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Evidence of a recent decline in UK emissions of hydrofluorocarbons determined by the InTEM inverse model and atmospheric measurements

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Supplement

S1 Measurement Site Information

Table S1 gives details of the instruments used, over which time periods, at each observation site.

Table S1. Instruments at each observation site and when they operated

Site	Operator	Instrument	Years Operated	Sampling Period	Frequency
Mace Head	Uni. of Bristol	GCMS	1994-1998	40 mins	every 6 hr
		GCMS	1998-2003	20 mins	every 4 hr
		GCMS-Medusa	2003-2020	20 mins	every 2 hr
Tacolneston	Uni. of Bristol	GCMS-Medusa	2012-2020	20 mins	every 2 hr
Carnsore Point	Uni. of Bristol	GCMS	2005-2010	20 mins	every 4 hr
Jungfraujoch	Empa	GCMS	2003-2008	20 mins	every 4 hr
		GCMS-Medusa	2008-2020	20 mins	every 2 hr
Monte Cimone	Uni. of Urbino	GCMS	2003-2008	20 mins	every 3 hr
		GCMS	2008-2020	20 mins	every 2 hr
Taunus	Uni. of Frankfurt	GCMS	2013-2020	2 mins	weekly flask

S2 InTEM model updates since Arnold et al. (2018)

InTEM has been improved since it was reported in detail in Arnold et al. (2018). The significant updates are listed here:

- The prior estimate of the background has been refined further. A daily, rather than hourly, background value is calculated after selecting those 2-hourly windows classified as background by fitting a 4th-order, 2nd-order or 1st-order (previously just 2nd-order) polynomial depending on the number of background points in a moving 6-month window (40-150 days previously).

- Time-integrated mole fractions (mol mol^{-1} s) are output from NAME which internally used the modelled temperature and pressure at the output location. Previously time-integrated air concentrations (g s m^{-3}) were output and subsequently converted using the station temperature and pressure. The latter is far less accurate especially when pertaining to high altitude stations.

- NAME was run using 20,000 rather than 5,000 particles per hour to reduce computational noise.

- InTEM now solves for a bias between the different observation stations, applicable here as different observation stations are used.

- The model uncertainty applied to each model time-period (4-hours in this study) has been significantly revised and is detailed in the main text.

- The heights of the 11 directions related to where the air enters the computational domain have been modified from 0–6 km, 6–9 km and >9 km to 0–3 km, 3–8 km and >8 km, relating to boundary layer/lower tropospheric, free-tropospheric and upper-tropospheric respectively.

- Each inversion undergoes 24 ’zooming’ steps rather than 50, the extra steps were found to be irrelevant in the UK context.

S3 Background mole fractions at each station

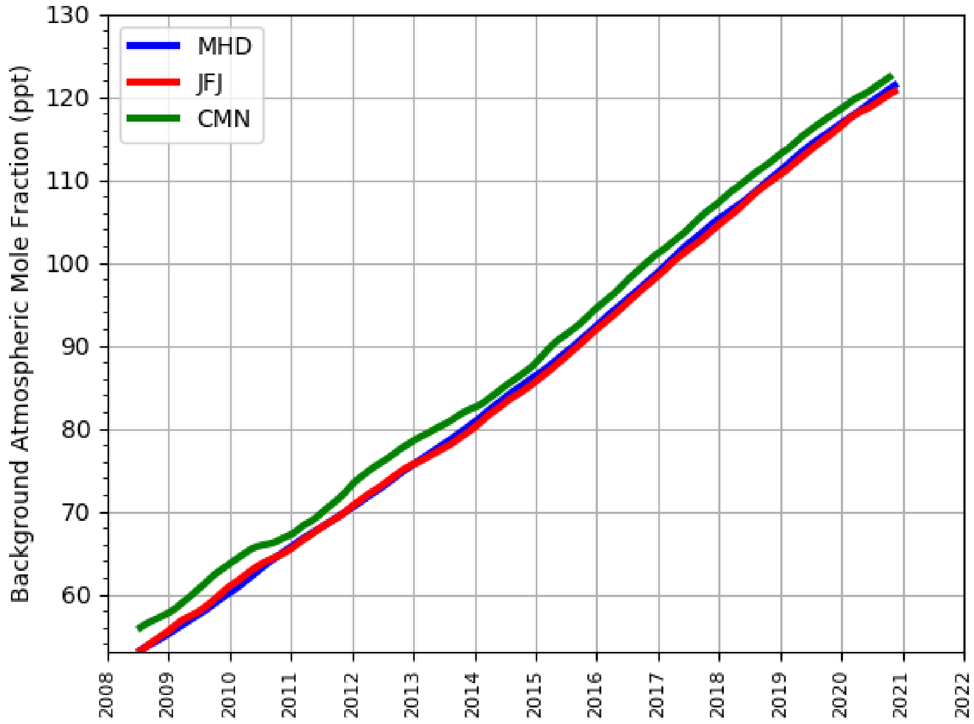

Figure S1. Comparison of prior background mole fractions of HFC-134a at MHD, JFJ and CMN 2008-2020

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Figure S2. Comparison of posterior background mole fractions of HFC-134a with observed data at CSP (2008–2010), TAC (2014–2016) and TOB 2014–2016

S4 Comparison of 1-year and 2-year inversion periods

Figure S3 shows the 1-year and 2-year inversion estimates for HFC-134a from 1994. The purpose of this figure is to demonstrate the unrealistic year-to-year variability in the 1-year inversion data when there is only one station operating (MHD). From 2003 data are available from JFJ and CMN, from CSP between 2005 and 2010, and from TAC and TOB from 2013. 2-year inversion periods are necessary up to 2012 to allow more data to be available to the inversion system to constrain the posterior UK emission estimate. 2-year inversion periods are necessary pre-2013 to increase the amount of data that the inversion system has to constrain UK posterior emission estimates. 1-year inversion UK estimates with TAC data give a more realistic, and thus smoother, year-to-year variability in the UK emissions. There is closer agreement in the 1-year and 2-year inversions as more data becomes available and hence the ability to present a 1-year inversion emission estimate for the UK from 2013.

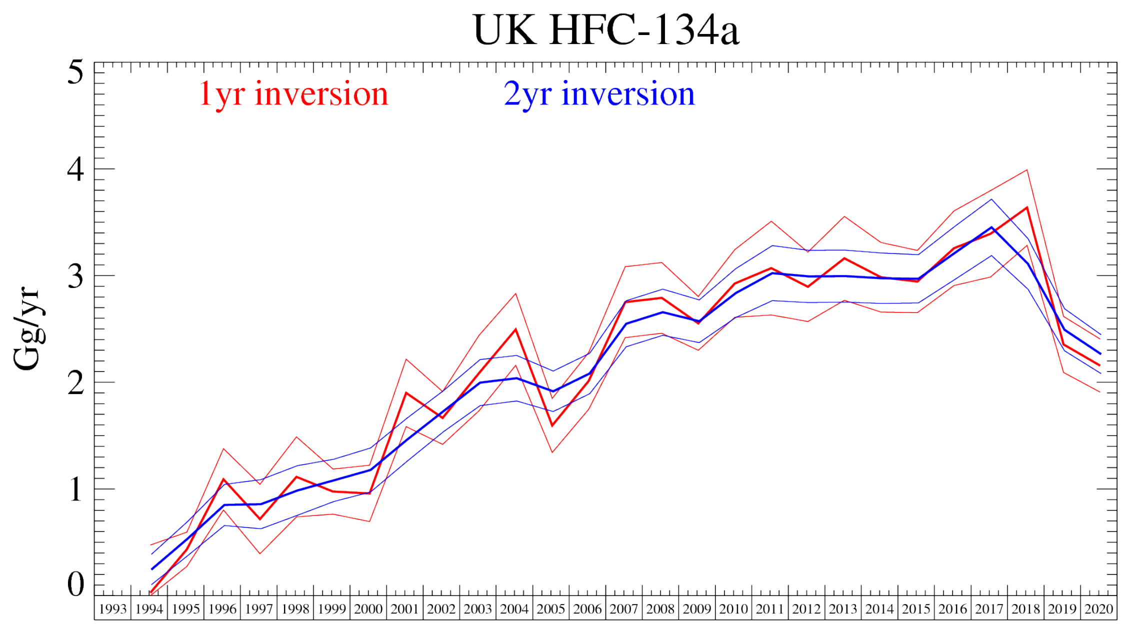

Figure S3. Annual UK InTEM emission estimates (Gg), annualised 2-year inversion (blue) and 1-year inversion (red) for HFC-134a. The uncertainty bars represent 1 σ.

S5 Impact of different measurement sites on UK HFC-134a emission estimates

The impact of adding measurement data from additional stations to the inversions on the UK emissions has been assessed by estimating HFC-134a UK totals with and without different measurement data. From 2006–2010 CSP data were included giving data from four sites (MHD, CSP, JFJ and CMN). With CSP data included the 2006–2010 average HFC-134a UK annual total was 3.45 $\pm$ 0.29 Tg CO_2-eq compared with 3.78 $\pm$ 0.34 Tg CO_2-eq without. The additional data-set from CSP has lowered the annual average emission estimate for the UK and the standard deviation but the uncertainty estimates still overlap. For the period 2013–2020, there are 5 sites available: MHD, JFJ, CMN, TAC and TOB. Using all data gives an average annual UK emissions estimate (2013–2020) of 4.06 $\pm$ 0.45 Tg CO_2-eq. Omitting data from TAC gives an estimate of 4.39 $\pm$ 0.64 Tg CO_2-eq and the removal of data from TOB gives 4.06 $\pm$ 0.45 Tg CO_2-eq. The effect of the additional data-set from TAC is therefore to lower both the annual average estimate and the standard deviation, but the uncertainties overlap. The addition of the TOB data-set has no impact on the UK estimates. The German station TOB provides only weekly flask data and therefore contributes far less data to the UK estimates than the other sites. The mountain stations (JFJ, CMN) are considerably more distant from the UK and the effect of their impact on the UK annual average 2013–2020 emissions estimate has also been considered. The 2013–2020 UK average without JFJ and CMN is 4.11 $\pm$ 0.47 Tg CO_2-eq, so again the loss of data from these stations slightly increases the UK estimate and standard deviation. This analysis does not assess the impact of the different data-sets on the spatial distribution of emissions which is much harder to assess quantitatively. The impact of each data-set on any individual annual UK estimate varies depending on data availability at each station. Additional data-sets, even if distant from the UK, allows the surrounding regions to be better constrained thereby improving the UK emission estimate. In all cases more data reduces the uncertainty of the UK estimate.

S6 Model versus observation timeseries statistics

Table S2 gives the correlation coefficient between the modelled data and the measurement data per gas per observation site for the InTEM-2yr data for 2018-2019. The 1-yr InTEM statistics are very much aligned to these values, for example the average 2019 and 2020 HFC-134a correlation coefficients for MHD, TAC, JFJ, CMN and TOB are 0.96, 0.80, 0.83, 0.71 and 0.43 respectively.

Table S2. Correlation coefficient (r) for the match between the observations and modelled time-series at the different sites. These are the results from the 2-yr inversion 2018-2019. NB for CSP used 2008-2009 as no data after 2010

Gas	MHD	TAC	JFJ	CMN	TOB	CSP
HFC-134a	0.97	0.80	0.87	0.74	0.47	0.82
HFC-125	0.96	0.81	0.92	0.80	0.73	0.79
HFC-143a	0.95	0.80	0.79	0.77	0.72	-
HFC-32	0.96	0.79	0.92	0.77	0.25	-
HFC-227ea	0.85	0.21	0.87	0.52	0.16	0.40
HFC-23	0.99	0.93	0.95	0.86	0.32	-
HFC-245fa	0.93	0.55	0.77	0.53	0.52	-
HFC-365mfc	0.87	0.64	0.69	0.60	-	0.71
HFC-152a	0.85	0.84	0.59	0.68	0.64	0.83
HFC-43-10mee	0.54	0.52	0.34	-	-	-

S7 Tabulated UK emission estimates for all HFCs

Table S3. UK emissions 2014 - 2020 estimated using InTEM (1-yr) in Tg CO_2-eq for each HFC and the composite total of all HFCs.

	2014	2015	2016	2017	2018	2019	2020
HFC-134a	4.05±0.44	4.00±0.40	4.43±0.48	4.61±0.55	4.95±0.48	3.20±0.36	2.94±0.33
HFC-125	2.79±0.43	3.42±0.40	3.21±0.40	3.28±0.50	3.38±0.43	2.52±0.33	2.21±0.29
HFC-143a	2.95±0.38	2.95±0.36	2.79±0.41	2.69±0.41	2.13±0.36	1.47±0.25	1.27±0.20
HFC-32	0.17±0.04	0.23±0.03	0.22±0.04	0.28±0.05	0.34±0.07	0.27±0.04	0.25±0.03
HFC-227ea	0.15±0.03	0.17±0.03	0.20±0.04	0.23±0.04	0.25±0.04	0.18±0.03	0.16±0.03
HFC-23	0.21±0.27	0.21±0.26	0.32±0.35	0.25±0.34	0.18±0.24	0.15±0.16	0.11±0.15
HFC-245fa	0.02±0.01	0.04±0.01	0.04±0.01	0.05±0.02	0.05±0.02	0.03±0.01	0.04±0.01
HFC-365mfc	0.09±0.01	0.08±0.01	0.09±0.01	0.06±0.01	0.07±0.01	0.04±0.01	0.04±0.01
HFC-152a	0.01±0.01	0.01±0.01	0.01±0.01	0.02±0.01	0.02±0.01	0.01±0.01	0.01±0.01
HFC-43-10mee	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01
Composite	10.46±0.77	11.10±0.72	11.32±0.82	11.48±0.91	11.38±0.78	7.89±0.58	7.04±0.51

Table S4. UK emissions 2008 - 2013 estimated using InTEM (2-yr: 2008 - 2012 & 1-yr: 2013) in Tg CO_2-eq for each HFC and the composite total of all HFCs.

	2008	2009	2010	2011	2012	2013
HFC-134a	3.62±0.29	3.50±0.27	3.86±0.31	4.11±0.35	4.07±0.33	4.30±0.53
HFC-125	2.38±0.19	2.35±0.19	2.66±0.24	3.10±0.28	3.28±0.29	3.62±0.50
HFC-143a	3.25±0.38	3.25±0.36	3.40±0.38	3.45±0.36	3.35±0.30	3.40±0.51
HFC-32	0.14±0.02	0.15±0.02	0.16±0.02	0.17±0.02	0.19±0.02	0.25±0.04
HFC-227ea	0.11±0.02	0.10±0.02	0.12±0.02	0.12±0.03	0.11±0.02	0.11±0.03
HFC-23	0.26±0.28	0.24±0.25	0.29±0.26	0.26±0.23	0.27±0.20	0.26±0.29
HFC-245fa	0.06±0.01	0.05±0.01	0.04±0.01	0.04±0.01	0.03±0.01	0.03±0.01
HFC-365mfc	0.09±0.01	0.06±0.01	0.06±0.01	0.07±0.01	0.06±0.01	0.06±0.01
HFC-152a	0.01±0.01	0.01±0.01	0.02±0.01	0.02±0.01	0.02±0.01	0.01±0.01
HFC-43-10mee				0.01±0.01	0.01±0.01	0.01±0.01
Composite	9.92±0.59	9.70±0.55	10.60±0.61	11.35±0.62	11.39±0.58	12.06±0.94

Table S5. Inventory reported UK emissions of the composite total of all HFCs 2006 - 2018 in Tg CO_2-eq.

2006	2007	2008	2009	2010	2011	2012
14.08±0.90	14.60±0.93	15.12±0.94	15.75±0.95	16.64±1.00	14.93±0.89	15.47±0.90

2013	2014	2015	2016	2017	2018	
15.85±0.88	16.04±0.88	15.96±0.85	15.10±0.81	14.00±0.75	12.86±0.68	

S8 UK emission estimates for the additional HFCs

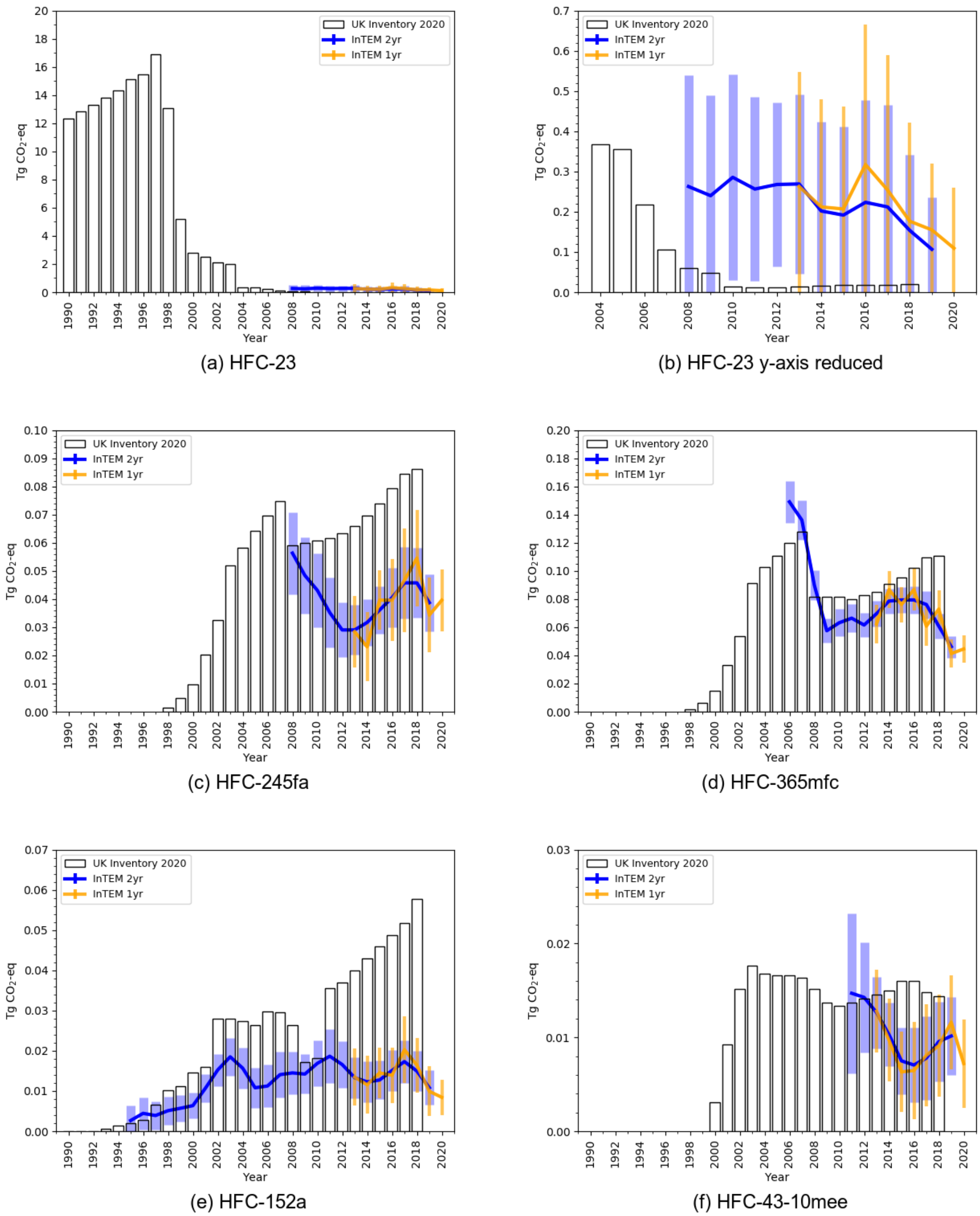

Figure S4. Annual UK emission estimates (Tg CO_2-eq) from the UK 2020 inventory (black), InTEM annualised 2-year inversion (blue) and InTEM 1-year inversion (orange) (a) HFC-23 (b) HFC-23 with y-axis reduced and x-axis starting in 2004 (c) HFC-245fa (d) HFC-365mfc (e) HFC-152a (f) HFC-43-10mee. The uncertainty bars represent 1 σ.

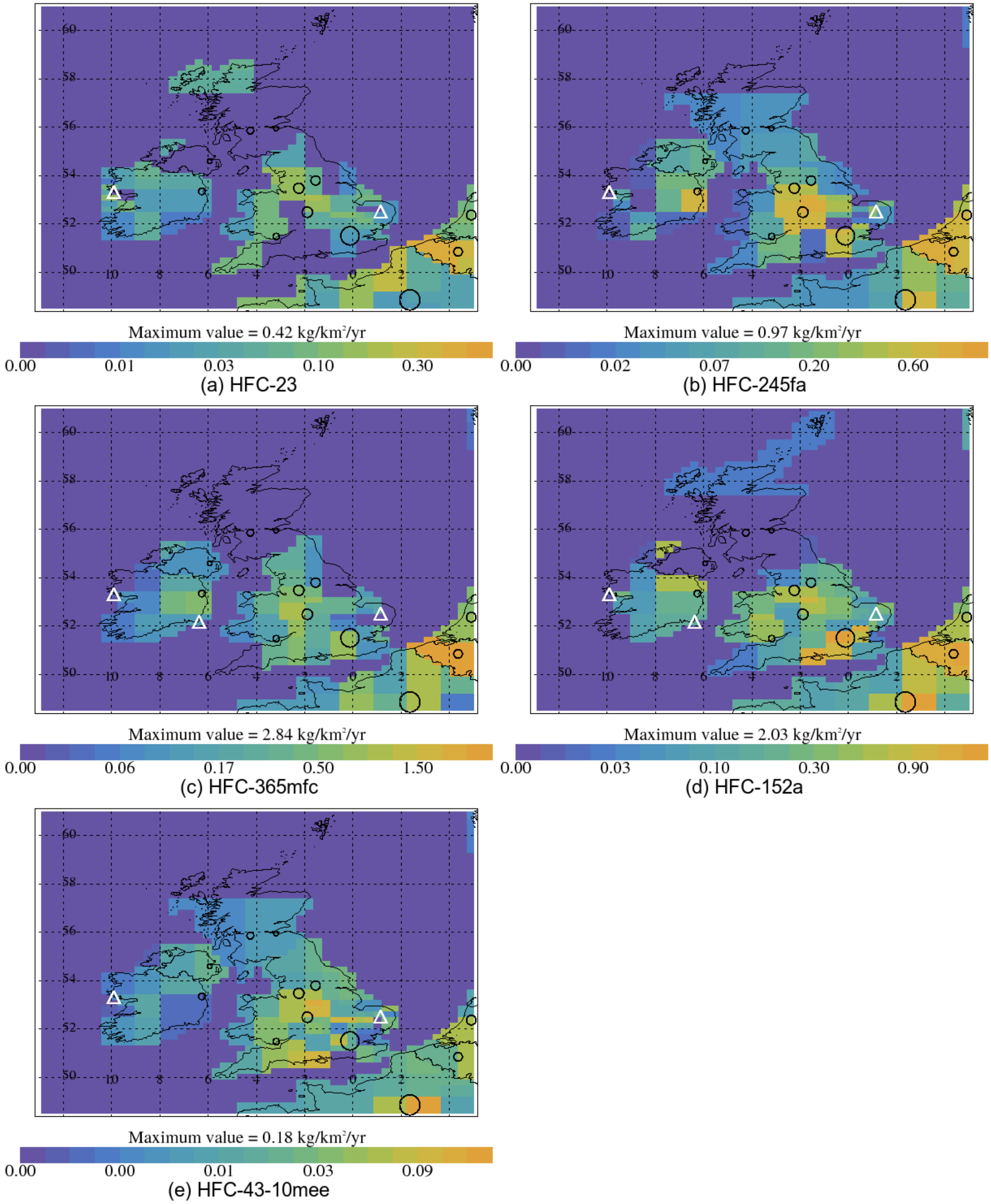

Figure S5. Two-year average InTEM emission estimates 2019–2020 (kg km^{-2} yr^{-1}) (a) HFC-23 (b) HFC-245fa (c) HFC-365mfc (d) HFC-152a (e) HFC-43-10mee. Black circles represent major cities and white triangles show the location of the observation sites.

S8.1 HFC-23

Future emissions of HFC-23, a by-product of HCFC-22 production, are expected to be limited by the Kigali Amendment to the Montreal Protocol, which mandates the destruction of HFC-23 to the extent that is practicable. Future global emission trends of HFC-23 will largely depend on the amount of HCFC-22 produced and the extent to which HFC-23 is destroyed by HCFC-22 production facilities. HCFC-22 is no longer produced in the UK. Fig. S4 shows the UK annual emissions estimated by InTEM plotted with the UK inventory 2020 values. InTEM emission estimates for the UK for HFC-23 from 2009 are higher than the emissions estimated by the inventory for this period, although the InTEM uncertainties are large and mostly extend down to zero. The spatial distribution of HFC-23 emissions over the UK is shown in Fig. S5. The levels of HFC-23 are fairly uniform over the UK. Higher emissions are indicated on the parts of the French coast, Belgium and the Netherlands.

S8.2 HFC-245fa

The InTEM estimates (Fig. S4) have significant uncertainty and are consistently lower than the inventory estimates, with the exception of 2008 and 2009. The inventory estimates show a significant decline of 0.02 Tg CO_2-eq from 2007 to 2008 and then a steady annual increase to 2018 reaching 0.09 Tg CO_2-eq. The InTEM estimates show a rapid decline from 2008, followed by a rise in emissions from 2014 with a peak in 2018 of 0.05 Tg CO_2-eq before a subsequent decline. Fig. S5 shows the spatial InTEM emissions estimate for HFC-245fa over the UK for 2019-2020. HFC-245fa generally follows the distribution of population over the UK. Higher emissions are indicated in Belgium and the Netherlands.

S8.3 HFC-365mfc

The inventory (Fig. S4) shows a sharp decline in emissions in 2008 and the InTEM 2-year estimates show a similar response. Post-2011 the inventory estimates rising UK emissions, a trend initially reproduced by InTEM, however the InTEM estimates then show a sharp decline from 0.09 Tg CO_2-eq in 2016 to 0.05 Tg CO_2-eq in 2020. The levels of HFC-365mfc emission (Fig. S5 are relatively uniform over England and Wales. Higher emissions are indicated on the near continent in Belgium.

S8.4 HFC-152a

Fig. S4 shows the InTEM and the inventory emission estimates for the UK for HFC-152a for the period 1990 onwards. Between 1999-2008 and from 2011 onwards the inventory estimates are significantly larger than those estimated through inverse modelling. It is also interesting to note the positive trend from 2011 until 2019 in the UK inventory conflicts with a much flatter InTEM trend followed by a decline of 0.01 Tg CO_2-eq from 2017 to 2020. The InTEM estimate is approximately one third of the inventory in 2018. Fig. S5 shows the spatial InTEM emissions estimate for HFC-152a over the UK for 2019-2020. The highest emissions are generally focused on the more populated areas, with the highest emission region appearing over London and in the south of the UK.

S8.5 HFC-43-10mee

As estimated by both methods, the UK emissions of this gas are small (Fig. S4. The inventory estimates are initially in agreement with those estimated by InTEM, but the inventory then has a small rise in 2015 and 2016, just as the InTEM emission drops to a low point in 2015 and 2016 (0.006 Tg CO_2-eq) before rising back up until 2019 (reaching 0.012 Tg CO_2-eq) and then dropping in 2020 to 0.007 Tg CO_2-eq. Throughout, the InTEM uncertainty estimates ($\sim$0.01 Tg CO_2-eq) are large relative to the emission. The spatial distribution is shown in Fig. S5 and is largely distributed by population.