Long-Term Atmospheric Measurement and Interpretation of Radiatively Active Trace Gases

September 2019 – August 2020

Executive Summary

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Photo of Winnats Pass courtesy of @grantrichie/Unsplash

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1 Introduction

1.1 Project Summary

Monitoring the atmospheric concentrations of gases is important for policy makers in assessing the impact of national and international policies related to the atmospheric environment. The effects of control measures on the principle greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), nitrogen trifluoride (NF_3) and sulphur hexafluoride (SF_6), are now observable. Likewise, measures introduced under the Montreal Protocol to protect the stratospheric ozone layer are also being observed in the atmosphere.

This project has two principle aims:

- Estimate the background atmospheric concentrations of the principle greenhouse and ozone-depleting gases from the UK and wider network of observations.
- Estimate the UK emissions of the principle greenhouse gases using the UK network of observations and compare these to the reported inventory.

Since 1987, high frequency, real time measurements of the principal halocarbons and radiatively active trace gases have been made as part of the Global Atmospheric Gases Experiment (GAGE) and Advanced Global Atmospheric Gases Experiment (AGAGE) at Mace Head, County Galway, Ireland. For much of the time, the Mace Head measurement station (MHD), which is situated on the Atlantic coast, monitors clean westerly air that has travelled across the North Atlantic Ocean. However, when the winds are easterly, MHD receives substantial regional scale pollution in air that has travelled from the populated and industrial regions of Europe. The site is therefore uniquely situated to record trace gas concentrations associated with both the Northern Hemisphere background levels and with the more polluted air arising from European emissions.

Building on the success of using the MHD observations in addressing the two principle aims of the project, the UK has developed a network of observation stations called the UK Deriving Emissions related to Climate Change (UK DECC) network. Along with MHD, it consists of four tall tower stations: Ridge Hill (RGL), Herefordshire; Tacolneston (TAC), Norfolk; Bilsdale (BSD), North Yorkshire (originally Angus (TTA), Angus, Scotland); and Heathfield (HFD), West Sussex. RGL became operational in February 2012 and TAC in July 2012. TTA began operating for the network in April 2012 but was decommissioned and replaced with BSD in September 2015 (BSD began operation in Jan 2014 under the NERC GAUGE programme). HFD began operation in Nov 2013 under the NERC GAUGE programme but became fully part of the network in Sept. 2018. The expanded network makes it possible to resolve emissions on a higher resolution, both spatially and temporally, across the UK.

The UK DECC network measures, to very high precision, all of the principle greenhouse gases in the inventory as well as many ozone-depleting gases. The Inversion Technique for Emission Modelling (InTEM) has been developed to use these observations to estimate both mid-latitude Northern Hemisphere concentration trends and UK emissions of each gas. The atmospheric measurements and resulting emission estimates of greenhouse gases provide an important independent cross-check for the national GreenHouse Gas Inventory (GHGI) of emissions submitted annually to the United Nations Framework Convention on Climate Change (UNFCCC). The GHGI are estimated through in-country submissions of Activity Data and Emission Factors that are, in some cases, very uncertain. The comparisons between the GHGI and InTEM estimates enable BEIS to be more informed in their inventory improvement programme and is also considered good practice by the Intergovernmental Panel on Climate Change (IPCC).

The UK is one of only three countries worldwide (Switzerland and Australia are the others) that currently routinely verify their reported inventory emissions as part of their annual UNFCCC submission of emissions. The UK is the only country to do so for all of the principle GHG gases and has done so for longest, since 2003.

1.2 Summary of Progress

Significant progress has been made during the second 12 months of the current contract period. The main points are summarised below but for further information and more in-depth discussion please refer to the companion, more detailed, report (referred to as the 'Detailed' report).

- Mace Head continues to be a baseline station at the forefront of global atmospheric research. This is evident through the high volume of peer-reviewed publications related to work using the MHD observational record. The recent publications related to this contract are detailed in the publication section of this report. In addition, the inclusion of MHD in many EU funded atmospheric research programmes, such as ICOS and ACTRIS, and continued support from other global programmes such as AGAGE and NOAA-ESRL indicates its international significance.
- Three radon (^{222}Rn) detectors from ANSTO, Australia were installed in the network; at HFD, TAC and RGL (as part of the NERC Advanced UK Observing Network for Air Quality, Public Health and Greenhouse Gas award NE/R011532/1). These ANSTO instruments allow for the continuous detection of ^{222}Rn to very low levels. We have developed the data analysis procedure to compare ^{222}Rn concentrations alongside the greenhouse gases with the aim of improving our understanding of how atmospheric mixing impacts observations.
- Meteorological equipment has been installed on the tall towers at TAC, RGL, (not yet at HFD) as part of the NE/R011532/1 award. This will allow wind speed and direction, temperature,

humidity, and barometric pressure to be measured at each of these UK DECC sites.

- Optical N_2O and CO analysers installed. The Picarro G5310 cavity ring down spectrometers (installed at Heathfield in 2018 and Bilsdale in 2019 as part of the NE/R011532/1 award) are running well and providing the network with continuous higher precision measurements.
- Mid-latitude Northern Hemisphere baseline trends have been updated. The trends have been extended from observations up to and including August 2020.
- UK emission estimates for the UK are reported up to and including 2020 and have been compared to the UK GHGI inventory submitted in April 2020 (covering UK emissions up to and including 2018).
- The verification appendix chapter for the UK National Inventory Report (NIR) submitted to the UNFCCC was delivered (February 2020).
- InTEM has been improved, the model now has a better fit to the observed data and the uncertainty bounds have been more robustly quantified.
- In the first quarter of 2020 RGL become an ICOS (Integrated Carbon Observation Network) observatory, feeding CO_2 and CH_4 observations from the on-site Picarro G2301 into the ICOS Carbon Portal. Data from this European portal supports climate science that informs scientists and society on natural and human emissions and uptake of these greenhouse gases from ocean, land ecosystems and atmosphere.

1.3 Future Plans

- High resolution NAME modelling (∼5 km compared to the current ∼25 km) of the areas directly surrounding each station may improve the overall modelling of the observations. This will be investigated at TAC.
- An improved ECMWF meteorological re-analysis data product (ERA-5) is available. This is at a higher resolution (∼30 km compared to ∼80 km) compared to the ERA-Interim that is currently used 1989-2002. NAME will be run for this period using the improved meteorology and the InTEM estimates compared to the current results.
- The UK DECC network will be utilised within DARE-UK (Detection and Attribution of Regional greenhouse gas Emissions in the United Kingdom), a 4-year NERC funded research project seeking to develop systems for estimating and improving GHG emissions from atmospheric observations. Additional instruments will complement the existing UK DECC network; Radiocarbon (^{14}C) flask measurements at TAC and HFD for the estimation of fossil fuel CO_2 emissions; Measurements of oxygen at HFD and the Weybourne observatory (WAO) to partition CO_2 fluxes; Measurements of δ^{13}C-CH_4 and δ^{2}H-CH_4 in CH_4 at HFD and TAC to improve our understanding of biogenic and fossil sources. DARE-UK focuses on the three major greenhouse gases responsible for global warming: CO_2, CH_4 and N_2O.

- Explore the use of HUGS (A HUb for Greenhouse gas data Science funded by NERC). HUGS is a cloud-based data analysis 'hub' for GHG measurements, modelling and data analysis and will streamline the process for data sharing, analysis and visualisation.
- NPL are developing a new instrument to measure isotope ratios in CH_4 at high frequency with the aim to help distinguish emissions sources at regional scales. This instrument will initially be set up at the laboratory at NPL before moving to HFD (DARE-UK funded).
- There are two instruments at HFD and BSD capable of measuring N_2O: the GC-ECD and the Picarro G5310. The Picarros are an upgrade and provide higher precision measurements. Analysis of the overlapping data has provided a quantitative insight into the value of high-frequency measurements in capturing short duration pollution events.
- NPL is organising a measurement intercomparison exercise for completion in 2021 to study instrument linearity differences across the network and resolve the reason for any systematic offsets in N_2O, CO and SF_6 observed between sites and instruments. This will also include WAO and CBW (Cabauw, The Netherlands) and will improve the uncertainty and inter-comparability of the observations across the network.

2 Summary of Instrument Performance

2.1 Mace Head

- The installation of two new air-conditioning systems was completed on the 4^{th} Dec 2019
- The Medusa GCMS experienced only one major issue - a fractured chromatographic column which led to 40 days of data loss between Oct-Sept 2019
- The GC-MD experienced no significant periods of data loss over the reporting period

2.2 Tacolneston

- All instruments were relocated to a new permanent room in Nov 2019
- A new radon detector and meteorological sensors were installed in Jul 2020
- The LGR, CRDS and Medusa GCMS performed well over the reporting period

2.3 Ridge Hill

- A new radon detector and meteorological sensors were installed in Jun 2020
- The G2301 CRDS performed well over the reporting period. Ridge Hill is currently progressing through the labelling process required to become an ICOS station

- The GC-ECD experienced no major issues over the last year

2.4 Bilsdale

- The G2401 CRDS suffered from a failed hotbox fan module on the 20^{th} Oct 2019, resulting in the loss of 18 days of data
- The G5310 performed well throughout the reporting period
- The GC-ECD suffered from chromatographic instability, which led to the loss of 139 days of N_2O data starting in Apr 2020.

2.5 Heathfield

- A new radon detector was installed in Jan 2020
- Two new air-conditioning modules were installed in Jun 2020, providing improved laboratory temperature control
- The G2401 CRDS suffered from a failed hotbox fan module in Jul 2020.
- The G5310 did not experience any significant issues during the reported period
- The GC-ECD has suffered from deteriorating N_2O precision over the last year. Investigation into the cause of this deterioration is ongoing.

3 Regional Emission Estimation

3.1 Introduction

This chapter presents the InTEM inversion results, showing the global atmospheric trends and comparisons of UK emissions of the gases that are measured in the UK DECC network and reported to the UNFCCC (April 2020 submission). For some of the gases InTEM estimates for North West Europe (NWEU = IRL + UK + FRA + BEL + NLD + LUX + DEU) are also discussed compared to UNFCCC estimates (April 2020 submission).

InTEM is briefly presented but for more information the reader is referred to the Detailed report or the Methodology report. The uses, atmospheric lifetimes, and global warming potentials for the different gases reported under the UNFCCC are presented in Table 1.

3.2 Summary of InTEM inverse modelling

Each observation is comprised of two parts; a time-varying Northern Hemisphere baseline concentration and a perturbation above baseline. The perturbations above baseline, observed across the UK DECC network, are driven by emissions on regional scales that have yet to be fully mixed on the hemisphere scale and are the principle information used to estimate surface emissions across North West Europe. A method for estimating emissions from observations, referred to as 'Inversion Technique for Emission Modelling' (InTEM) (Manning et al. 2011; Arnold et al. 2018), has been developed over many years and is used here to estimate UK and NWEU emissions using the observations from the UK DECC network and other European networks where available.

InTEM uses a Bayesian statistical technique with a non-negative least squares solver to find the emission distributions that produces the modelled times-series at each observation station that has the best statistical match to the observations. For CH_4 and N_2O prior emissions are used that are generated from combining the NAEI and a global emission database. For the HFCs a population-weighted prior is used and for the PFCs, SF_6 and NF_3 a simple land-based prior is employed. However, to preserve the independence of the inversion results presented here from the prior estimates, the priors were given large uncertainties thus ensuring the inversion results are dominated by the observations not the prior. For CH_4 and N_2O, where the inversion time window was set to one month, the prior was given more weight but the solutions were still dominated by the observations.

For each gas two sets of inversions are performed with the inversion time-frame changing from 2-years to 1-year. The 2-year inversions started in the year MHD started observing the gas, the 1-year inversions started in 2012 to coincide with the UK DECC network. Each inversion covers an entire calendar year (or two) and is repeated 24 times to explore the uncertainty. Annual emission estimates were made by averaging the inversion results covering the appropriate year. Observations from Jungfraujoch (JFJ, Switzerland) and Monte Cimone (CMN, Italy), Taunus (TOB, Germany), Carnsore Point (CSP, Ireland), Cabauw (CBW, The Netherlands) and Weybourne (WAO, Norfolk, UK) were used where available and complemented those in the UK DECC network. For CH_4, N_2O and SF_6, where observations are available from many sites in the UK, the second inversion time-frame was set to 1-month rather than 1-year.

3.3 Summary of the GHG reported to the UNFCCC

Table 1 describes the principle uses of each of the gases reported to the UNFCCC and observed in the network, their radiative efficiency, atmospheric lifetime and global warming potential in a 100-year framework (GWP_{100}).

Table 1: Principle uses of each of the gases, their radiative efficiency, atmospheric lifetime and global warming potential in a 100-year framework (GWP_{100}) (Chapter 8, Working Group 1, 5th Assessment Report of the IPCC, (Myhre et al. 2013)).

Gas	Chemical Formula	Main Use	Radiative Efficiency ($Wm^{-2}ppb^{-1}$)	Atmospheric lifetime (yr)	GWP_{100}
Methane	CH_4	Landfill, farming, energy, wetlands	0.000363	12.4	28
Nitrous Oxide	N_2O	Nylon manufacture, farming	0.00300	121	265
Carbon Dioxide	CO_2	Combustion	0.0000137	indefinite	1
HFC-125	CHF_2CF_3	Refrigeration blend, fire suppression	0.23	28.2	3,170
HFC-134a	CH_2FCF_3	Mobile air conditioner	0.16	13.4	1,300
HFC-143a	CH_3CF_3	Refrigeration blend	0.16	47.1	4,800
HFC-152a	CH_3CHF_2	Aerosol propellant, foam-blowing agent	0.10	1.5	138
HFC-23	CHF_3	Bi-product of manufacture of HCFC-22	0.18	222	12,400
HFC-32	CH_2F_2	Refrigeration blend	0.11	5.2	677
HFC-227ea	CF_3CHFCF_3	Fire suppression, inhalers, foam blowing	0.26	38.9	3,350
HFC-245fa	$C_3H_3F_5$	Blowing and insulation agent	0.24	7.7	858
HFC-43-10mee	$C_5H_2F_{10}$	Electronics industry	0.42	16.1	1,650
HFC-365mfc	$C_4H_5F_5$	Foam blowing	0.22	8.7	804
PFC-14	CF_4	Bi-product alum. production, electronics	0.09	50,000	6,630
PFC-116	C_2F_6	Electronics, bi-product alum. production	0.25	10,000	11,100
PFC-218	C_3F_8	Electronics, bi-product alum. production	0.28	2,600	8,900
PFC-318	C_4F_8	Semiconductor and electronics industries	0.32	3,200	9,540
Sulphur Hexafluoride	SF_6	Circuit breaker in high voltage switchgear	0.57	3,200	23,500
Nitrogen Trifluoride	NF_3	Semiconductor manufacture	0.20	500	16,100

3.4 Methane (CH_4)

- Methane (CH_4) is the second most important anthropogenic greenhouse gas after CO_2.
- After a decade of stability, global growth started again in 2007 (Figure 1) with a shift in the δ^{13}C-CH_4 isotopic ratios to more negative values. This suggests a change in the global makeup of sources and/or sinks.
- Currently there is an accelerating global trend upwards, currently increasing by ∼9 ppb yr^{-1}. The average mid-latitude Northern Hemisphere mole fraction was 1938 ppb in 2019.
- There is a strong latitudinal gradient of ∼120 ppb (Figure 1) indicating most of the emissions are in the Northern Hemisphere.
- The background Northern Hemisphere concentration has a strong seasonal cycle (∼25 ppb).
- UK GHGI and InTEM are in good agreement from 2012 (Figure 3).
- InTEM shows little change in emissions from 1990 whereas the GHGI has fallen by more than 50% since 1990 (Figure 2).
- There is little evidence of a seasonal cycle in UK emissions although there is year-to-year variability e.g. suppressed in 2014-15 and 2019, more activity in 2012 and 2018 (Figure 3).
- There is little change in the distribution of UK emissions over a year (Figure 4). The emissions are broadly uniform across the UK.

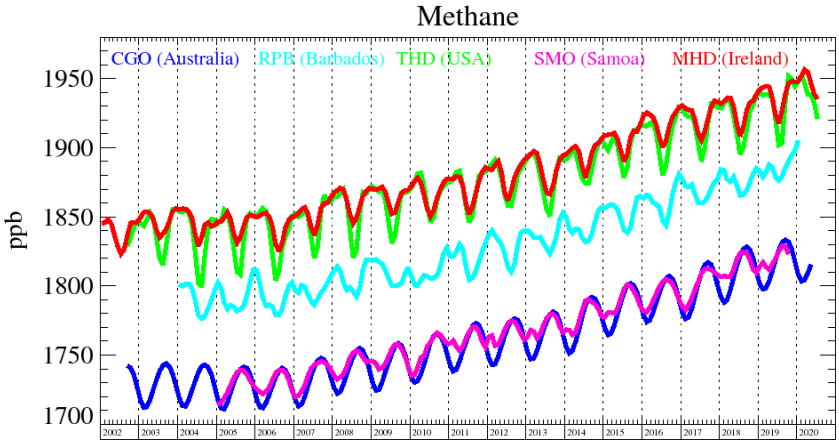


Figure 1: Background mole fractions at 5 AGAGE global stations

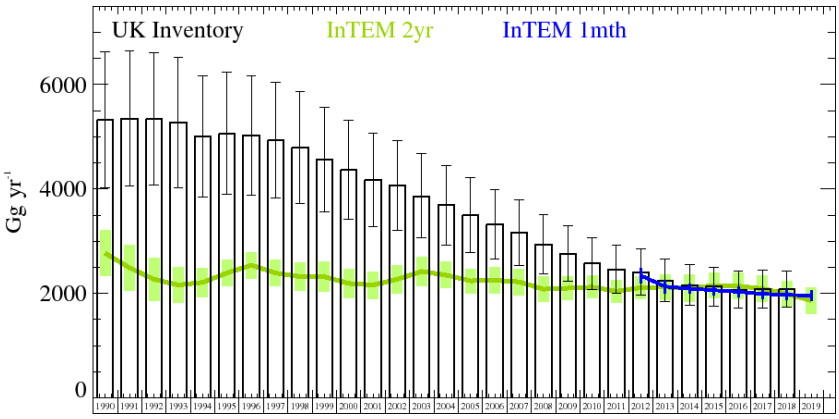


Figure 2: CH_4 UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black) and InTEM (a) Annualised 2-year inversion (green) (b) Annualised 1-month inversion (blue). The uncertainty bars represent 1-σ.

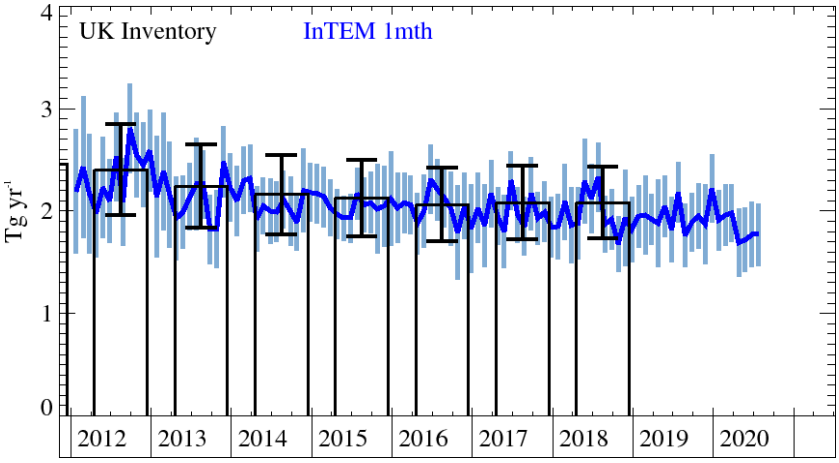


Figure 3: CH_4 UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black) and InTEM (monthly) DECC + CBW + WAO (blue). The uncertainty bars represent 1-σ.

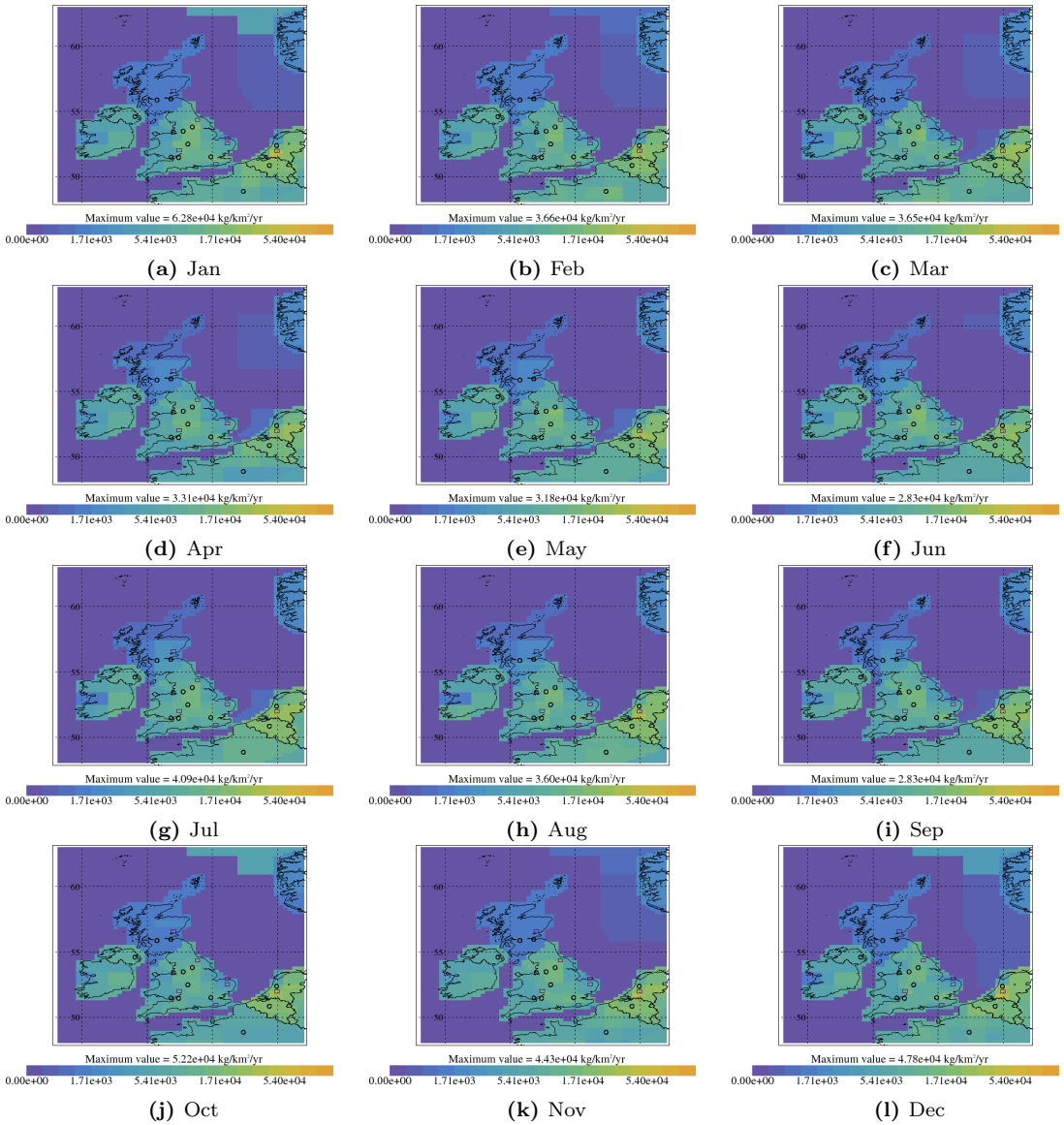


Figure 4: Average monthly InTEM CH_4 emission estimates (kg km^{-2} yr^{-1}) 2012-2019

3.5 Nitrous Oxide (N_2O)

- N_2O is the third most important anthropogenic greenhouse gas after CO_2 and CH_4.
- N_2O emissions, weighted by ozone depletion potential, currently exceed those of all other substances and is the main natural catalyst for stratospheric ozone destruction.
- Anthropogenic sources are dominated by agriculture, followed by industrial and fossil fuel sources, biomass burning, rivers and estuaries.
- The N_2O global mole fraction is increasing by ~0.85 ppb yr^{-1}. The average mole fraction in 2019 in the mid-latitude Northern Hemisphere was 332.6 ppb (Figure 5).
- The background mole fraction has a pronounced seasonal cycle (amplitude of ~0.8 ppb).

- UK GHGI estimates are lower than InTEM by ∼15% 2012-2019 (Figure 6).
- UK emissions are spread across the country (Figure 7). Emissions from Belgium are consistently high throughout the year.
- UK emissions have a very strong seasonal cycle (amplitude of ∼80 Gg). Peak emissions are in May-Aug, minima in Jan-Feb (Figure 8). 2015 has a suppressed summer maximum. Emissions of N_2O following fertilizer application can exhibit major temporal and spatial variability because microbial processes that give rise to N_2O are strongly dependent on soil moisture, temperature and soil type.
- Estimating annual emissions without the full 5-site DECC network is difficult and could be biased because of the strong seasonal cycle in emissions, therefore InTEM estimates prior to 2012 are much more uncertain.
- Improvement in observation instruments (starting in 2016) has reduced InTEM UK emission uncertainty.

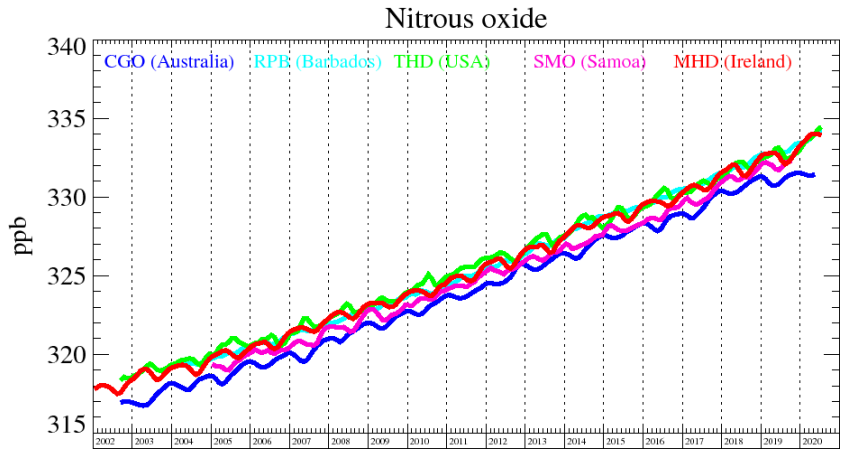


Figure 5: Background mole fractions at 5 AGAGE global stations

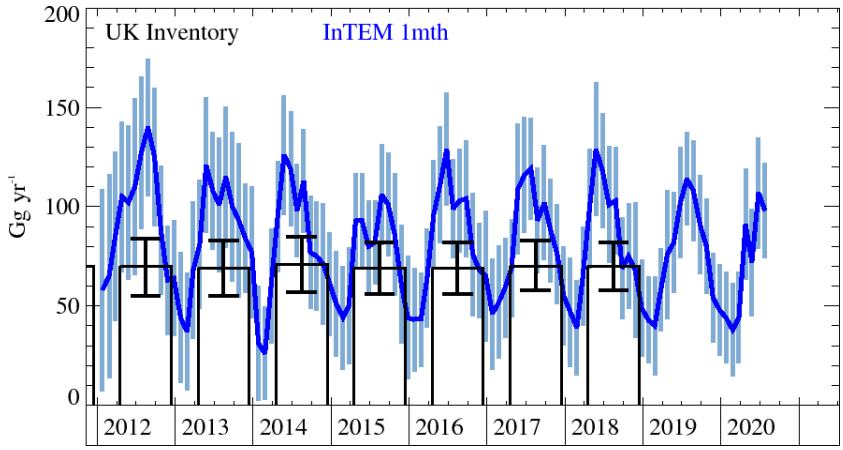


Figure 6: N_2O UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black) and InTEM (monthly) DECC network (blue). The uncertainty bars represent 1-σ.

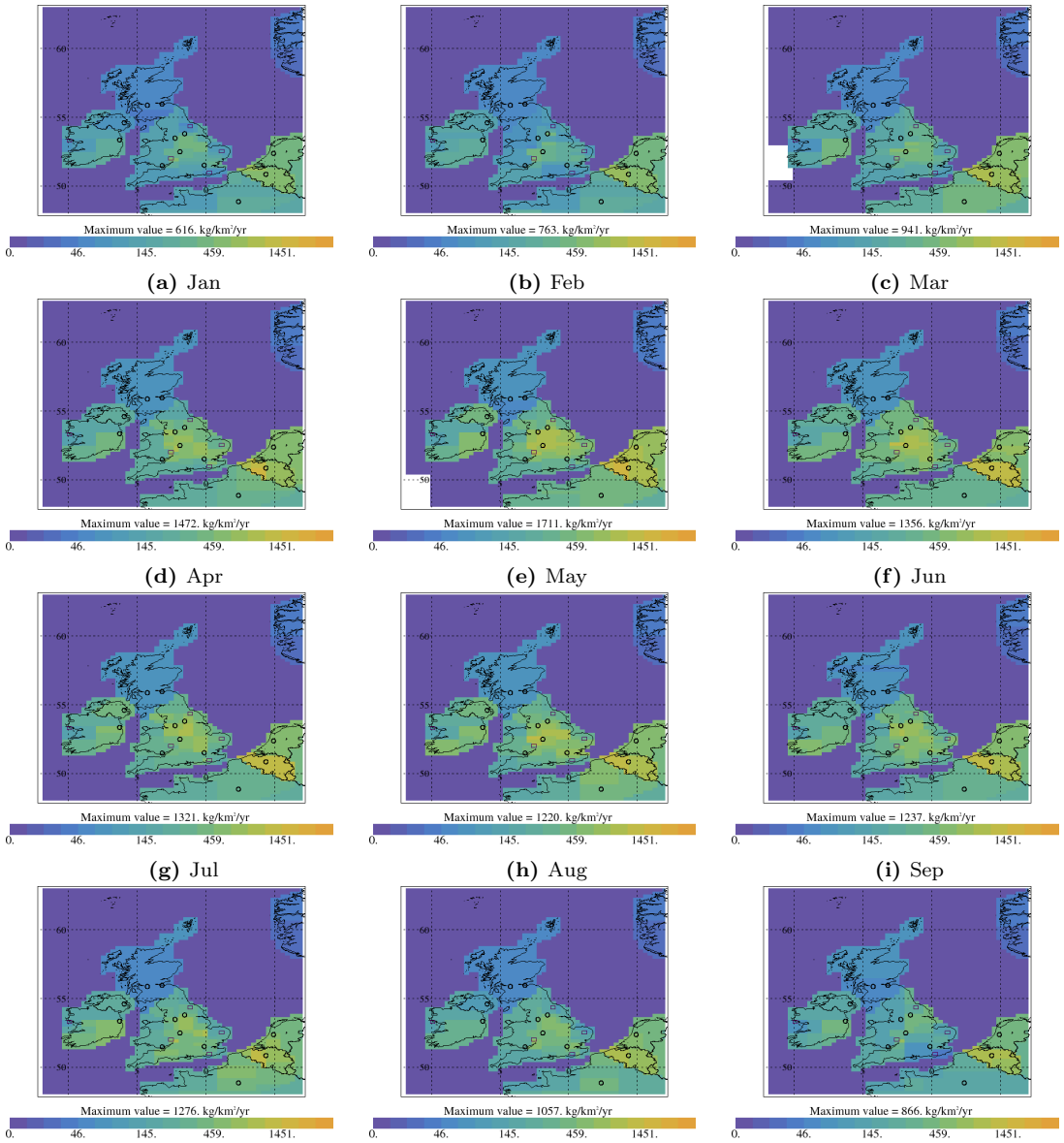


Figure 7: Average monthly InTEM N_2O emission estimates (kg km^{-2} yr^{-1}) 2012-2019

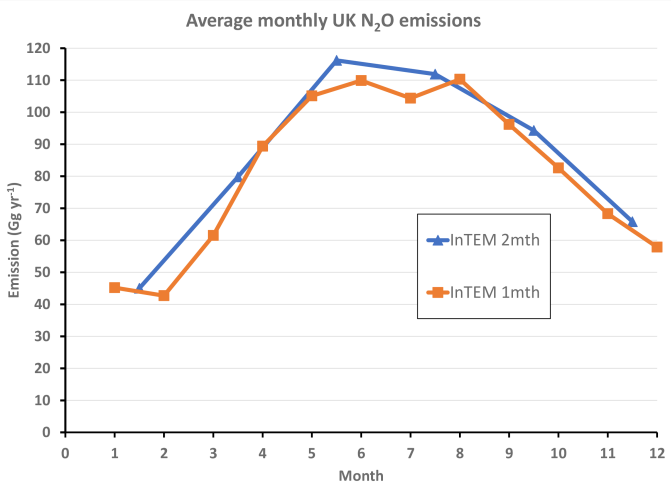


Figure 8: Average seasonal cycle in InTEM N_2O emission estimates (Gg yr^{-1}) 2014-2019. The results from a 1-month (orange) and a 2-month (blue) inversion are presented.

3.6 Carbon Dioxide (CO_2)

- The CO_2 global mole fraction is increasing by ~2 ppm yr^{-1}. The average mole fraction in 2019 in the mid-latitude Northern Hemisphere was 411 ppm (Figure 5).
- The background mole fraction has a pronounced seasonal cycle (amplitude of ~14.4 ppm)
- No UK emissions are estimated for CO_2 because of the complexities of estimating both natural and anthropogenic emissions that are varying on time-scales of less than a day. This is ongoing work.

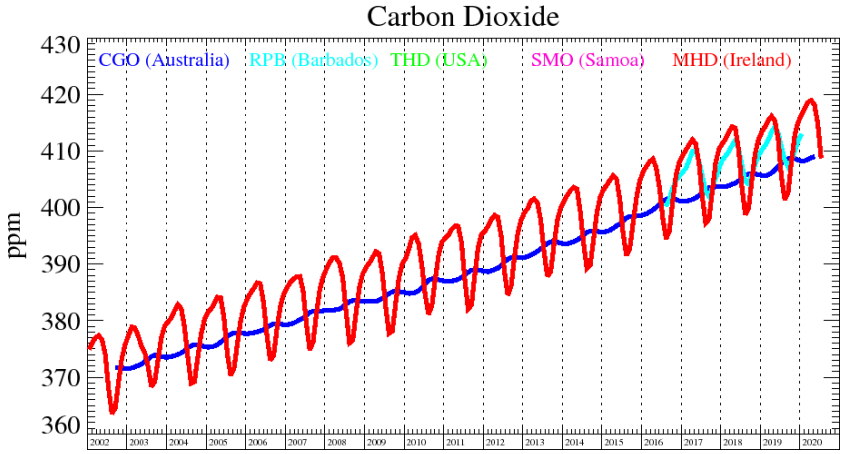


Figure 9: Background mole fractions at 5 AGAGE global stations

3.7 HFC Summary

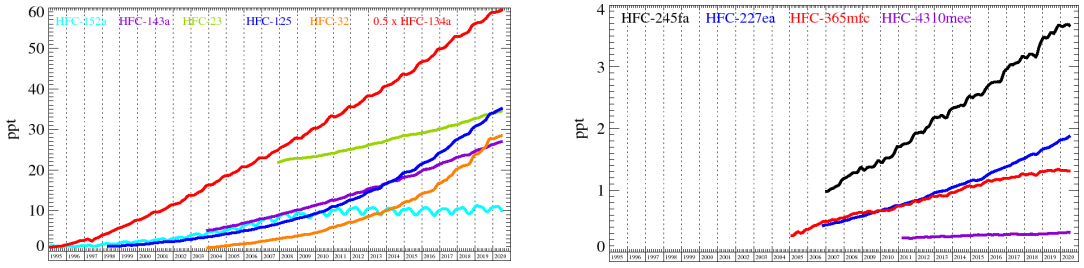


Figure 10: Northern Hemisphere Atmospheric Background Levels of HFCs as observed at the Mace Head observing station. Note the change in scale from the left to the right plot. For scale purposes the mole fractions of HFC-134a have been halved.

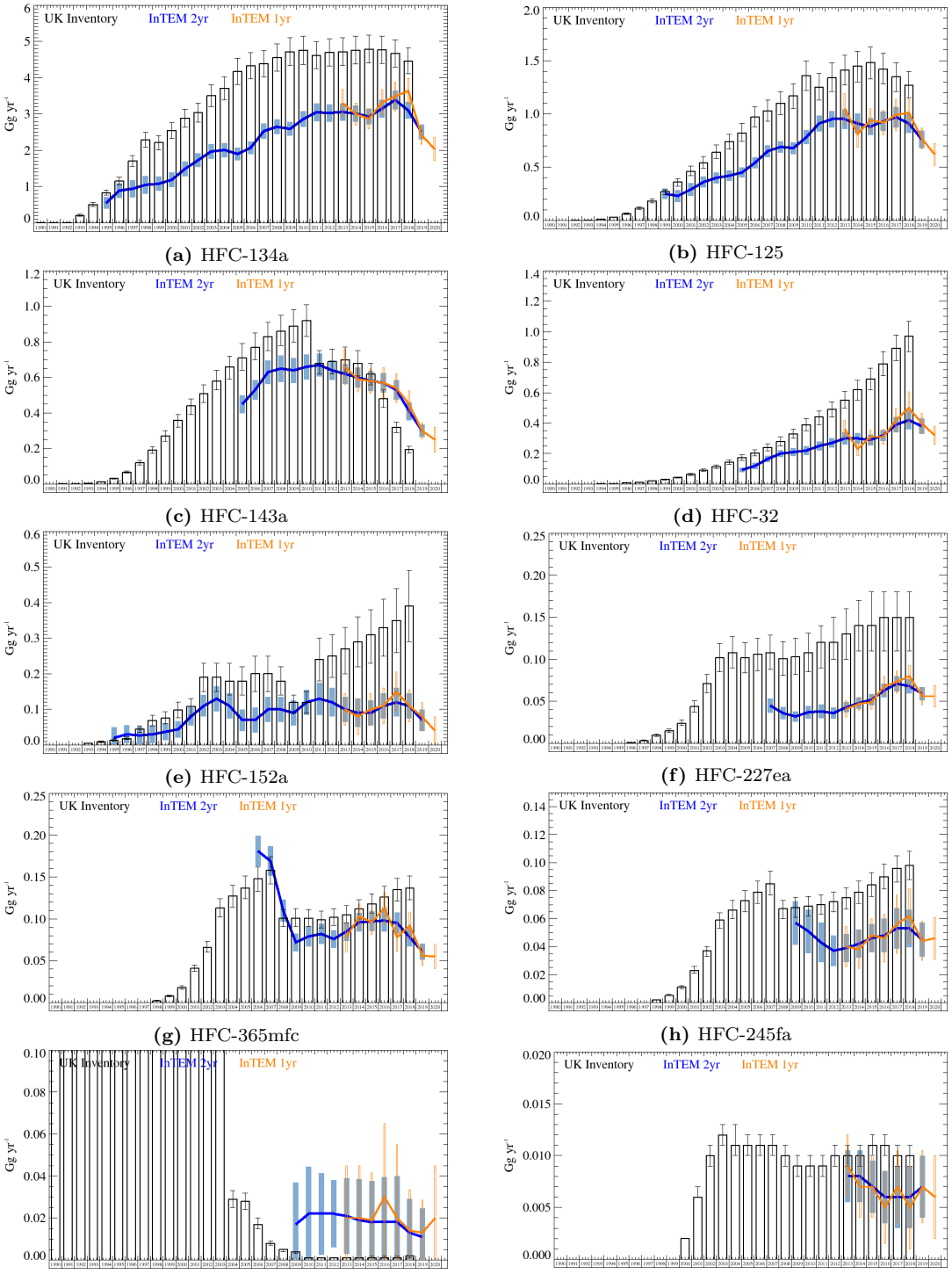
The atmospheric concentrations of all the HFC's reported here (HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-23, HFC-32, HFC-227ea, HFC-245fa, HFC-43-10mee and HFC-365mfc) are growing in the Northern Hemisphere as can been seen in Figure 10 and this is replicated in the Southern Hemisphere albeit with a time lag of 1-2 years. Some of the gases, notably HFC-134a, HFC-125, HFC-32, HFC-245fa and HFC-227ea, are growing very rapidly in the atmosphere. Others are growing much more slowly e.g. HFC-152a, HFC-43-10mee, HFC-365mfc. It is important to recognise that HFC-23 is the most important in terms of its impact on the climate as its GWP_{100} is by far the highest at over 12,000, the next most important gases, with GWP_{100} of 3,000-4,000, are HFC-125, HFC-143a and HFC-227ea and then HFC-134a with a GWP_{100} of 1,300.

Figure 11 shows the UK InTEM and GHGI (submitted April 2020 and includes estimates up to 2018) estimated annual emissions up to and including 2020. With the exception of HFC-23 and HFC-43-10mee which are constant, InTEM estimates that all of the UK HFC emissions have decreased over the last 2 years from 2018. Please note that data for 2020 should be treated as provisional as it is based on only 7 months of measurement data. For HFC-134a, HFC-125 and HFC-143a the 2018 GHGI estimate has decreased compared with that estimated for 2017, for HFC-32, HFC-152a and HFC-365mfc the GHGI has increased, and for the other gases they are broadly unchanged. The InTEM decline in UK HFC-143a emissions is slower than the GHGI predicts. For HFC-32, HFC-152a, HFC-365mfc and HFC-245fa the recent estimates are diverging when InTEM and the GHGI are compared, with the GHGI increasing and InTEM decreasing. It is also notable that, with the exception of HFC-143a and HFC-23, the InTEM estimates of UK emissions are smaller than those reported in the GHGI, sometimes strikingly so for example HFC-32, HFC-152a and HFC-227ea.

Figures 12a, 12b and 12c show 3-year average emission maps for 2017-2019 for HFC-125, HFC-134a and HFC-143a, and indicate that InTEM predicts the largest emission sources for these gases to be from a southern region of the UK, along with central regions of the UK, Belgium and The Netherlands. They also show evidence of emissions from the region around Paris which is more

pronounced for HFC-143a. The 3-year average maps from 2008 onwards (see Detailed report) show generally increasing emissions over the 3-year periods presented, until a decrease is evident in 2017-2019 for HFC-143a. The downward trend seen in the time-series of UK emissions for HFC-125 and HFC-134a is not easily apparent in the maps however, probably because the downturn is more recent than for HFC-143a and also less pronounced in the North West Europe region compared with the UK. Figure 12e for HFC-152a, shows strong evidence of a decrease over time in North West Europe when compared with the previous 3-year periods presented in the Detailed report. The 2008-2010 map shows a strong source of HFC-152a emission coming from Belgium, by 2017-2019 (Figure 12e) this is greatly reduced.

Figure 12g for HFC-365mfc and Figure 12h for HFC-245fa, show very similar spatial distributions, with the dominant emissions coming from Belgium. Lesser magnitude emissions are also predicted to come from the central and southern UK, the Paris region and The Netherlands. Figure 12f for HFC-227ea and Figure 12j for HFC-4310mee have similar spatial distributions to each other with similarly elevated regions in central and southern UK, Paris, Belgium and The Netherlands.



(a) HFC-134a **(b)** HFC-125

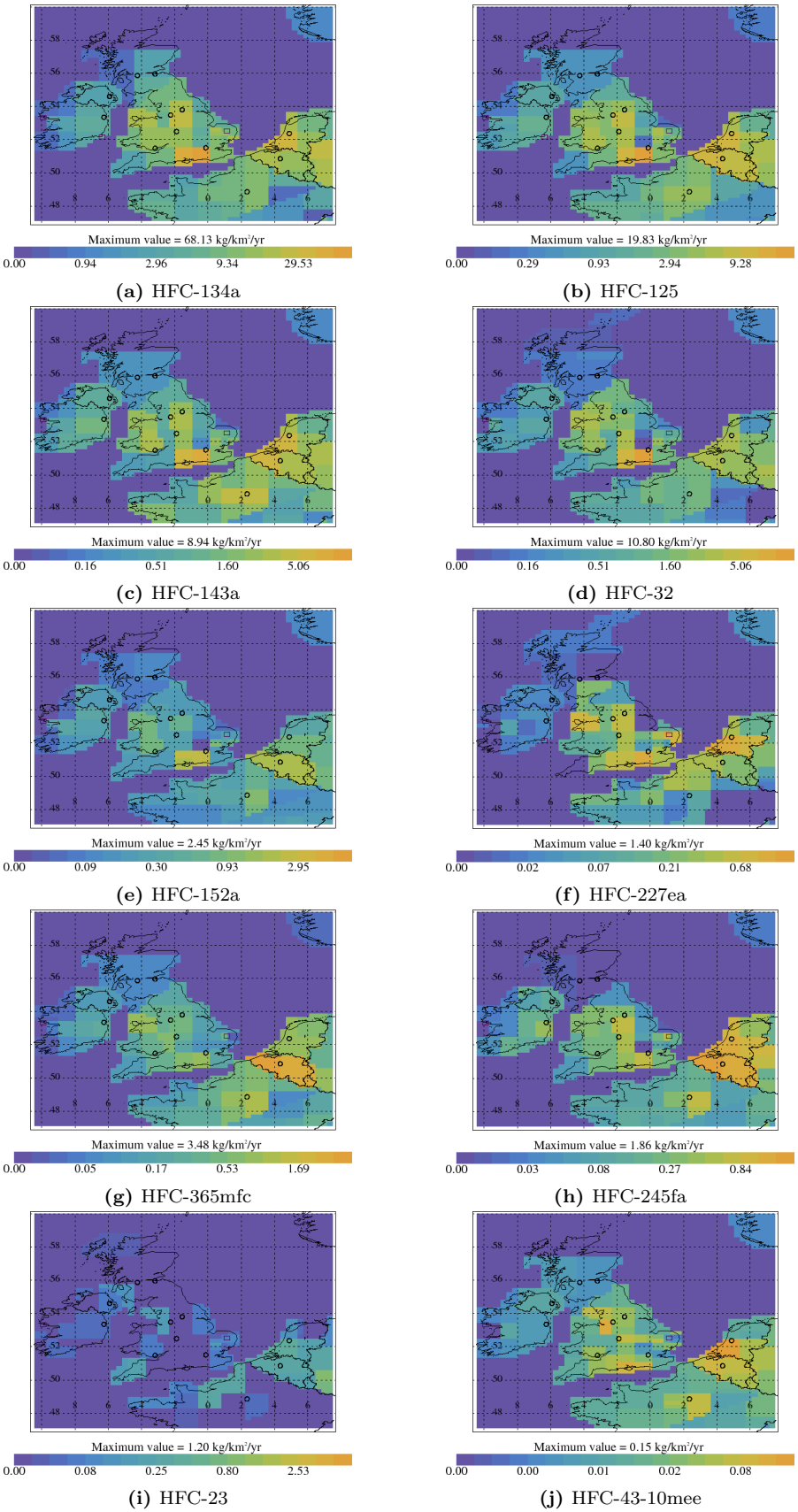
(c) HFC-143a **(d)** HFC-32

(e) HFC-152a **(f)** HFC-227ea

(g) HFC-365mfc **(h)** HFC-245fa

(i) HFC-23 **(j)** HFC-43-10mee

Figure 11: HFC UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black), InTEM Annualised 2-year inversion (blue) and InTEM Annual inversion (orange). The uncertainty bars represent 1-σ.



(a) HFC-134a **(b)** HFC-125

(c) HFC-143a **(d)** HFC-32

(e) HFC-152a **(f)** HFC-227ea

(g) HFC-365mfc **(h)** HFC-245fa

(i) HFC-23 **(j)** HFC-43-10mee

Figure 12: Three year average (2017-2019) InTEM HFC emission estimates (kg km^{-2} yr^{-1}). Note each plot has its own scale.

- HFC-134a: Atmospheric concentration increasing globally; UK InTEM emissions increased until 2018 but have since fallen dramatically; Similar pattern across NWEU but less dramatic; Populated areas of UK are the most significant sources.
- HFC-125: Atmospheric concentration increasing globally; UK InTEM emissions increased until 2012, remained flat until 2018, then drop dramatically; Similar pattern across NWEU but with a less dramatic drop; Populated areas of UK are the most significant sources.
- HFC-143a: Atmospheric concentration increasing globally but rate of increase now constant since 2016; InTEM UK emissions increased until 2007, fell slowly until 2017 and then fell more rapidly; GHGI has a dramatic decline in 2011 and a steep decline from 2015 onwards - much steeper than InTEM; Very good agreement between GHGI and InTEM 2014 onwards; Populated areas of UK are the most significant sources especially in the south.
- HFC-32: Atmospheric concentration increasing globally and accelerating with a widening hemispheric gradient; GHGI UK emissions increasing significantly in contrast to InTEM which shows a slow rise and a decline after 2018 with levels half that of GHGI; Similar picture across NWEU but UK numbers are 40% of the NWEU estimates; Figure 12d indicates that there has been an increasing emission source in southern England in the period 2017-2019 compared with previous 3-year averages (Detailed report), further years of data will be needed to understand this source of HFC-32.
- HFC-152a: Atmospheric concentration constant since 2012 but signs of a rise in the last 2 years; Background has a strong seasonal cycle and large inter-hemispheric gradient due to its short lifetime; UK emissions are very different when InTEM is compared to GHGI - InTEM stable 2013-2017 then falling rapidly, whereas GHGI rising steadily from 2010; Southern England and Belgium are the most significant sources.
- HFC-227ea: Atmospheric concentration increasing globally and accelerating with a widening hemispheric gradient; UK GHGI emission estimates are more than twice InTEM; InTEM showing a decline after 2018; UK emissions are about half of NWEU emissions in both estimates; InTEM estimates largely reflect population; highest emissions from Benelux countries.
- HFC-365mfc: Atmospheric concentration appears to have reached a plateau at 1.4 ppt; UK GHGI emission estimates in very good agreement to InTEM except InTEM shows a decline after 2016 not seen in the GHGI; For NWEU InTEM emissions are higher than reported but modestly so, both estimates are now declining; InTEM estimates significant emissions from Belgium.
- HFC-245fa: Atmospheric concentration increasing globally with a widening hemispheric gradient; UK GHGI emission estimates are higher than InTEM; InTEM showing a decline after 2018; For NWEU there is a very good match between estimates except in 2018 where InTEM shows a steep decline in emissions; InTEM estimates significant emissions from Benelux countries.

- HFC-23: Atmospheric concentration increasing globally; UK emissions in GHGI are negligible after 2009 but intermittent pollution events are still seen in the observations; Germany and Italy are estimated to have the most significant modelled emissions in recent years; UK emissions of HFC-23 have greatly reduced since the 1990's and have remained largely flat since 2009.
- HFC-43-10mee: Atmospheric concentration slowly increasing globally; Given the uncertainties UK GHGI emission estimates are similar to InTEM; In recent years, only the UK reports emissions for this gas; InTEM estimates are broadly in line with population.

3.8 PFC Summary

Globally, atmospheric concentrations of all the PFC's are growing (Figure 13). They all have long atmospheric lifetimes and high GWP_{100}'s (Table 1). They originate as by-products from the production of aluminium and from the electronic and semi-conductor industries. Over the UK the emissions of these gases have been quite stable, at low levels, for the last few years (Figure 14), however there is now some evidence from the InTEM estimates that PFC-218 emissions may have increased in the last 2 years. Within the area of North West Europe modelled by InTEM there are also emerging indications of small increases in PFC-14, PFC-116 and PFC-218 emissions.

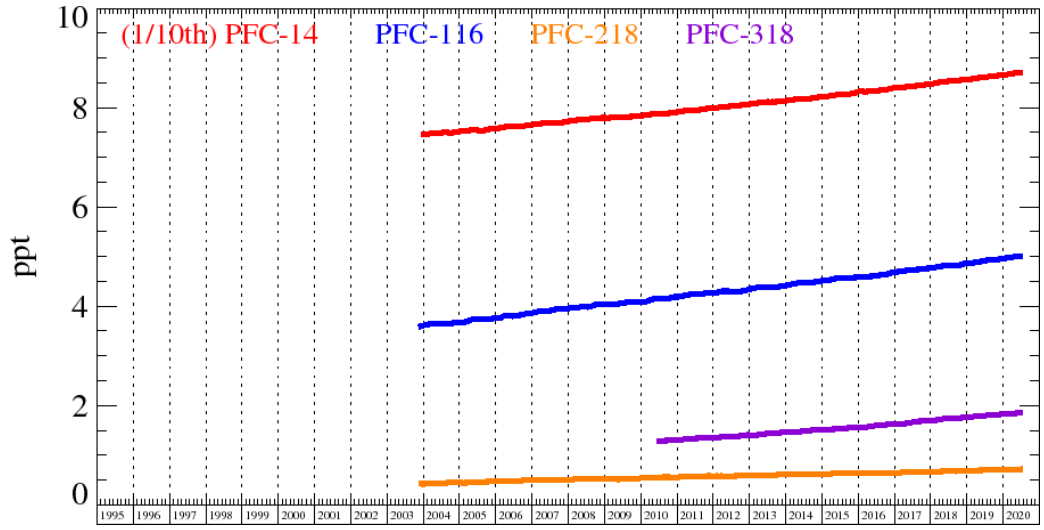
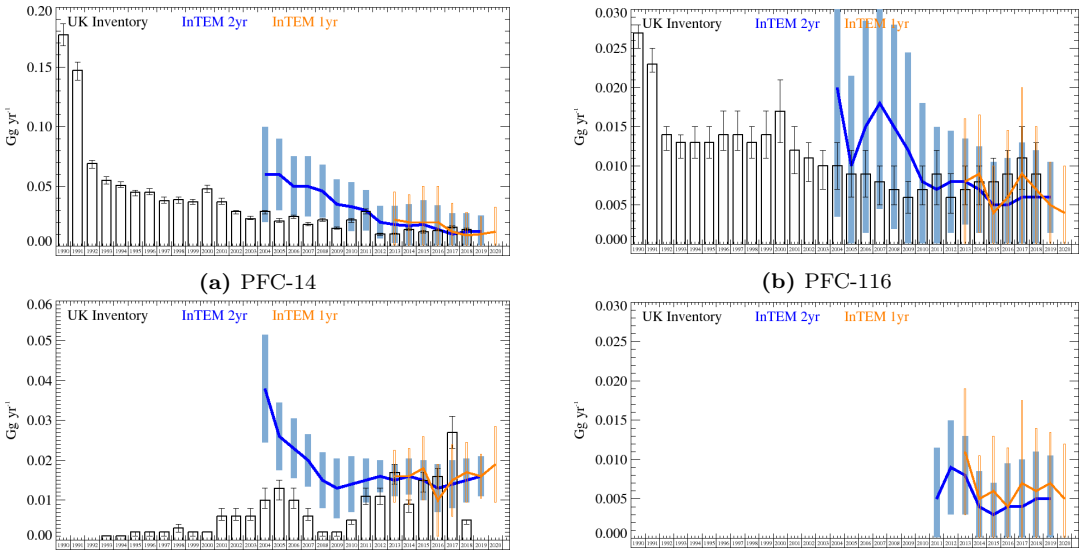


Figure 13: Northern Hemisphere Atmospheric Background Levels of PFCs as observed at the Mace Head observing station. Note that for scale purposes the atmospheric mole fractions of PFC-14 have been divided by 10.

- PFC-14: Atmospheric concentrations are growing globally (Figure 13), the growth rate is constant with a constant inter-hemispheric gradient; UK InTEM emissions are higher than the GHGI estimates from 2004-2010; Recent years show very close agreement between InTEM and the GHGI estimates (Figure 14a); UK emissions remain flat; North West Europe results show a similar pattern.

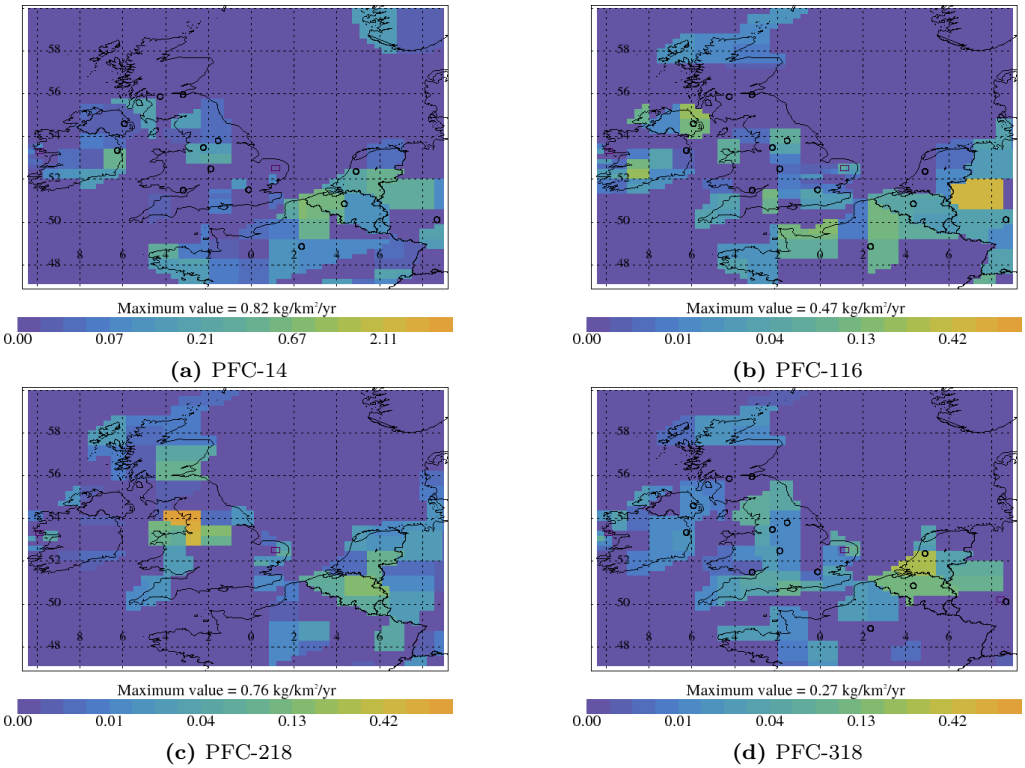
- PFC-116: Atmospheric concentrations are growing globally (Figure 13), the growth rate is constant with a constant inter-hemispheric gradient; Prior to the inclusion of TAC in 2012, the InTEM estimates have large uncertainty; The last 10 years show good agreement between UK InTEM and GHGI estimates (Figure 14b); InTEM estimates for North West Europe have remained flat for many years, however the 1-year InTEM results for 2019 and 2020 indicate a possible upturn; The largest source of emissions in the 2017-2019 average is estimated to be in Western Germany (Figure 15b).
- PFC-218: Atmospheric concentrations are growing globally (Figure 13), the growth rate is constant with a constant inter-hemispheric gradient; UK InTEM estimates (Figure 14c) are generally higher than GHGI, for 2018 the InTEM value is more than double the GHGI; In 2019 and 2020 InTEM results indicate a possible increase in UK emissions; The largest source of emissions very consistently occurs in North West England (Figure 15c).
- PFC-318: Atmospheric concentrations are growing globally (Figure 13), the growth rate is constant with a constant inter-hemispheric gradient; InTEM predictions for the UK are uncertain but greater than the very small GHGI estimates (Figure 14d); North West European estimates are dominated by an estimated emission source in The Netherlands (Figure 15d).



(a) PFC-14 **(b)** PFC-116

(c) PFC-218 **(d)** PFC-318

Figure 14: PFC UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black), InTEM Annualised 2-year inversion (blue) and InTEM Annual inversion (orange). The uncertainty bars represent 1-σ.



(a) PFC-14 **(b)** PFC-116

(c) PFC-218 **(d)** PFC-318

Figure 15: Three year average (2017-2019) InTEM PFC emission estimates (kg km^{-2} yr^{-1}). Note each plot has its own scale.

3.9 Sulphur Hexafluoride (SF_6)

The atmospheric concentrations of SF_6 are growing globally (Figure 16). There is overall good agreement between InTEM and GHGI for UK emission estimates. InTEM estimates the occasional significant enhancements in emissions e.g. Dec 2016 (Figure 17). A significant source is estimated for Southern Germany (Figure 18).

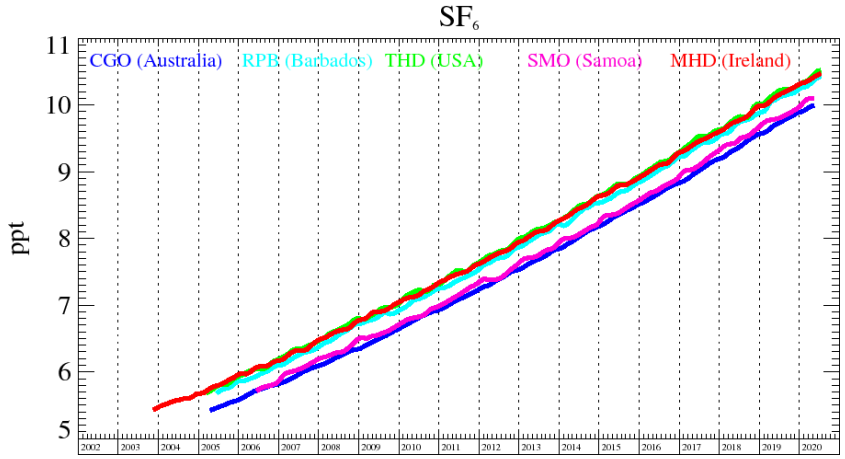


Figure 16: Background mole fractions at 5 AGAGE global stations

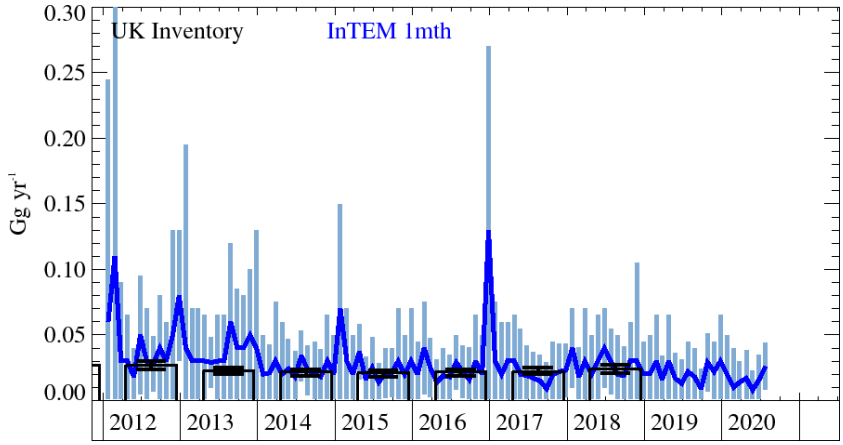


Figure 17: SF_6 UK emission estimates (Gg yr^{-1}) from the UNFCCC inventory (black) and InTEM (monthly) DECC network (blue).The uncertainty bars represent 1-σ.

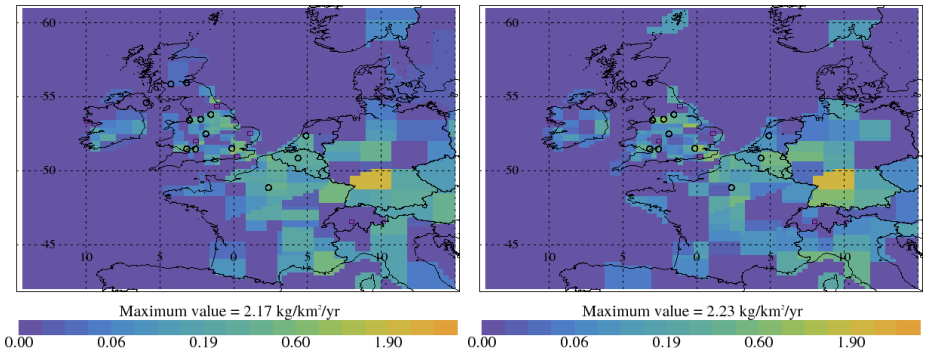


Figure 18: SF_6 InTEM emission estimates (kg km^{-2} yr^{-1}) 3 year averages (left) 2014-2016 (right) 2017-2019

3.10 Nitrogen trifluoride (NF_3)

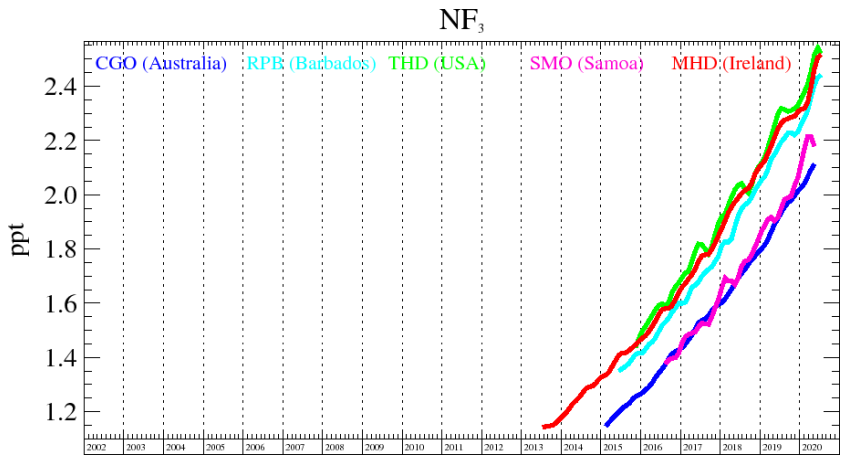


Figure 19: Background mole fractions at 5 AGAGE global stations

There is strong global growth of NF_3 as shown in Figure 19. UK emissions as estimated in the GHGI are very small and this is in line with what is observed in the atmosphere. The InTEM results for both the UK and NWEU are very small and uncertain.

4 2019 and 2020 Publications

A list of current publications and presentations resulting from AGAGE and other research are summarized below.

Claxton, T., R. Hossaini, C. Wilson, S. A. Montzka, M. P. Chipperfield, O. Wild, E. M. Bednarz, L. J. Carpenter, S. J. Andrews, S. C. Hackenberg, J. Mühle, D. Oram, S. Park, M.-K. Park, E. Atlas, M. Navarro, S. Schauffler, D. Sherry, M. Vollmer, T. Schuck, A. Engel, P. B. Krummel, M. Maione, J. Arduini, T. Saito, Y. Yokouchi, S. O'Doherty, D. Young, and C. Lunder (2020). "A Synthesis Inversion to Constrain Global Emissions of Two Very Short Lived Chlorocarbons: Dichloromethane, and Perchloroethylene". In: *Journal of Geophysical Research: Atmospheres* 125.12. ISSN: 2169-897X, 2169-8996. DOI: 10.1029/2019JD031818.

Derwent, R., D. Parrish, P. G. Simmonds, S. J. O'Doherty, and T. G. Spain (2020). "Seasonal Cycles in Baseline Mixing Ratios of a Large Number of Trace Gases at the Mace Head, Ireland Atmospheric Research Station". In: *Atmospheric Environment* 233, p. 117531. ISSN: 13522310. DOI: 10.1016/j.atmosenv.2020.117531.

Droste, E. S., K. E. Adcock, M. J. Ashfold, C. Chou, Z. Fleming, P. J. Fraser, L. J. Gooch, A. J. Hind, R. L. Langenfelds, E. Leedham Elvidge, N. Mohd Hanif, S. O'Doherty, D. E. Oram, C.-F. Ou-Yang, M. Panagi, C. E. Reeves, W. T. Sturges, and J. C. Laube (2020). "Trends and Emissions of Six Perfluorocarbons in the Northern Hemisphere and Southern Hemisphere". In: *Atmospheric Chemistry and Physics* 20.8, pp. 4787–4807. ISSN: 1680-7324. DOI: 10.5194/acp-20-4787-2020.

Kuyper, B., H. Wingrove, T. Lesch, C. Labuschagne, D. Say, D. Martin, D. Young, M. A. H. Khan, S. O'Doherty, M. T. Davies-Coleman, and D. E. Shallcross (2020). "Atmospheric Toluene and Benzene Mole Fractions at Cape Town and Cape Point and an Estimation of the Hydroxyl Radical Concentrations in the Air above the Cape Peninsula, South Africa". In: *ACS Earth and Space Chemistry* 4.1, pp. 24–34. ISSN: 2472-3452, 2472-3452. DOI: 10.1021/acsearthspacechem.9b00207.

Macdonald, M. L., J. L. Wadham, D. Young, C. R. Lunder, O. Hermansen, G. Lamarche-Gagnon, and S. O'Doherty (2020). "Consumption of CH_3Cl, CH_3Br, and CH_3I and Emission of $CHCl_3$, $CHBr_3$, and CH_2Br_2 from the Forefield of a Retreating Arctic Glacier". In: *Atmospheric Chemistry and Physics* 20.12, pp. 7243–7258. ISSN: 1680-7324. DOI: 10.5194/acp-20-7243-2020.

Michalopoulou, E., D. E. Shallcross, E. Atkins, A. Tierney, N. C. Norman, C. Preist, S. O'Doherty, R. Saunders, A. Birkett, C. Willmore, and I. Ninos (2019). "The End of Simple Problems: Repositioning Chemistry in Higher Education and Society Using a Systems Thinking Approach and the United Nations' Sustainable Development Goals as a Framework". In: *Journal of Chemical Education* 96.12, pp. 2825–2835. ISSN: 0021-9584, 1938-1328. DOI: 10.1021/acs.jchemed.9b00270.

Pugsley, K. L., T. D. J. Knowles, and S. O'Doherty (2018). "Novel Method of Extraction for Radiocarbon Measurements of Atmospheric Carbon Dioxide". In: *Radiocarbon* 61.6, pp. 1867–1877. ISSN: 0033-8222, 1945-5755. DOI: 10.1017/RDC.2019.142.

Ramonet, M., P. Ciais, F. Apadula, J. Bartyzel, A. Bastos, P. Bergamaschi, P. E. Blanc, D. Brunner, L. Caracciolo di Torchiarolo, F. Calzolari, H. Chen, L. Chmura, A. Colomb, S. Conil, P. Cristofanelli, E. Cuevas, R. Curcoll, M. Delmotte, A. di Sarra, L. Emmenegger, G. Forster, A. Frumau, C. Gerbig, F. Gheusi, S. Hammer, L. Haszpra, J. Hatakka, L. Hazan, M. Heliasz, S. Henne, A. Hensen, O. Hermansen, P. Keronen, R. Kivi, K. Komínková, D. Kubistin, O. Laurent, T. Laurila, J. V. Lavric, I. Lehner, K. E. J. Lehtinen, A. Leskinen, M. Leuenberger, I. Levin, M. Lindauer, M. Lopez, C. L. Myhre, I. Mammarella, G. Manca, A. Manning, M. V. Marek, P. Marklund, D. Martin, F. Meinhardt, N. Mihalopoulos, M. Mölder, J. A. Morgui, J. Necki, S. O'Doherty, C. O'Dowd, M. Ottosson, C. Philippon, S. Piacentino, J. M. Pichon, C. Plass-Duelmer, A. Resovsky, L. Rivier, X. Rodó, M. K. Sha, H. A. Scheeren, D. Sferlazzo, T. G. Spain, K. M. Stanley, M. Steinbacher, P. Trisolino, A. Vermeulen, G. Vítková, D. Weyrauch, I. Xueref-Remy, K. Yala, and C. Yver Kwok (2020). "The Fingerprint of the Summer 2018 Drought in Europe on Ground-Based Atmospheric CO $_2$ Measurements". In: *Philosophical Transactions of the Royal Society B: Biological Sciences* 375.1810, p. 20190513. ISSN: 0962-8436, 1471-2970. DOI: 10.1098/rstb.2019.0513.

Saunois, M., A. R. Stavert, B. Poulter, P. Bousquet, J. G. Canadell, R. B. Jackson, P. A. Raymond, E. J. Dlugokencky, S. Houweling, P. K. Patra, P. Ciais, V. K. Arora, D. Bastviken, P. Bergamaschi, D. R. Blake, G. Brailsford, L. Bruhwiler, K. M. Carlson, M. Carrol, S. Castaldi, N. Chandra, C. Crevoisier, P. M. Crill, K. Covey, C. L. Curry, G. Etiope, C. Frankenberg, N. Gedney, M. I. Hegglin, L. Höglund-Isaksson, G. Hugelius, M. Ishizawa, A. Ito, G. Janssens-Maenhout, K. M. Jensen, F. Joos, T. Kleinen, P. B. Krummel, R. L. Langenfelds, G. G. Laruelle,

L. Liu, T. Machida, S. Maksyutov, K. C. McDonald, J. McNorton, P. A. Miller, J. R. Melton, I. Morino, J. Müller, F. Murguia-Flores, V. Naik, Y. Niwa, S. Noce, S. O'Doherty, R. J. Parker, C. Peng, S. Peng, G. P. Peters, C. Prigent, R. Prinn, M. Ramonet, P. Regnier, W. J. Riley, J. A. Rosentreter, A. Segers, I. J. Simpson, H. Shi, S. J. Smith, L. P. Steele, B. F. Thornton, H. Tian, Y. Tohjima, F. N. Tubiello, A. Tsuruta, N. Viovy, A. Voulgarakis, T. S. Weber, M. van Weele, G. R. van der Werf, R. F. Weiss, D. Worthy, D. Wunch, Y. Yin, Y. Yoshida, W. Zhang, Z. Zhang, Y. Zhao, B. Zheng, Q. Zhu, Q. Zhu, and Q. Zhuang (2020). "The Global Methane Budget 2000–2017". In: *Earth System Science Data* 12.3, pp. 1561–1623. ISSN: 1866-3516. DOI: 10.5194/essd-12-1561-2020.

Say, D., B. Kuyper, L. Western, M. A. H. Khan, T. Lesch, C. Labuschagne, D. Martin, D. Young, A. J. Manning, S. O'Doherty, M. Rigby, P. B. Krummel, M. T. Davies-Coleman, A. L. Ganesan, and D. E. Shallcross (2020). "Emissions and Marine Boundary Layer Concentrations of Unregulated Chlorocarbons Measured at Cape Point, South Africa". In: *Environmental Science & Technology* 54.17, pp. 10514–10523. ISSN: 0013-936X, 1520-5851. DOI: 10.1021/acs.est.0c02057.

Simmonds, P. G., M. Rigby, A. J. Manning, S. Park, K. M. Stanley, A. McCulloch, S. Henne, F. Graziosi, M. Maione, J. Arduini, S. Reimann, M. K. Vollmer, J. Mühle, S. O'Doherty, D. Young, P. B. Krummel, P. J. Fraser, R. F. Weiss, P. K. Salameh, C. M. Harth, M.-K. Park, H. Park, T. Arnold, C. Rennick, L. P. Steele, B. Mitrevski, R. H. J. Wang, and R. G. Prinn (2020). "The Increasing Atmospheric Burden of the Greenhouse Gas Sulfur Hexafluoride (SF_6)". In: *Atmospheric Chemistry and Physics* 20.12, pp. 7271–7290. ISSN: 1680-7324. DOI: 10.5194/acp-20-7271-2020.

Stanley, K. M., D. Say, J. Mühle, C. M. Harth, P. B. Krummel, D. Young, S. J. O'Doherty, P. K. Salameh, P. G. Simmonds, R. F. Weiss, R. G. Prinn, P. J. Fraser, and M. Rigby (2020). "Increase in Global Emissions of HFC-23 despite near-Total Expected Reductions". In: *Nature Communications* 11.1. ISSN: 2041-1723. DOI: 10.1038/s41467-019-13899-4.

Wenger, A., K. Pugsley, S. O'Doherty, M. Rigby, A. J. Manning, M. F. Lunt, and E. D. White (2019). "Atmospheric Radiocarbon Measurements to Quantify CO₂ Emissions in the UK from 2014 to 2015". In: *Atmospheric Chemistry and Physics* 19.22, pp. 14057–14070. ISSN: 1680-7324. DOI: 10.5194/acp-19-14057-2019.

Western, L. M., Z. Sha, M. Rigby, A. L. Ganesan, A. J. Manning, K. M. Stanley, S. J. O'Doherty, D. Young, and J. Rougier (2020). "Bayesian Spatio-Temporal Inference of Trace Gas Emissions Using an Integrated Nested Laplacian Approximation and Gaussian Markov Random Fields".

In: *Geoscientific Model Development* 13.4, pp. 2095–2107. ISSN: 1991-9603. DOI: 10.5194/gmd-13-2095-2020.

5 Bibliography

Arnold, T., A. J. Manning, J. Kim, S. Li, H. Webster, D. Thomson, J. Mühle, R. F. Weiss, S. Park, and S. O'Doherty (2018). "Inverse Modelling of CF_4 and NF_3 Emissions in East Asia". In: *Atmospheric Chemistry and Physics* 18.18, pp. 13305–13320. ISSN: 1680-7324. DOI: 10.5194/acp-18-13305-2018 (cit. on p. 8).

Manning, A. J., S. O'Doherty, A. R. Jones, P. G. Simmonds, and R. G. Derwent (2011). "Estimating UK Methane and Nitrous Oxide Emissions from 1990 to 2007 Using an Inversion Modeling Approach". In: *Journal of Geophysical Research: Atmospheres* 116.D2, p. D02305. ISSN: 2156-2202. DOI: 10.1029/2010JD014763 (cit. on p. 8).

Myhre, G., D. T. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura, and H. Zhang (2013). "Anthropogenic and Natural Radiative Forcing". In: *Climate Change 2013 - The Physical Science Basis*. Cambridge: Cambridge University Press, pp. 659–740. ISBN: 978-1-107-41532-4. DOI: 10.1017/CBO9781107415324.018 (cit. on p. 9).