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Re-Evaluation of the UK's HFC-134a Emissions Inventory Based on Atmospheric Observations

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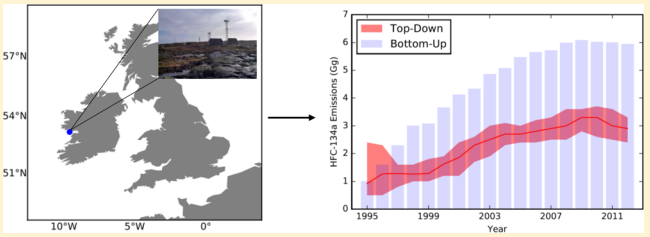
Supporting Information

ABSTRACT: Independent verification of national greenhouse gas inventories is a vital measure for cross-checking the accuracy of emissions data submitted to the United Nations Framework Convention on Climate Change (UNFCCC). We infer annual UK emissions of HFC-134a from 1995 to 2012 using atmospheric observations and an inverse modeling technique, and compare with the UK's annual UNFCCC submission. By 2010, the inventory is almost twice as large as our estimates, with an "emissions gap" equating to 3.90 (3.20−4.30) Tg CO_2e. We evaluate the RAC (Refrigeration and Air-Conditioning) model, a bottom up model used to quantify UK emissions from refrigeration and air-conditioning sectors. Within mobile air-conditioning (MAC), the largest RAC sector and most significant UK source (59%), we find a number of assumptions that may be considered oversimplistic and conservative; most notably the unit refill rate. Finally, a Bayesian approach is used to estimate probable inventory inputs required for minimization of the emissions discrepancy. Our top-down estimates provide only a weak constraint on inventory model parameters and consequently, we are unable to suggest discrete values. However, a significant revision of the MAC servicing rate, coupled with a reassessment of non-RAC aerosol emissions, are required if the discrepancy between methods is to be reduced.



INTRODUCTION

As a result of the Montreal Protocol on Substances that Deplete the Ozone Layer and subsequent amendments,[1−3] the production and consumption of ozone-depleting chlorofluorocarbons (CFCs), and their interim replacements hydrofluorochlorocarbons (HCFCs), is now prohibited in Annex 1 nations for all dispersive nonessential use. As a direct consequence, emissions of the third generation of fluorinated compounds, hydrofluorocarbons (HFCs), have risen dramatically.[4] Owing to an absence of chlorine, HFCs do not appreciably deplete stratospheric ozone.[5] However, long atmospheric lifetimes and strong infrared absorption profiles make them potent greenhouse gases. Typically, these gases have global warming potentials (GWP) many thousands of times greater than CO_2. As a result, HFCs were included within the Kyoto basket of greenhouse gases (GHGs), defined as one of six key groups of species deemed to have an adverse effect on global climate. According to a recent study by Rigby et al.,[4] HFCs accounted for 6% of radiative forcing incurred as a result of synthetic greenhouse gas emissions in 2012. By 2050, Velders et al.[6] estimate that HFC emissions may be equivalent to 9−19% of global CO_2 emissions in a business-as-usual scenario.

With a 2014 global mole fraction of 77.9 ppt,[4] HFC-134a ($C_2H_2F_4$) is the most abundant HFC in the global atmosphere. Due to the strength of sources above the equator, the Northern Hemispheric abundance is significantly higher, at 83.0 ppt. HFC-134a is a strong absorber of infrared radiation, with a GWP of 1300 (100-year time horizon).[7] In the UK, its predominant use is as a coolant in refrigeration systems and in particular, it is the refrigerant of choice for mobile air-conditioning (MAC) units of the type typically found in noncommercial vehicles.

As signatories to the Kyoto protocol, the UK must report annual emissions of HFC-134a to the UNFCCC.[8] These annual estimates are constructed using a bottom-up approach. In each emitting sector, the magnitude of the bank (product of the total number of sources and the average source unit volume), usually referred to as "activity data", is multiplied by an emissions factor and aggregated to generate a national estimate. However, bottom-up methods are subject to uncertainty.[9] Each sector is defined by three factors, representing the three key emissive stages in a products lifetime: manufacture, operation and disposal. At each loss stage, this factor is calculated as an average of the entire source sector and consequently, the resulting figure is often a disparate aggregation of local statistics scaled-up to national level. The complex nature of each refrigeration sector results in a number of assumptions being made, including unit lifetime and service rate, all of which increase the uncertainty of the final estimate. Consequently, independent assessment is required to verify

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each submission. In this study, we use high frequency atmospheric observations from the Mace Head observatory, Ireland, coupled with a transport model and an inverse modeling framework, to estimate national HFC-134a emissions for comparison with the UK inventory.

The UK HFC-134a Inventory. The UK's annual GHG inventory must adhere to guidelines provided by the International Panel on Climate Change (IPCC).[10] The majority of UK HFC-134a emissions are reported in UNFCCC category 2F: Consumption of Halocarbons and SF_6. A very minor contribution (<1%, reflecting the magnitude of UK halocarbon production) is observed in category 2E, Production of Halocarbons and SF_6. Here, we focus solely on consumption. The UK's annual submissions are available in Common Reporting Format (CRF) from the UNFCCC Web site (http://unfccc.int/ghg_data/items/3800.php). In 2010, the UK reported HFC-134a emissions of 6.0 Gg.

A graphical representation of UK HFC-134a emissive sectors (omitting production losses) is shown in Figure 1. Emissions

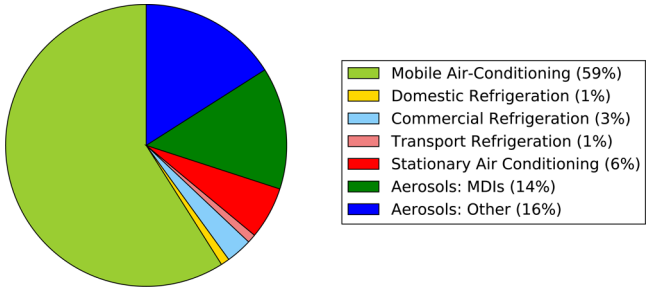

Figure 1. UK HFC-134a 2010 total emissions (UK NIR, 2014) by source sector (%). (MDI: metered dose inhaler).

from MAC units dominate the market both in the UK (59%) and across Europe, determined by the size of the respective automotive fleet. In 2010, the UK reported a MAC HFC-134a loss rate of 107 g vehicle^{-1} yr^{-1} (UK NIR, 2014 and SMMT), 27 g greater than the nearest comparable European nation. Refrigerant loss from a typical MAC unit occurs at three distinct stages of the product life-cycle: (1) initial emissions during unit manufacture, (2) operational emissions, occurring as a result of system leakage throughout unit lifetime, (3) disposal (end of life) emissions, predominantly due to the release of HFC-134a from a MAC unit upon scrapping/recycling. Losses occurring as a result of unit refill (MAC servicing) are included within stage two. Of the three emissive processes, over 90% of HFC-134a losses occur during the operational lifetime of the units (UK NIR, 2014).

The remaining 41% (2010) of UK HFC-134a emissions are split between six sectors. Refrigeration (domestic, commercial and transport) accounts for a combined 5% of the total inventory estimate, equivalent to 0.3 Gg. Stationary air-conditioning units, a diverse sector combining units of varying sizes (from small household to large commercial systems), commands a 6% share of HFC-134a emissions, equivalent to 0.36 Gg in 2010. The remaining 30% arises as a result of aerosol discharge (MDI (metered dose inhalers) and other). Aerosol emissions occur sporadically, and in comparison to refrigeration/air-conditioning units, operational loss is near total; when the propellant is exhausted, the aerosol canister is disposed of. To the best of our knowledge, the UK does not use HFC-134a as a blowing agent in foam manufacture. Subsequently, in contrast to a number of other EU states, no emissions are reported from this sector.

The Refrigeration and Air-Conditioning (RAC) Model. UK emissions from refrigeration and air-conditioning systems are quantified and collated using the RAC model (ICF International, AEA Ricardo). Combined RAC sectors account for over 70% of HFC-134a emissions, excluding only those from aerosols. The RAC model is split into 13 independent sectors based on source (as shown in Table 1); here we focus

Table 1. Summary of RAC Sectors, Including 2010 UK HFC-134a Emission Estimates (UK NIR, 2014) and Sector Contribution to Total RAC HFC-134a Emissions (%)

RAC sector	source	2010 emissions/tonnes
RAC-1	domestic refrigeration	171.92 (4.3%)
RAC-2	small hermetic stand-alone refrigeration units	49.33 (1.2%)
RAC-3	condensing units	37.73 (1.0%)
RAC-4	centralised supermarket refrigeration systems	34.73 (0.9%)
RAC-5	industrial refrigeration	8.52 (0.2%)
RAC-6	small stationary air-conditioning	5.01 (0.1%)
RAC-7	medium stationary air-conditioning	13.54 (0.3%)
RAC-8	large stationary air-conditioning (chillers)	97.35 (2.5%)
RAC-9	heat pumps	0.07 (0%)
RAC-10	land transport refrigeration	10.41 (0.3%)
RAC-11	marine transport refrigeration	0 (0%)
RAC-12	light-duty mobile air-conditioning	3127.93 (79.0%)
RAC-13	other mobile air-conditioning	401.80 (10.2%)
total RAC		3958.34

predominantly on the sectors of greatest combined magnitude, RAC-12/13: Light and other mobile air-conditioning, respectively. The light mobile air-conditioning (LMAC) sector encompasses units contained within cars and small vans, whereas other MAC (OMAC) collates refrigerant emissions from larger vehicles, typically including buses, trains and HGVs (heavy goods vehicles). LMAC accounts for roughly 90% of total MAC emissions in the UK (UK NIR, 2014). Each RAC sector is modeled independently, relying on a single template that incorporates activity data, emission factors (manufacture, operation and disposal) and market assumptions.

MATERIALS AND METHOD

Atmospheric Observations. We use high frequency in situ measurements from the Mace Head observatory, a fully intercalibrated[11] monitoring site located on the west coast of County Galway, Ireland (Latitude 53.3°, Longitude −9.9°). Mace Head is one of 12 remote AGAGE (Advanced Global Atmospheric Gases Experiment)[12] sites, providing long-term in situ atmospheric measurements since 1987. Meteorological records (2012) show that roughly 50% of air arriving at the site comes from the marine sector; the Atlantic Ocean. Of the remaining samples, 35% are influenced by the UK prior to arrival at Mace Head. The analysis of HFC-134a began in 1994 and was originally achieved using a Finnigan Magnum Ion Trap coupled with a custom-built adsorption/desorption system (ADS).[13] In 1998, the instrument was upgraded to an Agilent quadrupole mass selective detector (MSD, Agilent 5973) and in 2003, the ADS setup was replaced by the Medusa GCMS, an automated preconcentration system providing a greater range of trace gas measurements. An exhaustive description of the

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Environ. Sci. Technol. 2016, 50, 11129−11136

Medusa GCMS setup and analysis routine can be found elsewhere.[11]

At Mace Head, a sample module draws air into the inlet at a high flow rate (~10 L min^{-1}). The height of this inlet is 10 m above ground level. Prior to analysis, each 2 L real air sample is preconcentrated by the Medusa system. Reference gas analyses, which determine and correct for small variations in detector sensitivity, bracket each ambient sample; due to the optimization of instrumental sampling parameters, a sample is acquired approximately every hour. At Mace Head, HFC-134a is reported relative to the SIO-05 (Scripps Institute of Oceanography) gravimetric calibration scale (as dry gas mole fractions in pmol mol^{-1}). A more complete description of the calibration procedure has been reported previously.[11,14]

RESULTS

Deriving HFC-134a Emissions Using Atmospheric Concentration Data. We infer UK HFC-134a emissions by combining atmospheric measurements with simulations from the Lagrangian particle dispersion model, NAME (numerical atmospheric-dispersion modeling environment)[15,16] within the Met Office's inversion modeling system, InTEM (inversion technique for emission modeling).[16,17] Similar regional modeling techniques have been described previously.[18,19] Simulations from NAME are used to generate recent (30-day) histories of air mass arriving at Mace Head for each 2 h measurement window. Using an iterative best-fit technique, simulated annealing,[20] InTEM searches for the emissions map that minimizes the difference between model and atmospheric observations. Emissions are output on a grid with an intrinsic horizontal resolution of 0.352° longitude by 0.234° latitude, with a single grid cell roughly equal to an area of 25 × 25 km. The geographical domain of the inversion grid is significantly smaller than that of the NAME air-history maps, ensuring that recirculating air-masses are accurately represented. Since very distant sources have little influence on UK observations, and are often indiscernible from background noise, we assume that air entering the inversion domain is of hemispheric baseline concentration. For a single 3 year inversion, the estimate for each grid cell is considered constant and geographically static within the domain. However, since all 3 year periods which completely overlap a calendar year are used, grid cells may be reassigned between inversions to account for new observations; the median of each set of inversions is then used to estimate the annual value. Due to the long atmospheric lifetime of HFC-134a, all loss processes are assumed negligible over the course of each 30 day simulation.[16] We assign infinite uncertainty to the a priori emissions and hence, their influence is considered negligible. Using InTEM, we estimate the spatial distribution of HFC-134a emissions across the modeled domain (14.30° W to 30.76° E and 36.35° N to 66.30° N). An estimate of UK emissions is obtained via aggregation of those grid cells that lay within the UK's borders and surrounding waters.

The uncertainty bounds of our top-down estimates represent a one sigma confidence interval. An in-depth description of the uncertainty estimation in InTEM has been discussed previously.[16] In short, the uncertainty space is explored using two methods. (1) Each inversion is solved multiple times using a range of baseline mole fractions within the baseline uncertainty. This uncertainty is estimated during the baseline fitting process applied to the HFC-134a observations at Mace Head. (2) By varying each 3 year inversion window by a month throughout the data period, each year is solved for multiple times, using a different set of observations in each case.[21] Since there is no correlation between inversions, multiple estimates are generated; the spread of standard deviations may be used to assign an uncertainty to each annual estimate.

Our annual UK estimates indicate a steady rise in the emission rate of HFC-134a between 1995 and 2010, corresponding well with its use as the dominant refrigerant gas (replacing first-generation CFCs) in UK markets and a steady increase in the magnitude of the UK's air-conditioned automotive fleet. There are indications that the growth rate may have diminished post-2010, although the trend is not statistically significant. The reduced emissions rate may reflect the introduction of low GWP fourth generation refrigerants, hydrofluoroolefins (HFOs). In particular, HFO-1234yf (CH_2 = $CFCF_3$) has been proposed as a potential "drop-in" replacement for HFC-134a,[22,23] with an estimated 15% share of the UK MAC sector in 2012.[24] The onset of the EU MAC Directive,[25] which bans the use of HFC-134a in new type-approved vehicles within the EU as of January 2011, may also be influential. A complete ban on HFC-134a as a refrigerant in new MAC systems comes into force in 2017.

Regional and global top-down/bottom up HFC-134a emission estimates have been compared previously.[9,26−28] Comparison of our estimates (red trend, Figure 2) with the UK's annual UNFCCC submission (blue trend, Figure 2) indicates a significant discrepancy. While the UNFCCC estimates follow a similar trend to the derived emissions, a notably greater growth rate results in an increasing emissions gap throughout the reporting period. In the first four years, our flux estimates show modest average growth of 0.11 Gg yr^{-1}, while the inventory grew at a rate of 0.66 Gg yr^{-1}. The rate deficit is greatest during the initial reporting period. However, the UNFCCC data exhibits greater annual growth in all but two years where emissions increased upon the previous year. As a consequence, 2012 inventory emissions of HFC-134a (5.92 ± 0.53 Gg) were approximately 3.12 Gg in excess of those inferred from atmospheric measurements (2.80 ± 0.10 Gg).

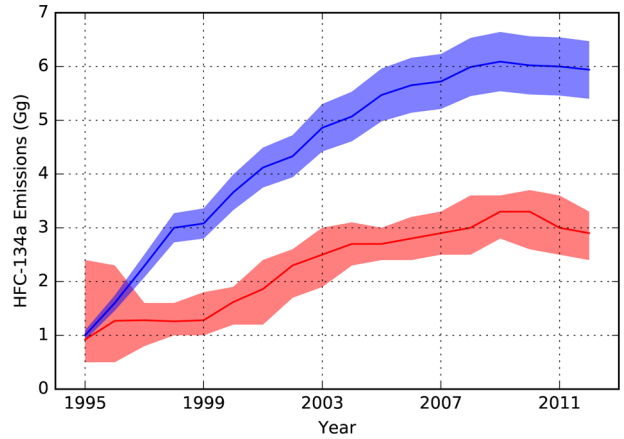

Figure 2. Annual UK HFC-134a emission estimates (Gg) from 1995 to 2012. In red, the results of our study using the Met Office' inversion modeling system, InTEM. In blue, the UK's UNFCCC submission (2014). Shaded regions indicate the respective uncertainty bounds. Inventory uncertainty is provided by the Department of Energy and Climate Change, whose estimation is described in detail elsewhere (UK NIR, 2014).

RAC Model Sensitivity Analysis. Each sector of the RAC model is comprised of input assumptions. Individual parame-

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Environ. Sci. Technol. 2016, 50, 11129−11136

Table 2. RAC-12 (LMAC) Input Assumptions

parameter	description
Refill	A yes/no input set to yes as default. when yes; all MAC units are assumed to be refilled (serviced) annually, when no; no refill of MAC units within unit lifetime. Refill refers to the 'topping off' of each MAC unit. Since operational losses are a percentage of the refrigerant charge, operational emissions are related to the refill frequency. The model does not account for refrigerant losses incurred during the service procedure itself.
penetration	The percentage of automobiles fitted with a MAC unit. Default values of 5% in 1990 and 80% in 2008, other years linearly interpolated.
lifetime	The assumed lifetime of MAC units in the UK automotive fleet.Default value of 15 years
life-cycle emission factors	Emission factors used to estimate refrigerant loss during the three stages of the MAC unit life-cycle; manufacture, operation and disposal. Default values (% yr^{-1}) of 0.5, 20, and 50 in 1990, and 0.5, 10 and 30 in 2010 respectively. Other years linearly interpolated.

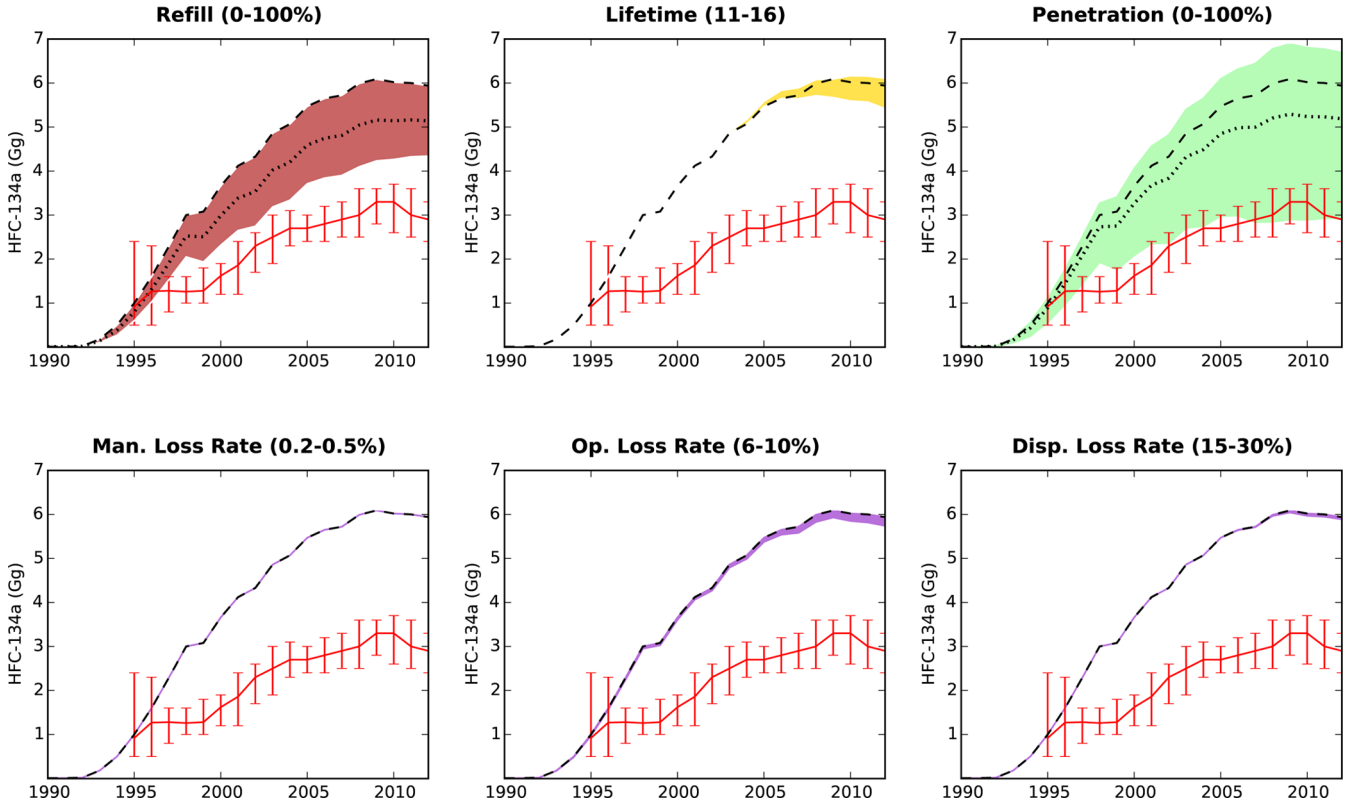

Figure 3. Summary of RAC model sensitivity to various RAC-12 input parameters, presented in the context of total HFC-134a emissions. Top Left; The unit refill parameter varied between 0 and 100%. The dotted line indicates a 50% refill rate, Top Center; Unit lifetime varied within recommended limits (11−16 years), Top Right; 2008 penetration rate varied between 0 and 100%. Values in other years are interpolated by assuming linear annual increase. The dotted line shows a penetration rate of 60%. Bottom Left; Manufacturing loss rate, varied between 0.2 and 0.5% (2010), Bottom Centre; Operational loss rate, varied between 6 and 10% in 2010, Bottom Right; Disposal loss rate, varied between 15 and 30% (2010). The dashed black line reflects the true inventory estimates, the solid red line with error bars indicates the estimates inferred from atmospheric data.

ters consist of a default value (Table 2) which may be varied by the user. Variation is subject to limits provided by the IPCC good practice guide,[10] in combination with recommendations from industry experts. Owing to the magnitude of the MAC market, small variations in each of these parameters, particularly when combined, can significantly influence the annual inventory totals.

To determine total MAC emissions, we first calculate the quantity of refrigerant contained within the market in a given year.

$$R = (S \times \mathrm{PR}) \times CS \quad (1)$$

Where R is the total amount (i.e., bank) of HFC-134a in MAC units in any given year, S is the vehicle stock and PR is the corresponding penetration rate. Charge size, CS, refers to the total volume of refrigerant in a single MAC unit, and decreases annually in line with assumed technological developments. Total operational emissions are then determined using eq 2.

$$E_{\mathrm{op}} = \left(\sum_{L} R_{\%r} \times O_{\mathrm{f}}\right) + \left(\sum_{L} R_{\%\mathrm{nr}} \times O_{\mathrm{f}} \times (1 - O_{\mathrm{f}})^{L}\right) + F_{\mathrm{ret}} \quad (2)$$

We define operational emissions, E_{op} as the sum of refrigerant contributions from refill ($R_{\%r}$), no-refill ($R_{\%\mathrm{nr}}$) and retrofit markets, where L is unit lifetime, O_{f} is the operational loss factor in a given year and F_{ret} are the retrofit emissions in that year. O_{f} was assumed to be 20% in 1990, and decreases

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Environ. Sci. Technol. 2016, 50, 11129−11136

linearly to a value of 10% in 2010, after which it remained constant. Retrofitting refers to the process by which MAC units, originally containing CFC-12, were modified to use HFC-134a in order to comply with environmental regulation and extend unit lifetime. Retrofit emissions peaked in 2002 at 0.095 Gg, and ceased in 2007 after all CFC-12 containing units had reached the end of their operational life. The contributions from refill and no-refill markets depend on the assumed servicing rate. In order to increase the flexibility of the model, we modify the Refill (YES/NO) parameter to allow variation between 0 and 100% (e.g., a 50% refill rate, representing annual servicing of half of the UK automotive fleet). The total new refrigerant is split based on the refill rate percentage, and calculated accordingly. Manufacturing and disposal losses are added to give total MAC emissions. We conduct a sensitivity analysis by varying the four input assumptions within their respective limits.

Refill. Changing the default refill setting (100%, annual service of all units) to 0% results in a theoretical emissions reduction of approximately 2 Gg in 2010, equivalent to a third of the inventory. While an assumption of no refill is implausible, varying the refill rate between extremes could significantly reduce the emissions total. Typically, leading car manufacturers (Volkswagen Group, Ford, Peugeot) recommend a 2 year MAC servicing frequency. The dotted line in Figure 3 (center) indicates an emission estimate trend generated by assuming a 1:1 ratio of units refilled to those not refilled, equivalent to annual servicing of half of the UK MAC fleet. The result of this modification is a 1 Gg reduction of the discrepancy in 2010.

Unit Lifetime. We vary the LMAC unit lifetime between 11 and 16 years, in accordance with IPCC (2006)[10] guidelines. Increasing the unit lifetime incurs a small increase in annual flux, however this is only observed after the expiration of the first generation of units. Increased theoretical emissions are observed due to a greater number of functioning MAC units in each reporting year. In contrast, reduction of the average unit lifetime limits the number of emissive units in each reporting year and subsequently, a small drop in emissions is observed. In 2010, lowering MAC unit lifetime to 11 years results in a 0.43 Gg reduction in HFC-134a emissions. Considering the strength of agreement between IPCC recommendations and industry estimates for LMAC unit lifetime,[24,29] coupled with the minimal influence of parameter fluctuations, we expect unit lifetime to be a minor contributor in efforts to reduce the emissions gap.

Penetration Rate. MAC market penetration rate is calculated by dividing the total number of MAC units in the UK automotive fleet by the size of the fleet itself. While the total number of cars in the UK is well-defined (Society of Motor Manufacturers and Traders (SMMT)), little information appears to exist regarding the number with an air-conditioning unit. The IPCC does not define a set range into which annual penetration rates should fall. Here, we vary the penetration in 2008 between 0 and 100%. Rates in other years are determined by interpolation, and assume linear market increase. Rate reduction reduces the number of light-duty MAC units on the UK market, therefore lowering emissions. We note that very low penetration rates are improbable, since these all but remove MAC's contribution toward total UK emissions. By applying a hypothetical penetration rate of 60%, emissions of HFC-134a were reduced by roughly 0.75 Gg in 2010. An increase in annual penetration rate results in the increased magnitude of reported emissions. Combining reduced unit refill with a lowered penetration rate significantly reduces emissions. While assuming 0% refill, setting a penetration rate of 60% generates a 2010 estimate only 0.3 Gg in excess of the InTEM uncertainty. Further research, in collaboration with DECC, is required to elucidate LMAC penetration rates fully representative of the UK market.

Life-Cycle Emission Factors. We vary the emission factors for manufacture (0.2−0.5%), operation (6−10%) and disposal (15−30%) in turn. Parameter uncertainty limits are specified within the model (AEA Ricardo). Minimal variation is observed within the recommended limits for manufacturing and disposal emission factors. This might be expected, given the limited (<10%) contribution of manufacture and disposal toward total MAC emissions. A small decrease in emissions is noted upon reduction of the operational loss factor. In 2012, this decrease was equivalent to 0.2 Gg; a minor decrement in comparison with the influence of refill and penetration rate. While we use 6% as the minimum operational emission factor, anecdotal advice from experts suggest this may be optimiztic; catastrophic losses involving total loss of refrigerant (vehicle collisions etc.) could prevent plausible reduction in this parameter below 8%, which may serve in limiting the influence of this parameter further.

BAYESIAN PARAMETER ESTIMATION

We can use the results from InTEM ($\mathbf{y}$) to update our understanding of the parameter estimates ($\mathbf{x}$), using Bayes theorem:

$$\rho(\mathbf{x}|\mathbf{y}) \propto \rho(\mathbf{y}|\mathbf{x})\cdot\rho(\mathbf{x}) \tag{3}$$

Based on our sensitivity analysis, we select the two most important RAC parameters, combine them with scalers for vehicle activity data and aerosol emissions and define their prior probability density functions (PDFs), $\rho(\mathbf{x})$. Refill: Defined previously. With no prior knowledge, we assume a uniform distribution between 0 and 100% inclusive. Penetration scaler: Defined previously. The default rate is 80% from 2008 onward. We set the lower bound to a scaling factor of 0.5. While we have no prior information regarding penetration rate, vehicle statistics are typically well-defined. Hence, we assume a Gaussian distribution centered on the default value (1) and a standard deviation of 0.1. Stock scaler: RAC vehicle activity data was originally provided by the SMMT. We compare this data with more recently available government statistics (www.gov.uk/government/collections/vehicles-statistics), and find these to be 10% lower than the SMMT projections for 2010. Henceforth, we introduce a scaler for vehicle stock, with a Gaussian distribution centered on the original SMMT estimate and a standard deviation of 0.1. Aerosol scaler: aerosols are a significant contributor of UK HFC-134a emissions, accounting for almost a third of the total inventory. We apply a scaling factor to the aerosol contribution, to account for uncertainty in the reporting method of these combined sectors (MDI and Other). We set the lower limit to 0, allowing maximum flexibility for the optimization routine, and the upper limit to 1.2. With no further knowledge to inform the model, a uniform distribution is assumed. Due to the limited sensitivity of the model, the influence of MAC unit lifetime variability, possible leak reduction technologies and emission factor uncertainties for manufacture, operation and disposal were omitted.

The likelihood function, $\rho(\mathbf{y}|\mathbf{x})$, compares the InTEM data to the output of the RAC model. It can be expanded, assuming each of the N data points (InTEM emissions) are uncorrelated:

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Environ. Sci. Technol. 2016, 50, 11129−11136

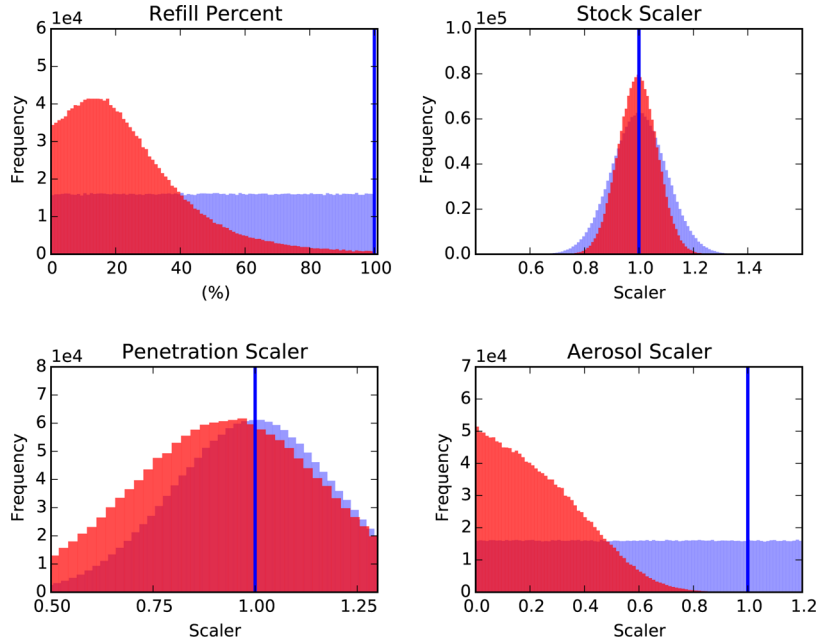

Figure 4. Parameter PDFs of the four selected model input parameters. In blue, the a priori PDFs for refill (uniform), stock (Gaussian), penetration (Gaussian) and aerosol scaling (uniform). The posterior PDFs are shown in red. The default parameter values are included as vertical blue lines.

$$\rho(\mathbf{y}|\mathbf{x}, \boldsymbol{\sigma}) \propto \exp\left(-\frac{1}{2}\sum_{n=0}^{N}\left[\frac{(\mathbf{y}_n - H(\mathbf{x})_n)^2}{\boldsymbol{\sigma}_n}\right]\right) \quad (4)$$

Parameters are stored in the vector $\mathbf{x}$, and the model is defined as $H(\mathbf{x})$. Sigma ($\boldsymbol{\sigma}$) is the uncertainty on each InTEM estimate, and n is the number of data points (InTEM years).

We can solve this system for arbitrary parameter PDFs and a nonlinear model using MCMC (Markov Chain Monte Carlo).[30] The posterior distribution was sampled using the Python package Emcee,[31] which uses an affine-invariant ensemble sampler.[32] This was run for 10 000 steps, with the first 5000 subsequently discarded to allow time for the Markov Chain to reach its equilibrium distribution.

The posterior PDFs (Figure 4) were found to be relatively broad for the refill, penetration rate and aerosol parameters, which indicates that the InTEM estimates provide only weak constraint on these parameters. Similarly, for the stock parameter, only a small reduction in the standard deviation of the posterior solution is found, compared to the prior. Given the lack of constraint, we cannot recommend specific parameter values here. However, what is clear from our analysis is that the rate of refill is likely to be significantly lower than the inventory default. Importantly, this will require a level of flexibility not available within the current model. As we argue above, a percentage refill input should be a minimum requirement, since neither 0 nor 100% refill rates are shown to be probable representations of the UK market. Our probability analysis indicates that refill is likely to be lower than 20% (median = 14%), however it should be noted that this parameter is significantly correlated with the derived penetration rate. A 20% refill rate corresponds to a refill frequency, averaged across the entire UK fleet, of approximately 5 years.

While no other studies appear to have been conducted with regards to UK refill rates, they have been estimated elsewhere. Papasavva et al.[33] projected high and low emission scenarios for US MAC units in 2017. In the high emission scenario, which we consider more likely to reflect vehicles in use between 1990 and 2012, a 15% refill rate was assumed. Under laboratory conditions, Hafner et al.[34] estimated that each MAC unit will receive 2 services during it is lifetime (in order to maintain the functionality of the unit). Given the assumed lifetime of a UK unit (15 years), this equates to a refill rate of approximately 14%. While this estimate, and that of the high emission scenario proposed by Papasavva et al. agree well with our median refill rate, further work is required to determine a true UK estimate. Climatic effects and differing refill modes (professional vs DIY) make comparison between countries difficult. By selecting the range of highest probability refill frequencies, centered on the median estimate of 14 ± 5%, we derive a 2010 operational emission rate of 56.2−62.3 g vehicle^{-1} yr^{-1} for the UK fleet. This compares well with Schwarz et al.,[35] who estimated an average leak rate of 52.4−53.9 g vehicle^{-1} yr^{-1} based on field measurements from across Europe, but less so with Papasavva et al., whose high emission scenario estimated a rate of 48.4 g vehicle^{-1} yr^{-1} for the US fleet. Further analysis of UK specific MAC emission characteristics is required to verify the results presented here.

As with refill, a lowering of the default input value for penetration rate is required to eliminate the emissions gap. However, the reduction is, statistically speaking, somewhat smaller, with the default penetration rate corresponding to the 61st percentile of our posterior PDF. The highest probability reduction in MAC penetration is 15%. In 2010, this results in a theoretical penetration rate of 68%.

Even with large emission reductions from MAC sectors (complete removal of MAC emissions would be required for the matching of InTEM and inventory absolute values), the magnitude of the emissions discrepancy is such that reduction in non-RAC sectors is needed. For the purpose of the current study, we merge MDI and other aerosol uses to form a single scalable sector. In practice, these independent sectors will be subject to different uncertainties and as such, unique scaling factors. Our analysis indicates the need for a significant reduction of UK aerosol emissions. We take the median value of 0.20 as the most probable parameter scaler, equivalent to an

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Environ. Sci. Technol. 2016, 50, 11129−11136

80% reduction in current UK HFC-134a aerosol emissions. In 2010, Germany reported aerosol emissions of 0.31 Gg (Germany NIR, 2014), while an 80% reduction in UK aerosol emissions (1.56 Gg) would yield an annual estimate of 0.32 Gg. Further work is required to explain the very large aerosol emissions reported by the UK (in comparison to other European nations). However, the matching of scaled UK emissions with the German equivalent suggest the results of our Bayesian analysis to be plausible.

DISCUSSIONS

Variation of key LMAC input parameters can result in significant alterations of the UK's HFC-134a inventory estimates. However, exclusive modification of the RAC model's largest sector, light mobile air-conditioning, does not yield a plausible scenario by which the inventory and our own top-down derived results show total agreement. In the initial analysis of the RAC model, we show the inventory to be particularly sensitive to changes in refill (servicing) and penetration rate. The refill assumption is of special interest, standing out as a notable oversimplification of the UK market. The current model accepts a single default value of 100%, assuming annual refill of all MAC units in the UK's automotive fleet. However, based on the recommendations of various manufacturers, it appears likely that the RAC model significantly overestimates the frequency of MAC servicing. A refill rate of 50% would represent the guidance of the automotive manufacturers, but our estimates show that this scenario may also be too high. Further research is required to develop this parameter. Owing to a lack of constraint provided by independent emission estimates inferred from atmospheric data, our Bayesian analysis provides only broad a posterior constraints. However, it is clear that significant revisions are required. If sufficient knowledge could be gained on refill trends, tightening the constraint on other parameters would be possible. Regardless, improving the flexibility of the refill parameter will be key in reducing RAC model uncertainty. As a minimum, we propose the substitution of the current parameter with a percentage type input (in addition to significant market research), but further development to allow annual rate variation would provide a more long-term solution.

As with refill rates, more research is required before we are able to make quantitative recommendations for a revised set of penetration rates, but reducing the number of air-conditioning units on the market in any given year has the potential to significantly reduce HFC-134a emissions from the MAC sector. In particular, combination with a revised refill rate estimate would drastically reduce reported emissions, bringing them further into line with our estimates. Analysis suggests a probable penetration rate reduction of up to 15%. While we stress the poor constraint on inventory model inputs, our work clearly defines the need for reassessment of the reporting method for HFC-134a. Analysis shows significant emission reductions will need to be found in multiple sectors, particularly MAC and aerosols, in order to reconcile the inventory with top-down estimates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03630.

Figure S1 showing a comparison of Mobile Air-Conditioning operating emission factors (by country), based on the relevant UNFCCC reports. Figure S2 showing a comparison of HFC-134a operating emissions per vehicle (by country) for 2010, based on UNFCCC emissions data and national vehicle statistics (PDF)

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Notes

The authors declare no competing financial interest.

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