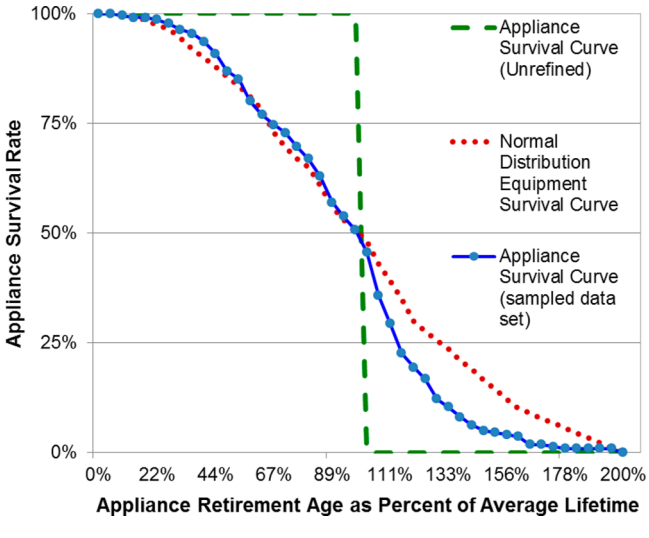

Figure 2. Equipment end-of-life function curve ("survival curve").

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time all equipment reaches EOL. The normal distribution survival curve is shown as a red dotted line. For comparison purposes, an average lifetime curve for household appliances (refrigerator-freezers) as sampled is shown as a blue line with blue dots, which compares closely to the normalized survival curve.[57]

The normal distribution survival curve indicates that half of all equipment are still in use at the time of average lifetime of equipment. Thus, the previously used equipment retirement model of 100% retirement at average equipment lifetime resulted in significant underestimates of CFCs (used in equipment manufactured prior to 1995), and overestimates of replacements to CFCs, primarily HFCs.

4.0. REFINED RESULTS AND DISCUSSION

The discrepancies between ambient-based and inventory-based emission estimates were reduced for the selected F-gases. The refined emission estimates for 2008 for the selected F-gases are shown in Figure 3.

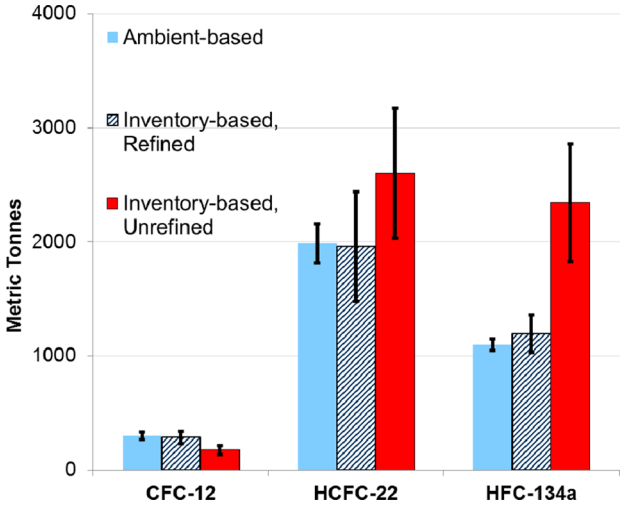

Figure 3. Los Angeles County, California; selected F-gas emissions estimates in metric tonnes for 2008, ambient-based vs inventory-based (unrefined and refined estimates).

Ambient air emission estimates shown in blue are compared to the refined inventory-based emission estimates (dark-striped bars) for selected F-gases. Unrefined estimates shown in red are also included for comparison to the refined estimates.

For the refined estimates, ambient estimates remain the same. CFC-12 ambient-based emissions estimates were 303 ± 33 MT vs 286 ± 57 MT for the refined inventory-based estimates. HCFC-22 ambient-based emissions estimates were 1987 ± 173 MT vs 1959 ± 480 MT for inventory-based estimates. HFC-134a ambient -based emissions estimates were 1097 ± 52 MT vs 1192 ± 165 MT for inventory-based estimates.

The discrepancies between inventory-based estimates and ambient-based measurements were reduced as follows: from −42% to −6% for CFC-12; from +31% to −1% for HCFC-22; and from +114% to +9% for HFC-134a. The reassessment of EOL emissions assumptions was the primary factor in reducing discrepancies in CFC-12 and HFC-134a, while the reduced discrepancy for HCFC-22 was primarily due to a refinement (decrease) in the number of facilities containing large HCFC-22 refrigeration or AC systems (based on CARB direct surveys on commercial business and industry refrigerant usage).[58] In addition to the three representative F-gases, all sectors and F-gas emission estimates were refined by applying EOL emission refinements and other emission estimate refinements as described in the Supporting Information document. Table 2 shows refined, inventory-based emissions estimates in California in 2008 for all 32 F-gases investigated.

In addition to closer agreement between inventory-based and ambient-based emission estimates in 2008 for CFC-12, HCFC-22, and HFC-134a; as a follow-up comparison to alternate ambient-based emissions estimates, we compared the 2010 inventory-based emission estimates to the findings of Barletta et al., 2013,[30] from the California Research at the Nexus of Air Quality and Climate Change (CalNex 2010) sampling, which showed a continuing close agreement for HCFC-22 emissions, with ambient-based measurements (in the Southern California Air Basin) of 3170 ± 340 MT, compared to inventory-based estimates 2985 ± 730 MT (6% less than ambient-based estimates). Additionally, there was close agreement for the ambient-based emissions estimates in 2010 of HCFC-124, HCFC-141b, HCFC-142b, and HFC-152a compared to the CARB inventory-based estimates.[30]

Refined emission estimates for F-gases have also been calculated for years 1990 through 2050 in California (back-cast revisions and forward projections were applied); the refined emissions estimates for years 2000−2011 have been used in the official CARB greenhouse gas inventory.[24] Emission trends are shown in Figure 4.

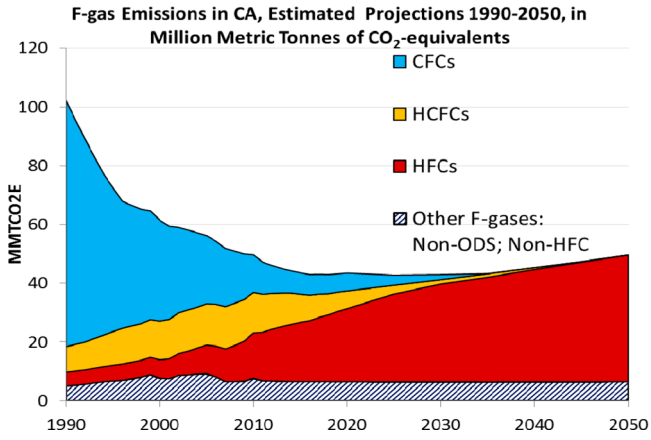

Figure 4. California estimated emissions, 1990−2050, for fluorinated gas groups of CFCs, HCFCs, HFCs, and all other F-gases.

The vertical axis shows emissions by $MMTCO_2E$ for the four main groups of F-gases studied: CFCs, HCFCs, HFCs, and all other non-ODS, non-HFC F-gases. GWP values are from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report of 2007 (AR4) 100-year GWP values. CFC emissions are shown in blue, HCFC emissions are shown in gold, HFC emissions are shown in red, and all other F-gases are shown in blue diagonal stripes. By 2050, ODS emissions will be negligible, but the HFC and ODS substitutes emissions are estimated to increase from 24.5 $MMTCO_2E$ in 2012 to approximately 50 $MMTCO_2E$, by 2050, a 100% increase.

The long-term GHG emissions goal in California is no greater than 85 $MMTCO_2E$ emissions annually from all sources by the year 2050 (80% reduction from baseline year 1990 levels of 427 $MMTCO_2E$).[7] However, if the emissions trends of ODS

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Table 2. High-GWP Emissions in California, 2008. Shown by Speciated Compound. Statewide Results Are Shown in $MMTCO_2E$, Kilograms, and kg/capita

F-gas or high-GWP gas inventoried	GWP value[a]	2008 $MMTCO_2E$ state[b]	percent of total high-GWP GHG emissions (by CO_2E)	2008 kg state[b]	2008 kg/capita[b]
CFC-11	4750	6.24	12.1%	1 300 000	0.035
CFC-12	10900	11.72	22.8%	1 100 000	0.028
CFC-113[c]	6130	0.09	0.2%	15 000	0.0004
CFC-114	10000	0.20	0.4%	20 000	0.0005
CFC-115	7370	0.50	1.0%	68 000	0.002
HCFC-22	1810	13.34	26.0%	7 400 000	0.19
HCFC-123	77	0.01	0.01%	80 000	0.002
HCFC-124	609	0.16	0.31%	260 000	0.007
HCFC-141b	725	0.26	0.5%	360 000	0.01
HCFC-142b	2310	0.17	0.3%	72 000	0.002
HCFC-225 ca/cb	359	0.02	0.04%	51 000	0.001
Halon 1211	1890	0.01	0.01%	3 600	0.0001
Halon 1301	7140	0.07	0.1%	10 200	0.0003
HFC-23[d]	14800	0.08	0.1%	5 100	0.0001
HFC-32	675	0.10	0.2%	150 000	0.004
HFC-43−10mee	1640	0.03	0.05%	17 000	0.0005
HFC-125	3500	2.11	4.1%	600 000	0.016
HFC-134a	1430	6.41	12.5%	4 500 000	0.118
HFC-143a	4470	2.23	4.3%	500 000	0.013
HFC-152a	124	0.40	0.8%	3 200 000	0.085
HFC-227ea	3220	0.14	0.3%	43 000	0.001
HFC-236fa	9810	0.10	0.2%	11 000	0.0003
HFC-245fa	1030	0.53	1.0%	520 000	0.014
HFC-365mfc	794	0.0003	0.001%	400	0.00001
PFC-14	7390	0.17	0.3%	23 000	0.001
PFC-116	12200	0.48	0.9%	39 000	0.001
PFC-218	8830	0.01	0.03%	1 600	0.00004
PFC-318	10300	0.01	0.02%	1 100	0.00003
PFC/PFPEs[e]	9300	0.002	0.004%	200	0.00001
NF_3	17200	0.17	0.3%	9 800	0.0003
SF_6	22800	1.02	2.0%	45 000	0.001
SO_2F_2	4780	4.60	9.0%	960 000	0.025
totals		51.4	100%	21 400 000	

[a]GWP values are 100-year time horizon GWP values from the IPCC Fourth Assessment Report of 2007.[3] [b]Refined emission estimates have the following uncertainties: ±20% for CFC-12 and ±17% for all other CFCs and Halons; ±25% for HCFC-22 and ±24% for all other HCFCs; ±14% for HFC-134a and ±15% for all other HFCs; and ±13% for all other F-gases (PFCs, PFC/PFPEs, NF_3, SF_6, and SO_2F_2). The unrefined emission estimates uncertainty had been aggregated for all F-gases at ±22%. [c]According to the California Office of Environmental Health Hazard Assessment (OEHHA), continuing illegal importation of CFC-113 from Mexico to California, used in the clandestine manufacture of methamphetamines, contributes an additional, but unknown amount of CFC-113 in California.[59] [d]In California, the minimal HFC-23 emissions are from its use in the semiconductor manufacturing industry, not from HCFC-22 production, which produces the majority of global HFC-23 emissions as an incidental and generally undesired byproduct. Although HCFC-22 will be phased out of production and import in the U.S. by 2020, it will continue to be produced globally for use as a feedstock for fluoropolymer production. Therefore, global HFC-23 emissions will continue to be a concern.[60] [e]For PFC/PFPEs, CARB follows the protocol established by the U.S EPA, which uses PFC/PFPEs as a proxy for a diverse collection of PFCs and PFPEs employed for solvent applications. For estimating purposes, the 100-year IPCC AR4 GWP value used for PFC/PFPEs was based upon C_6F_{14} (PFC-5-1-14, or perfluorohexane).[10]

substitutes continue, this emissions sector alone will comprise a full 59% of all GHG emissions in California.

4.1. Discussion. F-Gas emission estimates derived by inventory-based methods differed significantly for selected representative F-gases when compared to ambient-based measurements. A comparison between the results of the two methods led to a reassessment of all assumptions and input factors to estimate emissions using an inventory-based methodology. A systematic bias was revealed where it was assumed that all equipment would be removed from service once it had reached its average lifetime. Although the approach has been used to help simplify emission calculations in the past,[8,18] it leads to an underestimate of older chemicals phased out of production such as CFCs; and leads to an overestimate for newer replacement chemicals such as HFCs.

An implication of the findings is that inventory-based emission estimates must periodically be compared to actual ambient-based measurements and emissions estimates to assist in assessing the reasonableness of the inventory-based emission estimates. Another implication of the findings is that previously used inventory-based methods have likely underestimated ODS emissions, due to an underestimate of stockpiled chemicals and usage in older equipment.

Although a production and import phase-out of CFCs by December 31, 1995 was enacted in the U.S., CFCs continue to be a major source of GHG radiative forcing. We estimate that in 2010, CFC-12 contributed 3.2% of all F-gas emissions by mass, but due to its high GWP of 10900, comprised 16% of all GHG emissions by CO_2-equivalents from F-gases. If GHG and ODS reduction programs were to continue or expand their scope, they could further mitigate the continuing ODS emissions such as CFC-12, which will likely continue through 2020.[61]

The likely ongoing emissions of CFCs more than 25 years after final phase-out of production is a realistic model for expected and continued emissions of HCFCs, which were phased-down from maximum production between 2003 and 2010,[5] and may serve as a cautionary tale when developing phase-out schedules for HFC production and import, with global consumption and emissions expected to increase five to ten times the present levels by 2050.[2] Large commercial refrigeration equipment can still be in operation for up to 27 to 40 years.[54,62] Therefore, equipment manufactured prior to the 2010 phase-down of HCFC-22 could be expected to still be in use until 2036 to 2050. For the mobile vehicle AC emissions sector, we can expect HFC-134a emissions to continue many years after a complete conversion of new model year vehicles to low-GWP alternatives.

ODS no longer produced have proven to be more persistent in use and emissions than previously believed. As with the persistence of ODS emissions, it is also reasonable to expect a similarly lengthy impact from HFC-containing equipment, even if an HFC phase-down were to begin immediately. The mass of F-gas emissions continues to increase annually; therefore, if reduction of the GHG impact from HFC sources were to be made, a rapid transition to lower-GWP replacements would result in significant reductions of GHG impacts from F-gases, but not until existing banks of high-GWP F-gases become depleted, which would take several decades after complete phase-out of HFCs.

■ ASSOCIATED CONTENT

Supporting Information

Additional information for the F-gas inventory-based emissions estimates methodology and refinements: a comprehensive description of inventory-based emissions methodology, F-gas emission trends in California, and correlation charts for F-gases to carbon monoxide. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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