LONG-TERM ATMOSPHERIC MEASUREMENT AND INTERPRETATION
(OF RADIATIVELY ACTIVE TRACE GASES)

DECC contract number: GA0201

6-month Report (May 2014 - Oct 2014)

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2 Executive Summary

2.1 Project Summary

Monitoring of atmospheric concentrations of gases is important in assessing the impact of international policies related to the atmospheric environment. The effects of control measures on chlorofluorocarbons (CFCs), halons and HCFCs introduced under the 'Montreal Protocol of Substances that Deplete the Ozone Layer' are now being observed. Continued monitoring is required to assess the overall success of the Protocol and the implication for atmospheric levels of replacement compounds such as HFCs. Similar analysis of gases regulated by the Kyoto Protocol on greenhouse gases will likewise assist policy makers.

Since 1987, high-frequency, real time measurements of the principal halocarbons and other 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 measurement station, 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, Mace Head receives substantial regional scale pollution in air that has travelled from the industrial regions of Europe. The site is therefore uniquely situated to record trace gas concentrations associated with both the mid-latitude Northern Hemisphere background levels and with the more polluted air arising from Europe.

The observation network in the UK has been expanded to include three additional stations; Angus Tower near Dundee, Tacolneston near Norwich and Ridge Hill near Hereford. Ridge Hill became operational in February 2012, Tacolneston began operating in July 2012 and Angus Tower has been making measurements since late 2005.

The Met Office's Lagrangian atmospheric dispersion model, **NAME** (**N**umerical **A**tmospheric dispersion **M**odelling **E**nvironment), has been run for each 2-hour period of each year from 1989 so as to understand the recent history of the air arriving at Mace Head at the time of each observation. By identifying the times when the air, arriving at Mace Head, has travelled over un-populated regions, i.e. when the air has travelled across the north Atlantic and the air concentration reflects the mid-latitude Northern Hemisphere baseline value, the data collected have been used to estimate baseline concentrations, trends and seasonal cycles of a wide range of ozone-depleting and greenhouse gases for the period 1989-2014.

By removing the underlying baseline trends from the observations and by modelling the recent history of the air on a regional scale, estimates of UK, Irish and North West European (UK, Ireland, France, Germany, Denmark, the Netherlands, Belgium, Luxembourg) emissions and their geographical distributions have been made using **InTEM** (**In**version **T**echnique for **E**mission **M**odelling). The estimates are presented as yearly averages and are compared to the UNFCCC inventory.

The atmospheric measurements and emission estimates of greenhouse gases provide an important cross-check for the emissions inventories submitted to the United Nations Framework Convention on Climate Change (UNFCCC). This verification work is consistent with good practice guidance issued by the Intergovernmental Panel on Climate Change (IPCC).

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3 Overview of Progress

3.1 Update contract website

Atmospheric baseline concentrations for each gas reported at Mace Head have been estimated through to the end of September 2014 and are presented through the website:

www.metoffice.gov.uk/atmospheric-trends

3.2 Investigating uncertainties in inversion emission estimation

The inversion system (InTEM) uses uncertainty estimates from several sources:

a. Atmospheric baseline uncertainty
b. Degree of influence of the surface area local to the observation point
c. Repeatability uncertainty of the observation
d. Variability uncertainty of the observation within a 2-hour window

Uncertainty elements (a) and (b) are classed as model uncertainty as they relate to the ability of the model to correctly model the air flow to the observation point. Uncertainty elements (c) and (d) are classed as observation uncertainty as they relate to the uncertainty of the observation within a 2-hour window. The relative strengths of the model and observation uncertainties are reported for each year and station for the Kyoto basket of gases.

3.3 Reporting new Kyoto basket gases

Nitrogen Trifluoride (NF_3) inversions have been performed for the first time and are reported. The emissions of NF_3 from the UK are not significant relative to the magnitude of the uncertainties.

3.4 Investigating the sensitivities in the inventory model for estimating HFC-134a emissions

The inventory refrigerant model has been provided for investigation by DECC. The sensitivities of the model to the input parameters have been considered for the gas HFC-134a, the principle gas used as a mobile air conditioner, e.g. in cars. The results of this analysis are presented.

3.5 Report on the potential of isotope measurements

The potential for isotopic measurements to aid source-specific emission estimates of carbon dioxide (CO_2) and methane (CH_4) are summarised.

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4 Update on UK DECC network measurement sites

4.1 Ridge Hill

Operations at Ridge Hill have continued with no major issues to report for either the GC-ECD or the Picarro CRDS. The Picarro CRDS was upgraded to Windows7 software and set to be remotely controlled by GCWerks software from the hub computer. A peristaltic pump was installed to operate a secondary water drain inside the lab.

4.2 Tacolneston

The Picarro CRDS was upgraded to Windows7 software and set to be remotely controlled by GCWerks software from the hub computer. The Medusa cooling unit (Cryotiger) was removed from site to be recharged and reinstalled a month later, this resulted in 4 weeks of data loss. The reduction gas analyser, which measures hydrogen and carbon monoxide, broke its main circuit board and lamp. These were replaced by the manufacturers and equipment reinstalled resulting in 4 weeks for data loss. Communication to Tacolneston was lost for a period of three weeks and a new internet hub was installed to resolve this.

4.3 Angus

Operation of the Picarro-CRDS at Angus continued with no major issues to report. Upgrade to windows7 was attempted but unsuccessful due to issues with the new hard drive. The upgrade is scheduled for November 2014. A drying system for the Picarro CRDS was installed as well as a new set of calibration standards.

4.4 Mace Head

The instruments at Mace Head have experienced a few problems since the previous report. The AGAGE-MD suffered a broken valve, and no data was collected for CH_4, CO and H_2 from 30 July – 29 August 2014. The valve has now been replaced and data on this channel is now being collected again. On the 12 September the flame in the detector for CH4 went out (during a time when the station operator Gerry Spain was on holiday). The flame was relit on 23 Sept 2014. The Medusa-MS ran well for a majority of the reporting, the only data loss occurred between 19 September – 2 October 2014, when the backup UPS failed. The batteries on the UPS have been replaced and the Medusa-MS is now operational.

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5 Uncertainty analysis for use in InTEM

5.1 Introduction

In order to be useful and comparable to the UNFCCC inventory it is essential that the modelled inversion emission estimates from InTEM are understood and quantified as comprehensively as possible. Describing the uncertainty within InTEM is an on-going activity as it is has many potential sources and few, if any, are easy to quantify. This chapter describes the latest work on uncertainty in InTEM, in particular, the current uncertainty estimates associated with each observation at each station for each gas.

Currently all of the errors are considered to be uncorrelated, future work will consider the potential for describing the degree of correlation between error terms.

InTEM combines uncertainty estimates from several sources within its inversion framework:

a. Atmospheric baseline uncertainty
b. Degree of influence of the surface area local to the observation point
c. Repeatability uncertainty of the observation
d. Variability uncertainty of the observation within a 2-hour window

Uncertainty elements (a) and (b) are classed as model uncertainty as they relate to the ability of the model to correctly model the air flow to the observation point. Uncertainty elements (c) and (d) are classed as observation uncertainty as they relate to the uncertainty of the observation within a 2-hour window. Here the relative strengths of the model and observation uncertainties are reported for each year and station for the Kyoto basket of gases.

5.2 Uncertainty components

The cost function within an inversion framework is the tool used to assess the best-fit of the *a posteriori* emissions and allows the inversion process to iterate towards an emission map that has the best agreement with the observations and can be constrained, to some degree, by the *a priori* emissions, i.e. it cannot produce solutions that are radically different from the *a priori* information (depending on the uncertainty of the prior). The mis-match between the model time-series and the observations is assessed using the standard Bayesian formulation. J_1 is the fit between the observations (y) and the modelled time-series using the current *a posteriori* emissions (x), M is the transport matrix that dilutes emissions from source to station and is calculated by NAME and R is the uncertainty matrix expressing the uncertainty of the modelled transport and observations.

$$J_1 = (Mx - y)^T R^{-1} (Mx - y)$$

The model and measurement elements are assumed uncorrelated and therefore only the diagonal elements of R are required. This is a simplification, an observation in one 2-hour period will, to some degree, by correlated with the previous and next 2-hour period, equally there will be some correlation between adjacent grid boxes. These are not considered here but are being investigated.

R is the model-measurement uncertainty matrix and describes the uncertainty of the observations and the uncertainty of the transport modelling:

- Observation uncertainty ($\sigma_{repeatability}$ & $\sigma_{variability}$)

$\sigma_{repeatability}$ → Uncertainty describing the repeatability of the observations. This is the standard deviation of the measurements of the standard tank each day. On the Medusa system, between each air measurement, a measurement of the standard is performed. The variability of these measurements of the same tank over a day is assumed to represent the repeatability of the

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measurement system. On the Picarro system a similar process is followed where air from a standard tank is repeatedly measured over the course of a day.

$\sigma_{variability}$ → Uncertainty due to aggregating the observations over the time step of the air history maps, in this case 2-hours. All of the observations within each 2-hour period are averaged and the standard deviation of these observations is assumed to be the uncertainty in the measurements over this time window.

- Model Uncertainty ($\sigma_{baseline}$ & σ_{local})

$\sigma_{baseline}$ → Uncertainty of the Mace Head baseline for each 2-hour period when applied to each of the different measurement stations. The Mace Head baseline, as described in previous reports, is used to describe the mole fraction of the air entering the inversion domain at each of the different measurement stations. This baseline time-series is only an approximation of the actual mole fraction entering the domain and therefore an uncertainty is attached to it. The standard deviation of the observations classed as baseline at Mace Head within a several week window is used to describe this uncertainty. This uncertainty is also used to describe the error in the transport modelling.

σ_{local} → Uncertainty increases as local influence of observation increases. In conditions when the local wind speed or the boundary layer are low, it is known that the modelling is more uncertain because local effects, not captured by the driving 3-D meteorology, are more dominant, and therefore the modelling is less able to represent the local reality. The local influences of the nine surrounding grid cells are known for each 2-hour period. These values are normalised (arbitrarily divided by 1e-8) and used as a multiplier for the modelling uncertainty at this time.

The modelling uncertainty is usually significantly larger (by an order of magnitude) than the measurement uncertainty.

$$R = \sigma^2 = (\sigma_{repeatability})^2 + (\sigma_{variability})^2 + (\sigma_{baseline})^2 + (\sigma_{local})^2$$

The plots on the following pages show how the model and observation uncertainties vary over time (years) per gas (Kyoto Protocol basket) along with the relative magnitudes of the observations above baseline. The model uncertainties are shown in red with the variability taken as the 5th and 95th percentile over the year. The observation uncertainties are shown in green with the variability taken as the 5th and 95th percentile over the year. The magnitude of the observations above the Mace Head baseline are shown in blue, the positive variability is the 75th percentile, the low variability is always zero and is not shown. The values have all been normalised as a percentage relative to the magnitude of the annual baseline mole fraction.

The following sections are headed by gas with information for each station contained within.

5.3 Conclusions

The red columns (model uncertainties) are consistently (but not always) much larger than the green columns (observation uncertainties).

The uncertainties vary from year to year in both the model and the observations.

The observation uncertainty is, for many gases, decreasing with time, for instance the introduction of the new mass spectrometer in 2011 is clear to see for several gases, as is the significant upgrade in instrumentation in 1998.

The average observation above baseline gives an indication of the change in magnitude of the pollution events seen at the different stations, it varies significantly from year to year/.

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5.4 Carbon dioxide

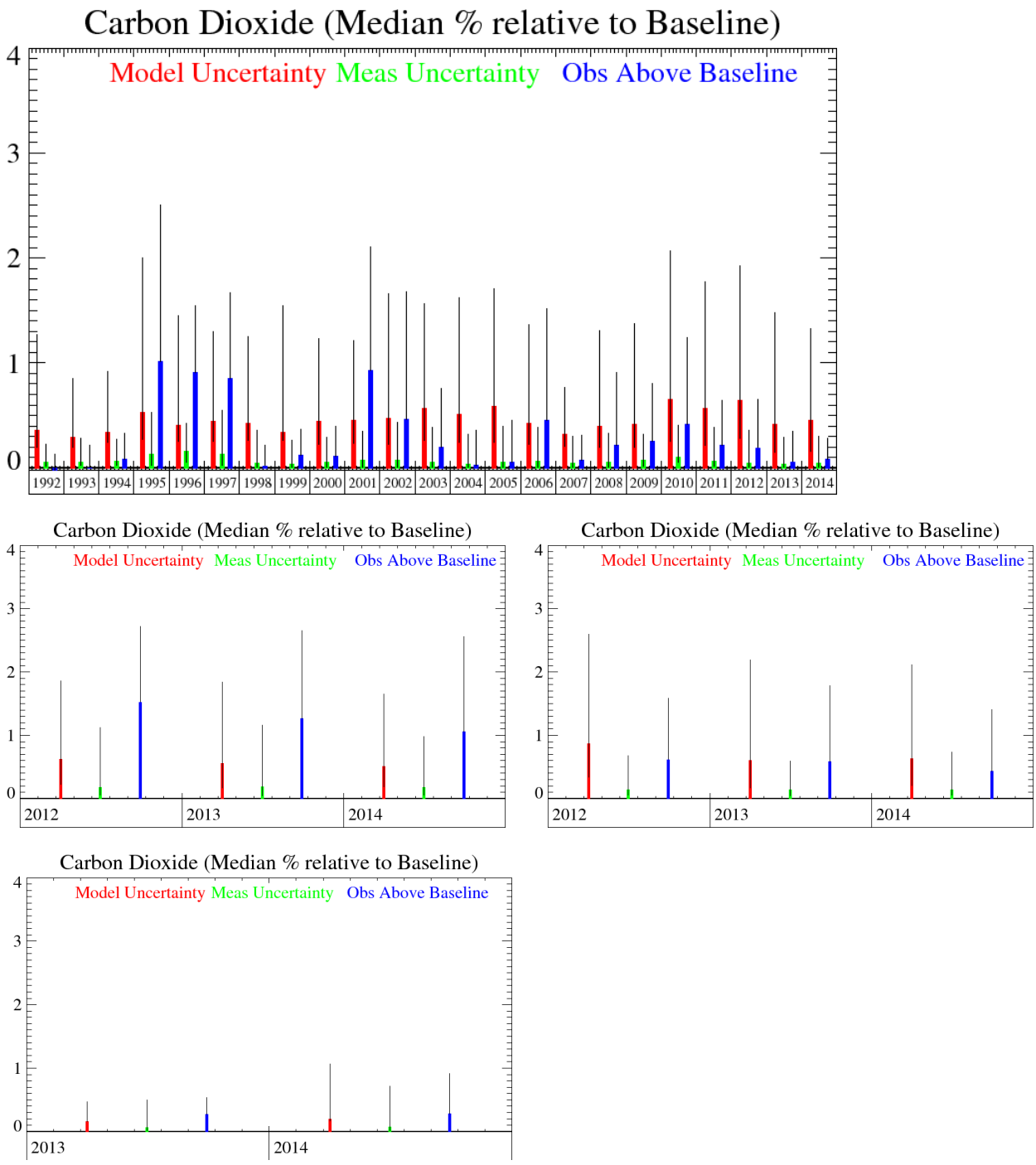

Figure 1: Carbon dioxide: Mace Head, Tacolneston, Ridge Hill and Angus. Pollution events are most significant at Ridge Hill and least significant at Angus. There is a strong variability in the strength of the pollution events at Mace Head when looked at over the whole record, 1995, 1996, 1997 and 2001 are the years with the strongest and long-lived of events.

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5.5 Methane

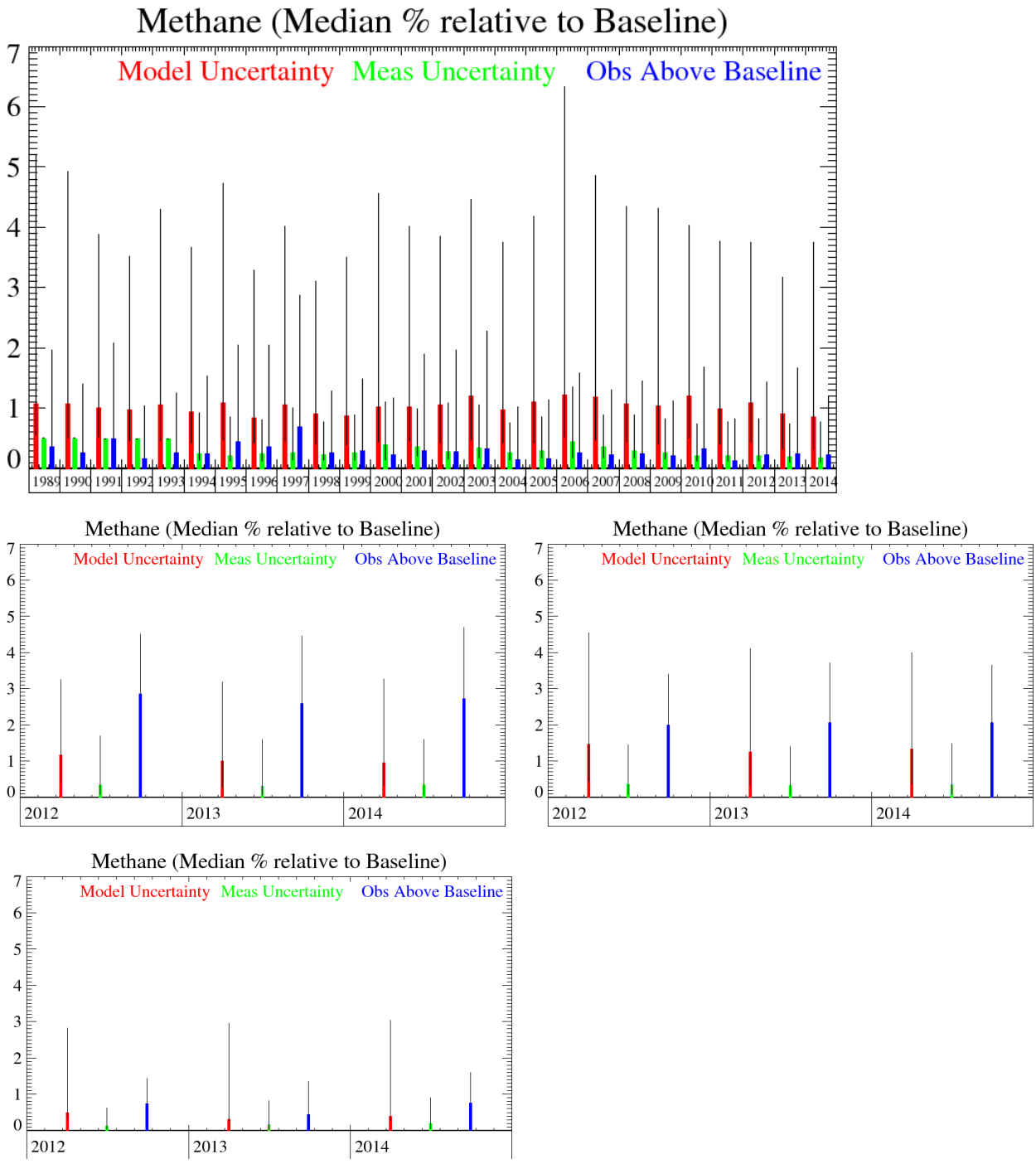

Figure 2: Methane: Mace Head, Tacolneston, Ridge Hill and Angus. Pollution events are most significant at Ridge Hill and least significant at Mace Head and Angus. There is a step change in the observation uncertainty at Mace Head when the instrument was changed in 1994.

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5.6 Nitrous oxide

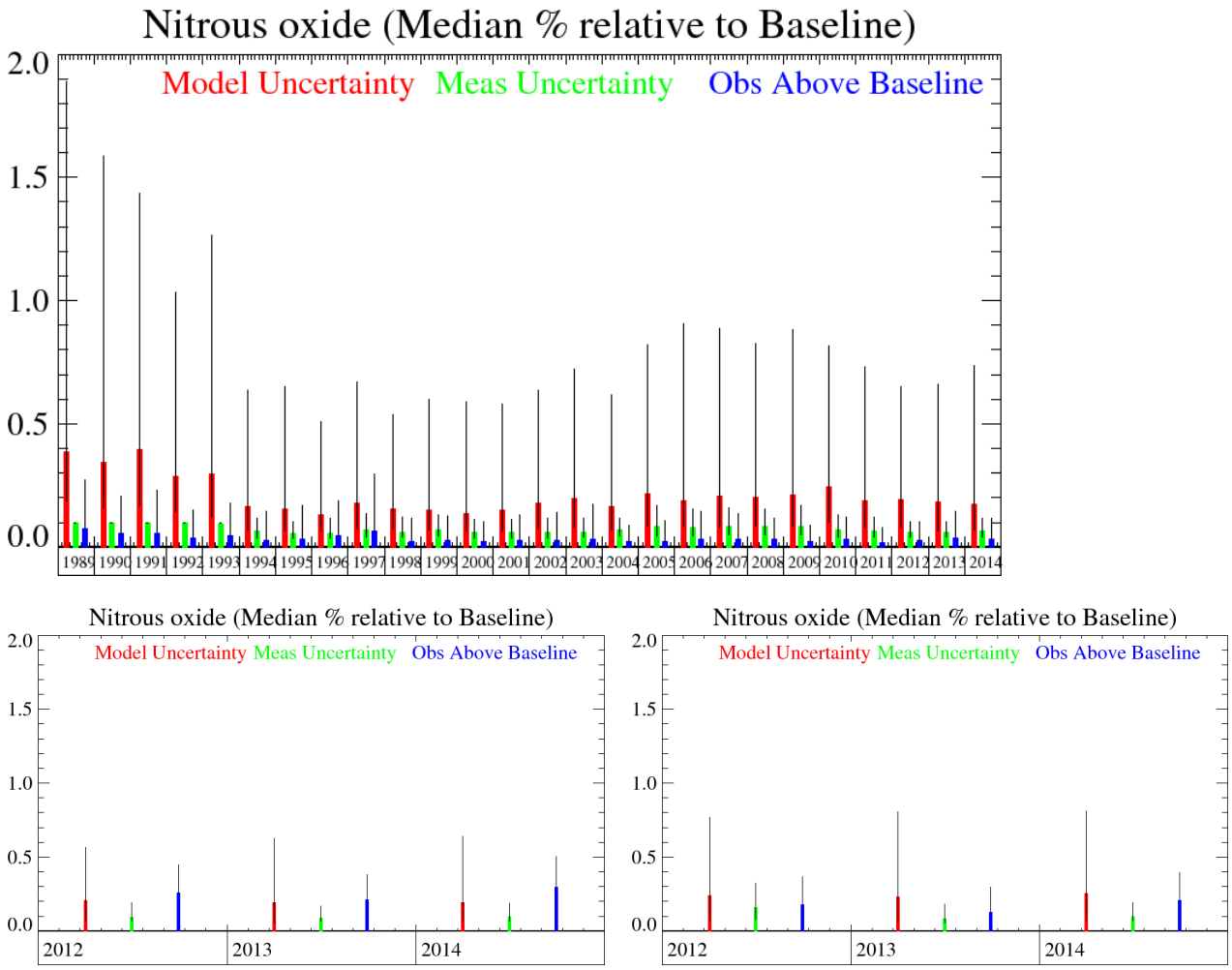

Figure 3: Nitrous oxide: Mace Head, Tacolneston and Ridge Hill. Note the different y-scale used for Tacolneston. The sizes of pollution events are similar at both UK stations. Observation uncertainty improved at Ridge Hill 2012-2013 as temperature stability in the cabin was improved.

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5.7 SF_6

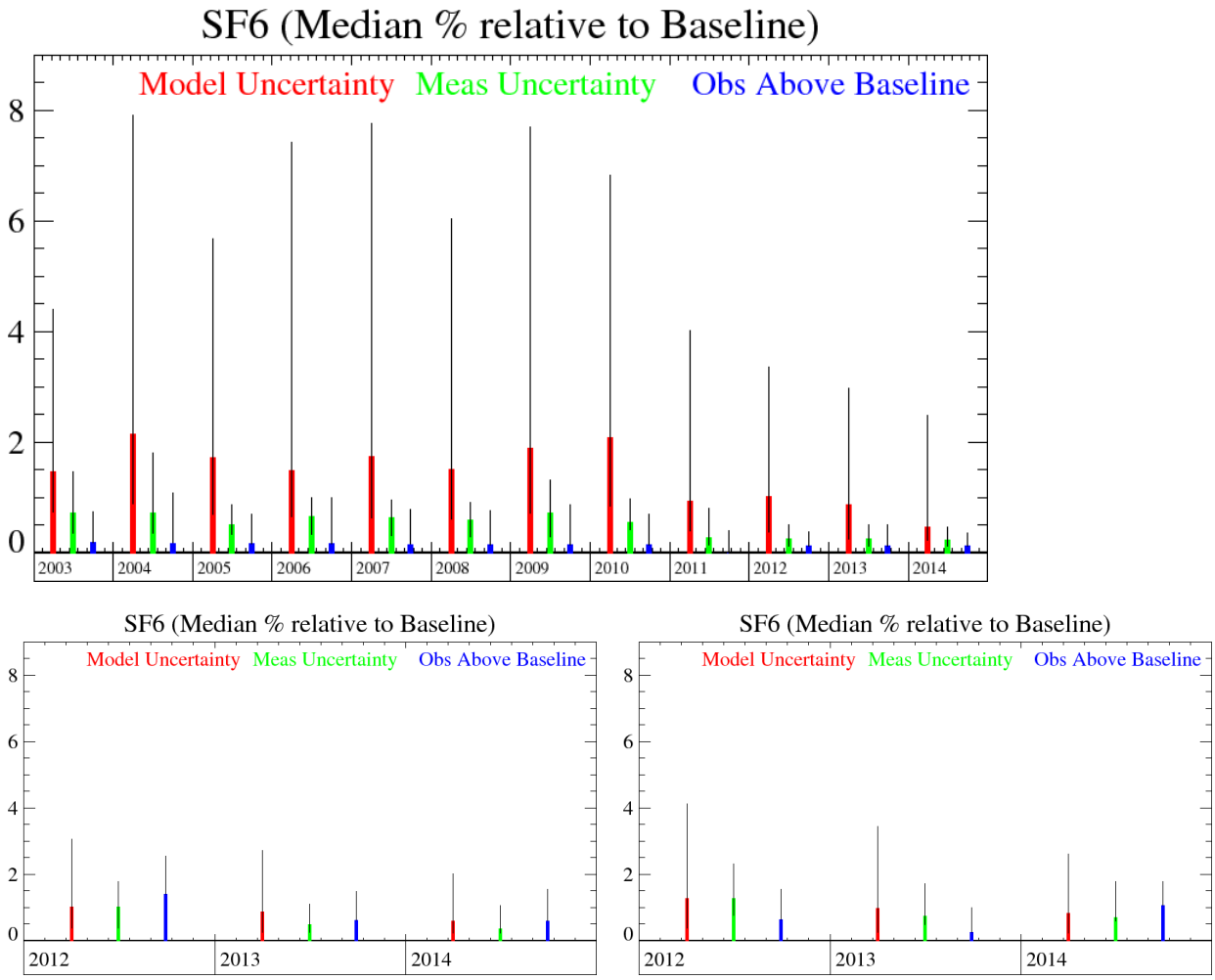

Figure 4: SF_6: Mace Head, Tacolneston and Ridge Hill. Note the different y-scale used for Ridge Hill. Model and observational uncertainty improved at Mace Head 2010 to 2011 after an upgrade to the Medusa-MS. Tacolneston GC-ECD observations used.

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5.8 Gases only measured at Mace Head and Tacolneston

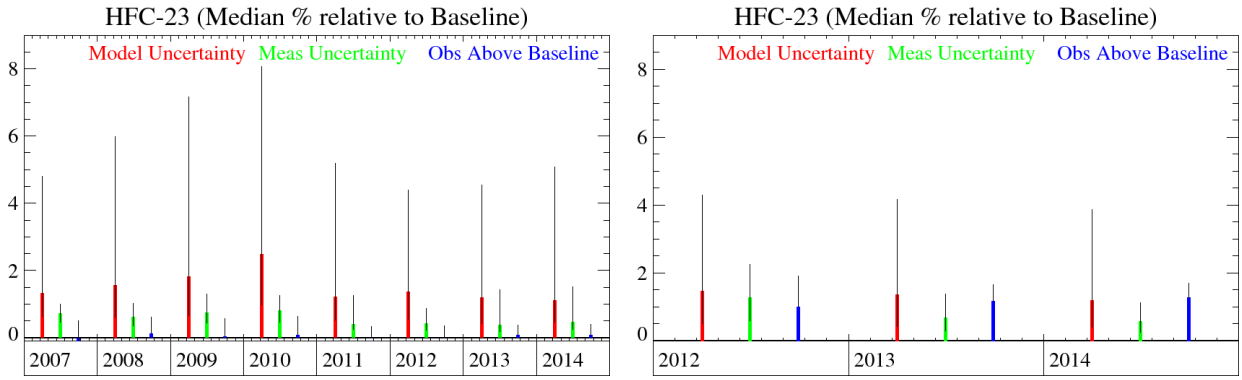

Figure 5: HFC-23: Mace Head and Tacolneston. Pollution events are considerably more significant at Tacolneston. The impact of an upgrade to the Medusa-MS 2010-2011 at Mace Head can be seen.

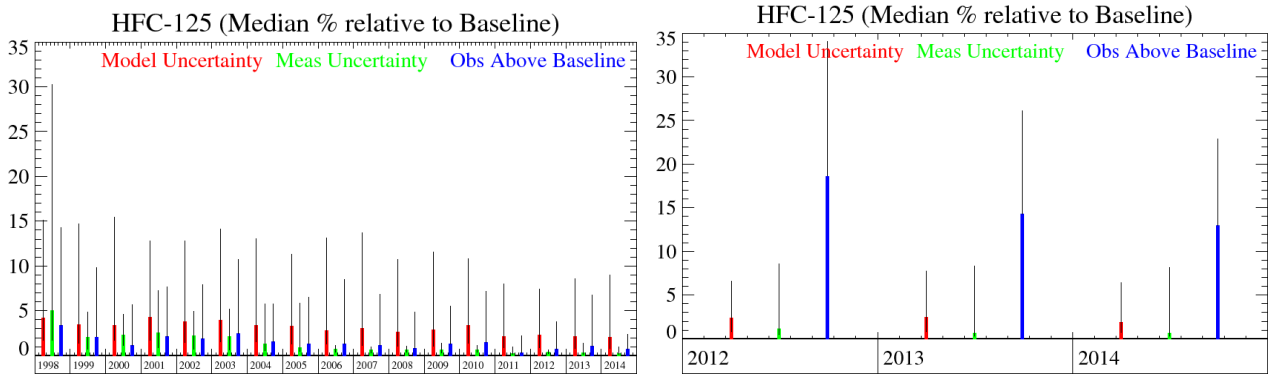

Figure 6: HFC-125: Mace Head and Tacolneston. There was considerable uncertainty at Mace Head, as a percentage, in the first year of observation at Mace Head. Observational uncertainty changed markedly in 2004 with the switch to the Medusa instrument. Pollution events at Tacolneston are considerably larger than at Mace Head.

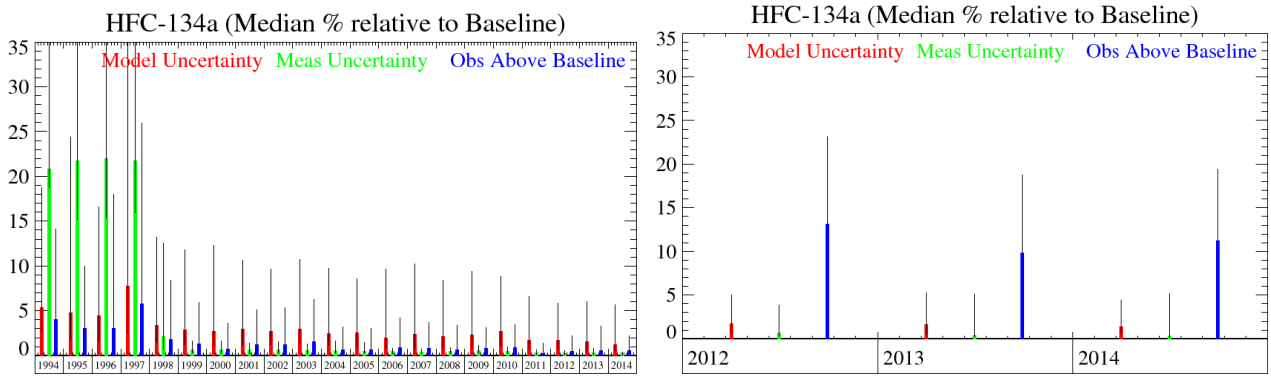

Figure 7: HFC-134a: Mace Head and Tacolneston. The early measurements at Mace Head, as a percentage, had high uncertainty; the model uncertainty only dominates after 1998. The Tacolneston pollution events are significantly larger than at Mace Head.

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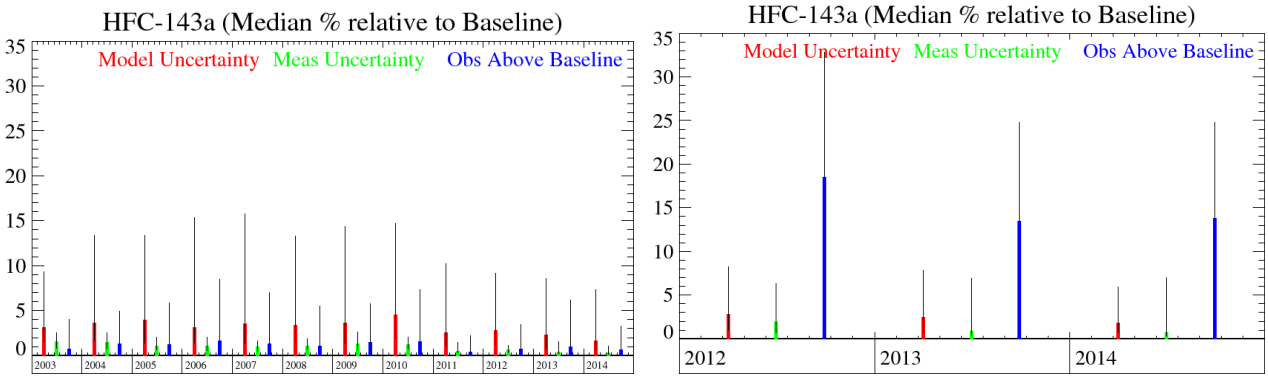

Figure 8: HFC-143a: Mace Head and Tacolneston. Mace Head observation and model uncertainty improved from 2011 onwards after an upgrade to the Medusa-MS. Pollution events are more significant at Tacolneston.

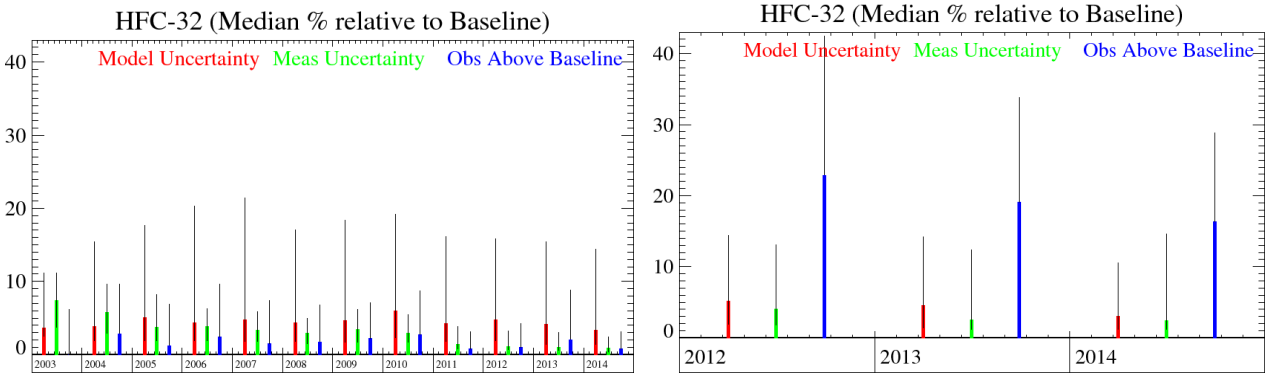

Figure 9: HFC-32: Mace Head and Tacolneston. The pollution events seen at Tacolneston are considerably larger than seen at Mace Head.

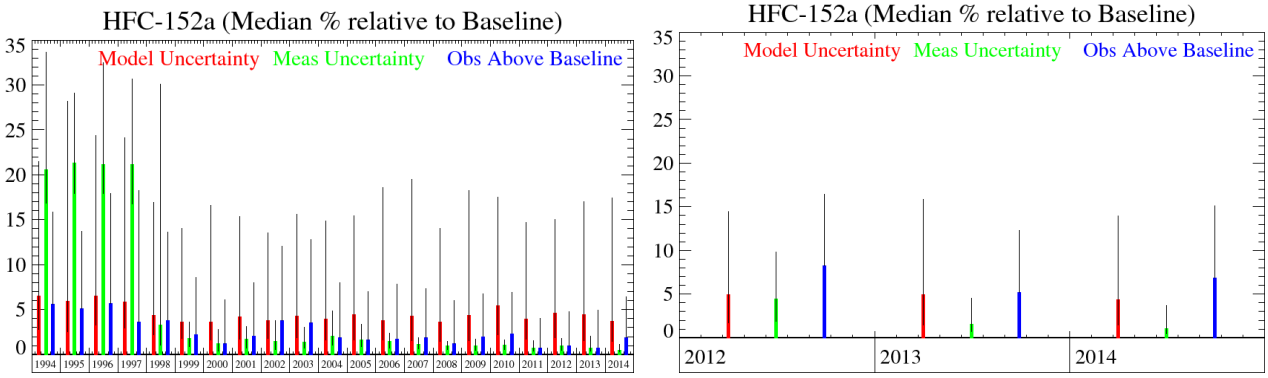

Figure 10: HFC-152a: Mace Head and Tacolneston. Similar to HFC-134a, the early observations as a percentage of the baseline were highly uncertain. The difference in the magnitude of pollution events between the sites is less striking compared to other gases.

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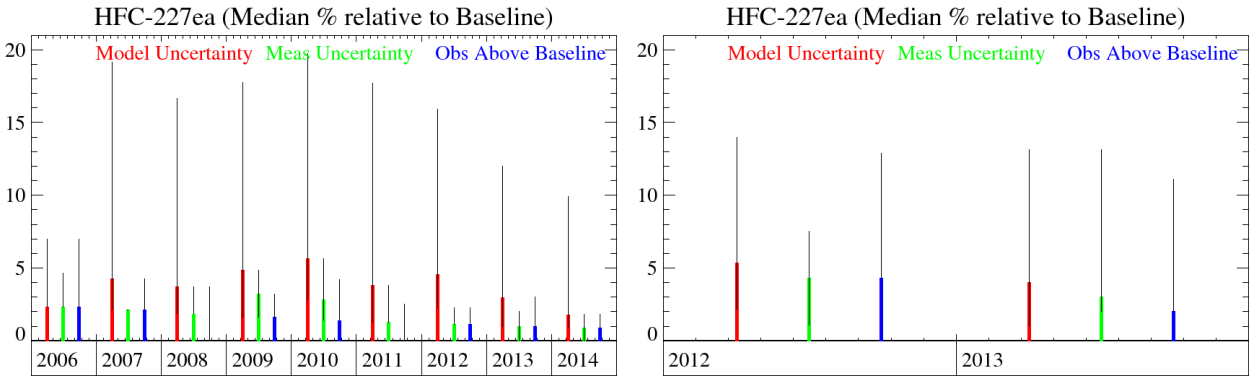

Figure 11: HFC-227ea: Mace Head and Tacolneston.

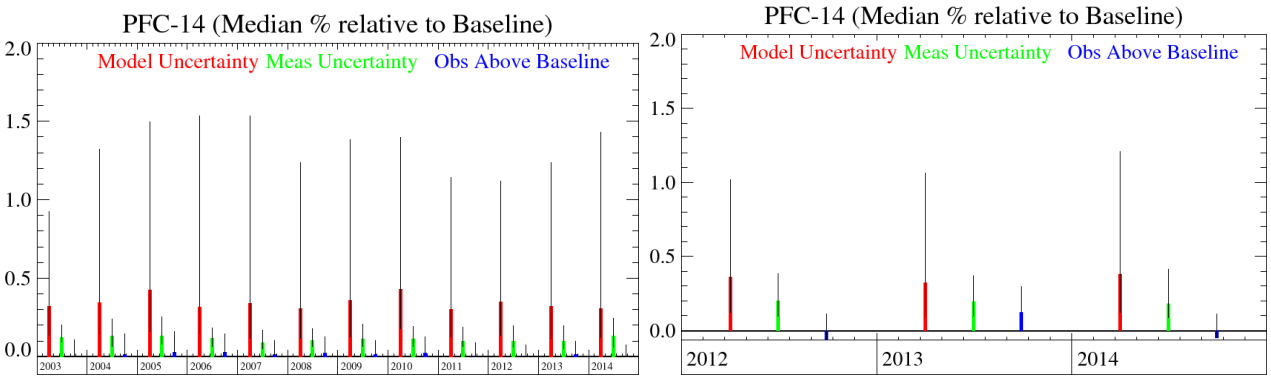

Figure 12: PFC-14: Mace Head, Tacolneston. Neither site sees prolonged pollution events.

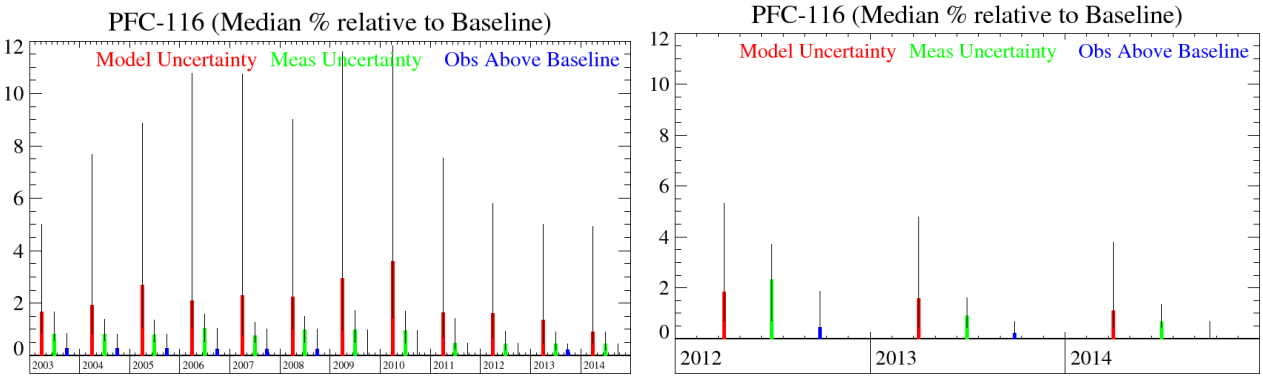

Figure 13: PFC-116: Mace Head, Tacolneston. Neither site sees prolonged pollution events.

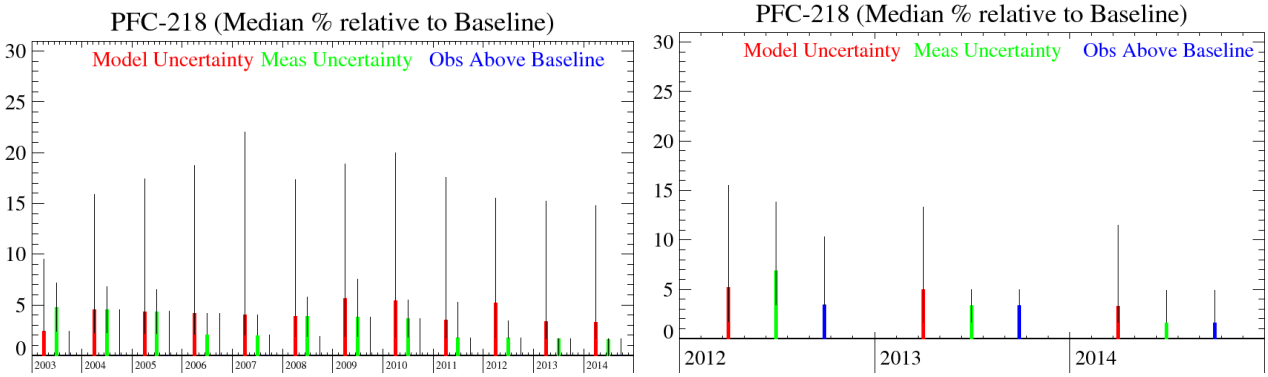

Figure 14: PFC-218: Mace Head and Tacolneston.

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6 Investigating UK HFC-134a emissions inventory

6.1 Introduction

HFC-134a (1,1,1,2-tetrafluoroethane) is a potent greenhouse gas. Over a 100-year period, it is 1200 times more effective at warming the atmosphere than CO_2. Controlled by legislation from the highly successful Montreal protocol, the production and use of ozone-depleting predecessors (CFCs and HCFCs), with the exception of existing banks, has been completely phased out in North Western Europe (NWEU). With little competition from other compounds, and despite recent EU regulation banning its use in all new automobiles as of 2010, HFC-134a has become the dominant source of fluorinated synthetic gas (F-gas) emission for the UK and much of Europe.

The UK reports emissions of HFC-134a from multiple sources. While the largest contribution originates from its use as a coolant in mobile air-conditioning systems (MAC), notable emissions are also recorded from a variety of other sources, including small and large scale refrigeration units, metered dose inhalers and a propellant for aerosols.

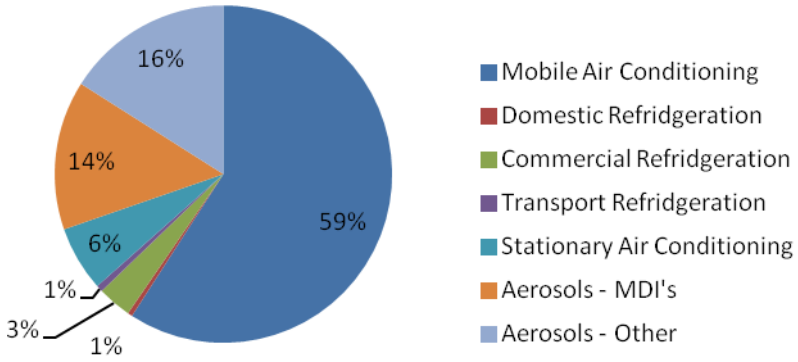

Fig 15: UK HFC-134a emissions by sector

Alike to many other European nations, the UK's emissions of HFC-134a are dominated by the MAC sector. Within the air-conditioning unit, HFC-134a is employed as a coolant: while use of the system is expected to be intermittent, continuous gradual leakage of coolant is expected.

6.2 The UK's HFC-134a inventory

In accordance with UNFCCC regulation, the UK and other nations that are parties to the Convention must submit national greenhouse gas (GHG) inventories to the UNFCCC. This annual submission incorporates emissions estimates for key gases highlighted under the Kyoto Protocol, including CO_2, CH_4, nitrous oxide and a number of fluorinated gases (including HFCs).

The UK's inventory report is compiled using 'bottom-up' methodologies. HFC-134a emission estimates are calculated by combining pre-determined emission factors with activity data; that is, the sum total of emission sources, i.e. automobiles. While bottom up efforts are able to provide estimations estimates, the method includes many uncertainties. In particular, emission factors are often considered overly simplistic for purpose; introducing potential error by means of generalisation. For example, MAC systems are represented by a single leak rate: given the broad range of vehicles within the UK fleet, this may be considered insufficient. Small changes in emission factors may have a notable influence on total emission estimates.

In order to validate these estimates, a 'top-down' approach has been employed. Via a combination of atmospheric observations (obtained from Mace Head, Ireland (AGAGE) and Tacolneston, Norfolk (University of Bristol/University of East Anglia)) with the Met Office' inversion

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modelling system, InTEM (Alistair Manning, Met Office), an independent estimate of the UK's HFC-134a emissions has been obtained.

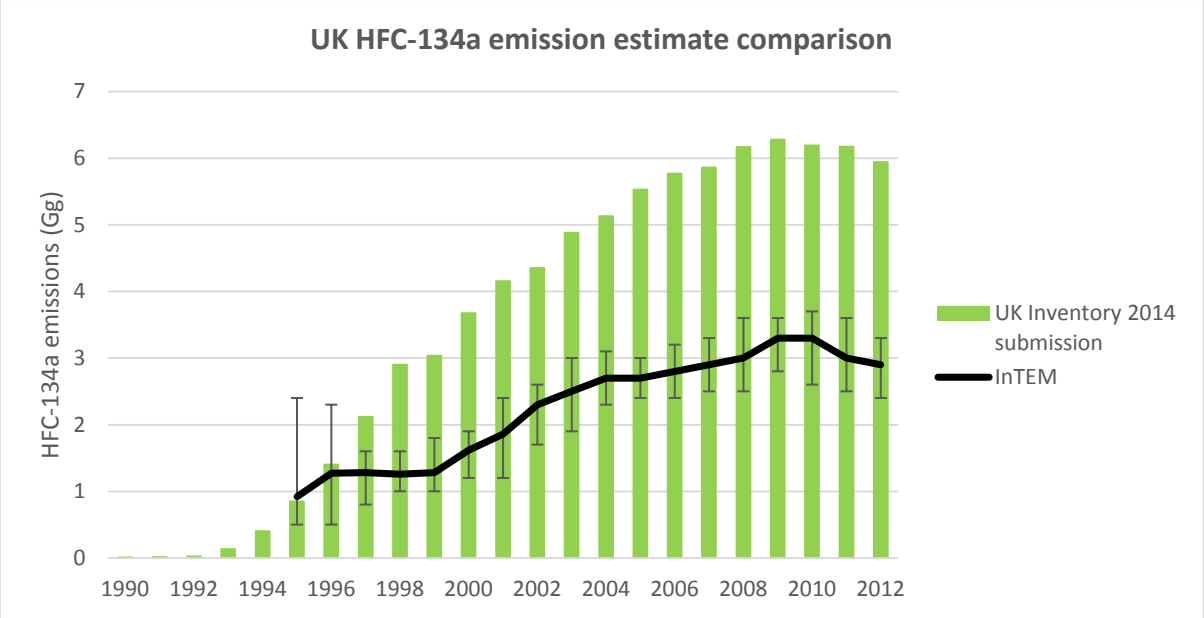

Fig 16: A comparison of UK HFC-134a emissions estimates, i) DECC compiled 2013 inventory, prepared for submission to the UNFCCC and ii) independent top down estimate compiled by InTEM

As illustrated in Fig 16, significant disagreement is observed between inventory and InTEM estimates; as of 2012, the magnitude of disagreement is estimated to be of the order of 3 Gg, almost half the inventory total in 2012. While both estimation methods carry notable margins of error, neither provides deviations large enough to justify such a discrepancy.

In order to determine a likely source of the disagreement, InTEM has been used to produce estimates for other fluorinated species, including HFC-125. Here, good agreement is observed between estimates, suggesting InTEM to be a reliable means of national emission estimation. In order to assess the likely accuracy of the inventory estimate, a provisional study was undertaken and described here in brief.

6.3 Comparing UK emission factors with those of other European nations

A key component of inventory methodology is the emissions factor and each HFC-134a inventory submission includes a factor in three sectors: manufacture, operation and disposal. These factors, expressed as percentages, govern emission totals in each sector (i.e. MAC), and are calculated based on study of the relevant sources. In order to estimate the accuracy of the UK's HFC-134a inventory, MAC (the largest contributing sector of HFC-134a emissions) emission factors were evaluated to gain an understanding of annual variations. (Emission factors, particularly from sectors incorporating automobiles, are likely to change annually as improvements in technology are implemented).

A useful means by which to gauge the likely accuracy of the UK's calculated MAC emission factors is by comparison with other European nations; in particular, an assessment of factors from countries with similar standards of living (and as a result, similar automobile fleets). For countries with similar fleets, it is provisionally expected that similar emission factor trends may be observed.

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Since the majority of MAC based emissions arise as a result of operating losses, manufacturing and disposal factors were omitted from the analysis.

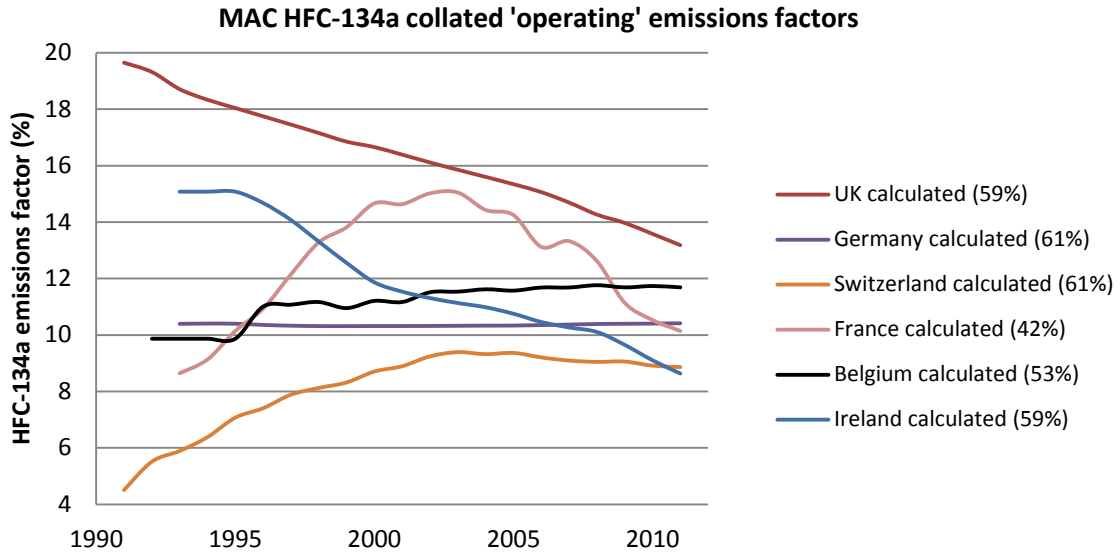

Fig 17: MAC operating emission factor trends from base year by nation. Bracketed percentages represent contribution from MAC sector to total national HFC-134a emissions

Contrary to expectations, MAC emission factor trends show significant and often unexplainable national variation. While the UK and Ireland show typically negative trend lines, which may be expected based on constantly improving technologies, and hence reduced emissions, trends from the continent do not reflect such improvements. Since the UK began reporting HFC-134a emissions in 1991, its MAC (operating) emission factor has consistently remained the factor of greatest magnitude in Western Europe. In 2011, the UK's MAC operating emissions factor was, at approximately 13%, over 4% greater than the comparable Irish factor and equivalent to over 122 Mg of HFC-134a.

In particular, a comparison of UK and German trends highlights the effectively unexplainable variation in MAC emissions factor by country. The UK and Germany have similar standards of living, but at no point during the last 20 years have these emission factors followed similar trends or any notable level of agreement. The German factor has shown almost no variation since its first submission, at an average value of around 10.5% operational loss. Given the equivalency of UK and German fleets, and that Germany has a greater number of cars per capita (572 compared to 519), it would be expected that national emissions from the MAC sector would be greater in Germany than the UK. However, this is not the case: in 2011, the UK reported 'operating' MAC emissions of 3.1Gg, while Germany reported just 2.6Gg. This difference can therefore only be accounted for by influences from emission factor variations.

In order to test the outcome of a continental scenario (i.e. a scenario by which the UK employs emissions factors more closely related to those in North West Europe), UK stock values (extracted from the UK's 2013 UNFCCC submission) were combined with German emission factors across all emitting sectors.

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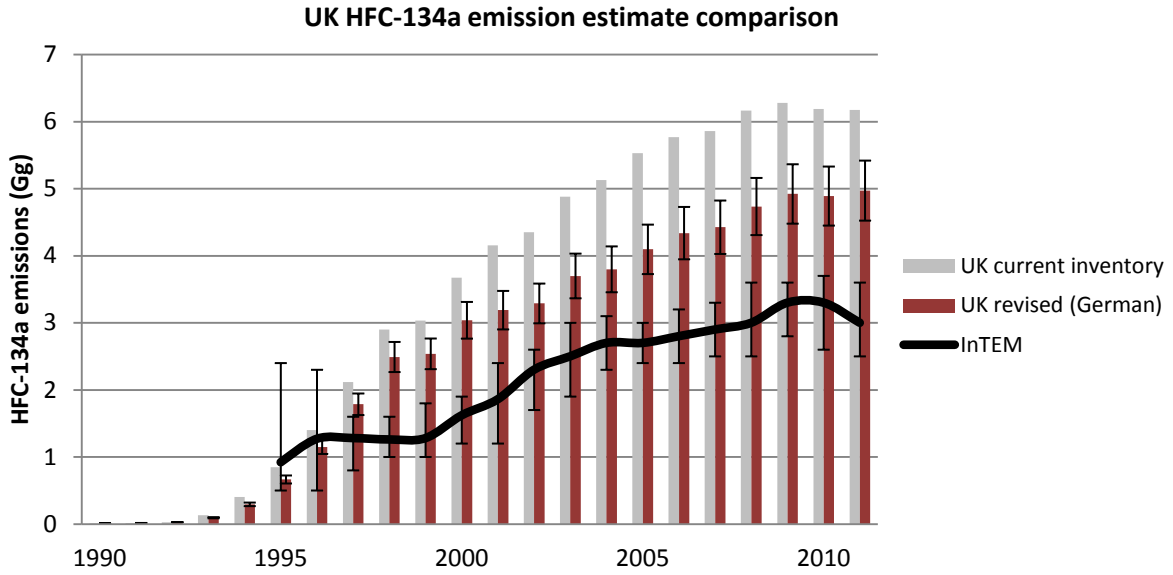

Fig 18: A comparison of InTEM estimates with i) the current UK inventory and ii) the revised UK inventory employing German emission factors. (For simplicity, original inventory error bars are retained)

A continental scenario has a significant impact on the UK inventory, as seen in *Figure 4*. In 2011, modification with German factors gave a hypothetical emissions reduction of over 1Gg, equating to in excess of 1300Gg CO_2eq. Clearly, nation based variation of emission factors can generate large differences in reported values, an inherent disadvantage of the bottom-up method of calculation.

While Fig 18 demonstrates the theoretical emission 'cuts' available through small changes to the UK's emission factors, this method alone remains short of providing any substantial agreement between inventory and InTEM estimates. In order to do this, a more in-depth study of the model used to calculate the UK's HFC-134a emissions (in key sectors) is required.

6.4 Introduction to the RAC model

Following discussions between the University of Bristol, UK Met Office, DECC and Ricardo-AEA (environmental consultants and contractors tasked with construction of the UK's annual inventory submission by DECC), we (the University of Bristol) were able to obtain a working copy of Ricardo-AEA's RAC model (RAC: Refrigeration and Air-Conditioning).

The RAC model, originally produced by ICF international in 2011, is used to calculate emissions of a number of gases from the refrigeration and air-conditioning (including MAC) sectors. It relies heavily on research based findings; the model facilitates the annual modifications to these findings by allowing model variables to be altered and total values to be re-calculated. The model itself is split into 13 distinct categories, ranging from light MAC, through domestic refrigerators and condensing units to industrial scale refrigeration. Based on the nature of RAC appliances, the model deals solely with emissions of fluorinated species, including CFCs and HCFCs (now banned under the Montreal protocol), HFCs and a number of refrigerant blends (a combination of 2 or more fluorinated gases selected for their combined properties). Hydrofluoroolefins (HFOs), designed as replacement compounds for HFCs, are also included as their emissions are predicted to rise steeply in coming years (Spatz et al., 2008).

While the RAC model does not account for the complete suite of HFC-134a sources, including, most notably, contributions from the aerosol sector, its inclusion of MAC makes it an ideal platform for exploring the effect of changes to emission parameters. The RAC model splits mobile

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air-conditioning into two categories: Light Mobile Air-Conditioning (LMAC, RAC12) and Other Mobile Air-Conditioning (OMAC, RAC13). While LMAC deals almost exclusively with cars and vans, OMAC incorporates emission contributions from a number of other sources, including trains, buses and trucks (over 3.5 tonnes). Since MAC demands such a significant portion of HFC-134a emissions, it is modifications in these sectors (LMAC, OMAC) that have been examined.

6.5 Modifying the AEA model

The RAC model is entirely dependent on a combination of findings from research and IPCC guidelines set out to quantify emission parameters. While these parameters are generated by comparison of information from a number of sources, each source contains uncertainty estimates; as a result, each variable is presented as range of plausible values from which the original value is chosen. As seen in the provisional study, small changes in emissions factor can hold notable influence over total inventory figures and therefore, selecting a set value from multiple specified ranges may have a significant impact on model output.

In addition to the RAC model, the University of Bristol was granted access to the accompanying ICF report. The report justifies the selection of model parameters, and includes the ranges from which they are chosen. The model was adjusted by incorporating, in turn, the minima of each of these ranges. A total minimum estimate was also calculated, in order to assess any potential agreement between updated scenarios and InTEM estimates. *Table 6.1* (below) summarises modifications made to the RAC model and presents them in descending order of relative impact (out of 10).

Modification	**Details**	**Impact**
No Refill	The RAC model accommodates for the refill of LMAC and OMAC systems via a simple YES/NO parameter. The default setting for the refill parameter is YES. In both categories, this variable was changed to NO	**10/10**. Removing the refill assumption significantly influences the inventory estimates
Penetration rate (1&60%)	Assesses MACs market penetration as a percentage (i.e. the percentage of automobiles containing an air-conditioning unit). The model facilitates the alteration of this parameter in 1990 (base year) and 2008, while interpolating other values. In both categories, penetration rate was reduced from 5% to 1% in 1990 and 80% to 60% in 2008	**5/10**. A notable reduction in reported emissions in observed. While significantly smaller than the 'no refill' variant, modification still results in ~1Gg theoretical reduction
Penetration rate (2&70%)	As above. In both categories, penetration rate was reduced from 5% to 2% in 1990 and 80% to 70% in 2008	**3/10**. A reduction is observed, however the result is less significant than the previous two modifications
Post '10 leak reductions	A post 2010 leak reductions parameter is included in LMAC and OMAC categories. It may be set to either YES or NO; its default setting is NO. The parameter is designed to account for significant technological improvements (resulting in leak reductions) after 2010. Its influence was examined by changing the variable setting to YES	**3/10**. Significant reductions are observed after 2010, however overall impact limited by time frame (no reductions pre-'10)
Max lifetime LMAC	Based on IPCC guidelines and research by	**2/10**. Limited

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	Oko-Recherche et al., the lifetime of LMAC is suggested to be between 9-16 years. This parameter was altered by changing the default LMAC lifetime (15) to its maximum potential value of 16 years	theoretical reductions observed
Minimum disposal (LMAC & OMAC)	The disposal parameter reflects HFC-134a losses at the disposal stage. As of 2011, the default disposal loss was set to 30% of the remaining charge. *Oko-Recherche* estimated that, if recovery procedures were followed without exception, that disposal losses could be limited to 6%. The disposal parameter of LMAC and OMAC categories was therefore modified to 6%	**2/10**. An extreme modification in terms of deviation from default value, yielding limited emission reductions
Max lifetime OMAC	Based on IPCC guidelines and research by *Oko-Recherche*, the lifetime of OMAC is expected to be between 9-16 years. This parameter was altered by changing the default OMAC lifetime (10) to its maximum potential value of 16 years	**1/10**. Reflecting the relatively small contribution of OMAC to the Mobile Air-Conditioning sector, increase of lifetime yields only small inventory variations
0.7kg charge 2010	An average unit charge size is assumed for all LMACs. This parameter is expected to decrease with time, reflecting technological advances. Values may be changed by decade, with other values linearly interpolated. Based on research from *Oko-Recherche,* the charge size in 2010 was reduced from its default value (0.73kg) to its potential minima, 0.7kg	**0.5/10**. Very limited influence
Manufacturing loss rate minimum	The manufacturing loss rate parameter determines the loss of total charge (%) during manufacture. The default setting for both LMAC and OMAC is 0.5%, and has remained constant since base year. The default value was reduced to 0.2%, in accordance with the lowest estimated loss rate provided by *Oko-Recherche.*	**0.1/10.** Almost no variation of inventory estimates observed

Table 6.1: A summary of modifications made to the AEA Ricardo RAC model MAC sectors, and an assessment of their relative impacts on the UK's HFC-134a inventory estimates

In order to calculate revised inventory estimates based on modifications to the RAC model, the difference between original MAC emission estimates and theoretically generated estimates were produced. This difference was then subtracted from total HFC-134a annual emission estimates, in order to produce a suite of revised trends, each related to a different RAC modification. The results of this study are reproduced in Fig 19.

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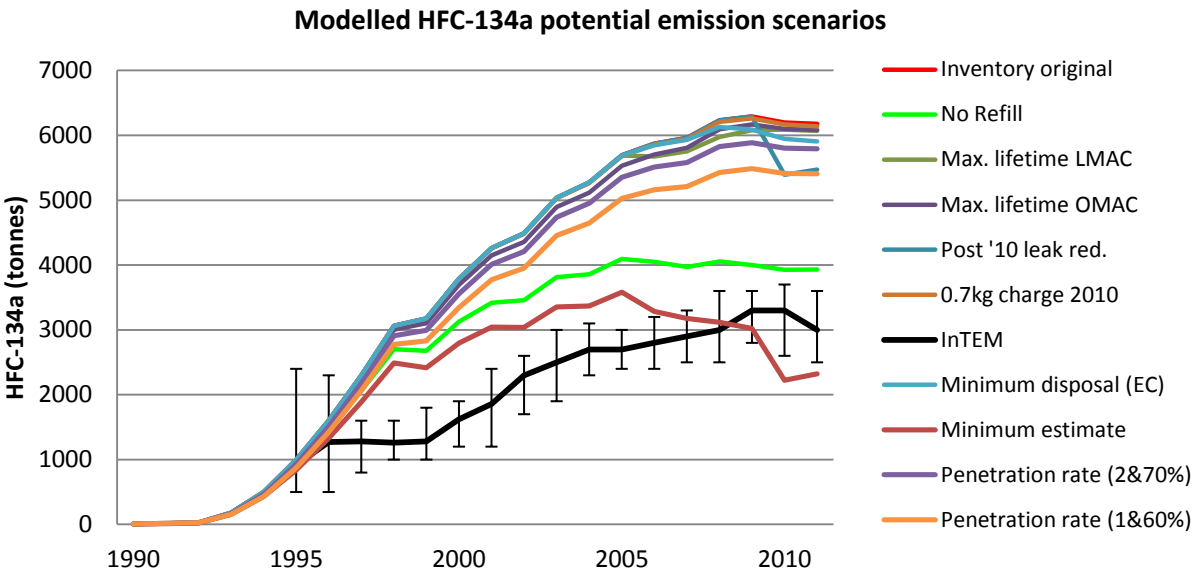

Fig 19: Collated HFC-134a emission scenarios, labelled according to their corresponding RAC model modification. Combined minimum estimate and InTEM values are included for comparison

NOTE: Results of the manufacturing loss rate minimum modification are omitted from Fig 19, since its limited impact produced a trend line indistinguishable from the original UNFCCC inventory.

By combining modifications the RAC model, partial agreement is observed between the theoretical UK inventory and InTEM estimates. As described in *Table 6.1* and demonstrated graphically above, rate of refill and penetration rate have the greatest influence on inventory estimates. While other modifications do offer some scope for varying the UK's HFC-134a inventory, our study will focus primarily on the likely accuracy of the aforementioned variables.

6.6 MAC Refill: A closer look

At the end of a MAC unit's lifetime, the unit may be refilled. This process replenishes the quantity of HFC-134a within the air-conditioning system to its approximate original volume. Given the total number of light automobiles within the UK, including nearly 32 million cars, the assumed rate of refill is expected to hold significant influence over total MAC emissions.

Our provisional analysis of the RAC (LMAC & OMAC) refill parameter suggests that the input system is inadequate for purpose. A simple YES/NO variable is not expected to facilitate an accurate refill estimate; in particular, with the default setting as YES, it is assumed that *all* vehicles in the UK fleet are refilled annually: this is not expected to be the case, with many AC units predicted not to be recharged for multiple years/not at all during product lifetime. Conversely, it is possible also that a vehicle may be filled multiple times a year. Fig 20 highlights 4 theoretical refill scenarios, generated by interpolation of the two potential model results; total annual refill (YES) or zero annual refills (NO).

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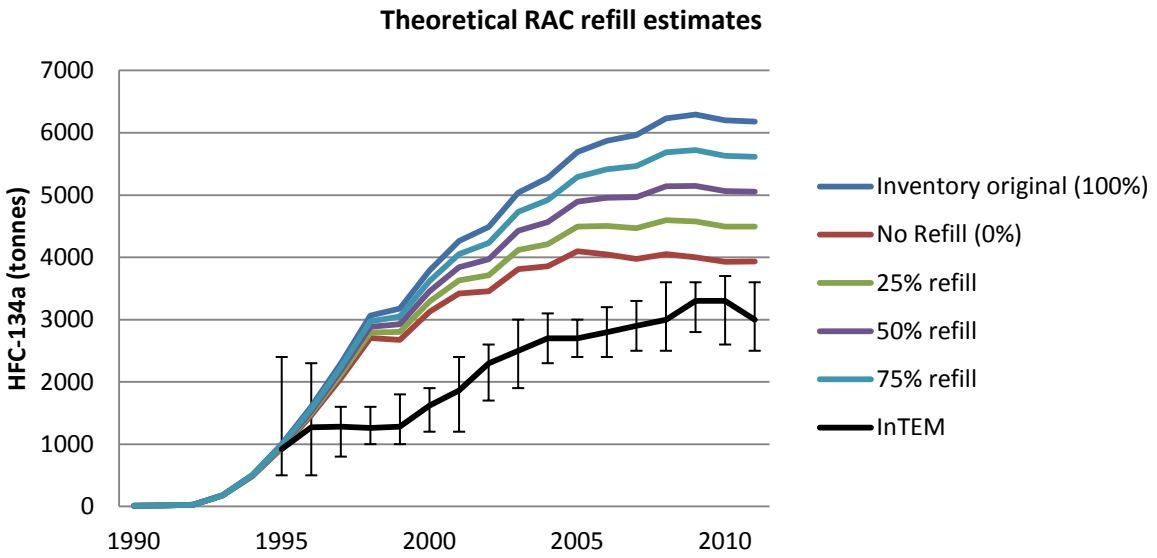

Fig 20: Theoretical emission estimates, based on interpolated variations of the RAC refill parameter. InTEM results are included for comparison

Significant HFC-134a emission reductions are observed upon modification of the RAC refill parameter (see Fig 20). A 25% reduction of annual refills would result in a loss of over 0.5Gg from the original inventory estimate for 2011, while complete removal of the refill parameter (equivalent to changing the default setting to NO) yields a potential saving of over 2.1Gg, a third of the total 2011 HFC-134a estimate.

In order to improve the accuracy of the HFC-134a inventory, it is recommended that the refill parameter should, as a result of this work, be revised. While a simple YES/NO variable offers simplicity, a distribution of refill rates, supported by a greater understanding of refill trends, will offer reduced uncertainty and better accuracy for the MAC sector.

6.7 MAC HFC-134a Penetration Rate: A closer look

Penetration rate determines, as a percentage, the total number of automobiles (in both LMAC and OMAC categories) with air-conditioning units. For the base year (1990), 5% of automobiles were assumed to contain a MAC unit. In correspondence with improving technologies and increased customer demand, the penetration rate is assumed to rise steadily to an estimated value of 80% in 2008, followed by a plateau. In order to estimate annual values, a linear interpolation is used, based on manually entered values for 1990 and 2008. (Resulting in an approximate annual increase of 4.5%)

By interpolating the majority of years, the RAC model introduces significant uncertainty to total MAC emission estimates. While manually entered values should provide a reasonable degree of accuracy (AC penetration rate can be determined by examination of relevant motor industry documentation), interpolated figures do not account for annual variations in uptake rate. A comparison of inventory and InTEM estimates, from 1995 to 2000 in particular, shows distinct disagreement in growth rate; inventory estimates show significant growth, while InTEM estimates remain relatively constant throughout the period. It is postulated that a generic interpolated penetration rate could account for such growth of the inventory estimate.

A more detailed study of MAC penetration rates will be used to quantify the potential impact of the ‘interpolation assumption.’ It is expected that access to the relevant data is possible, and could be used to better estimate annual penetration trends in future work.

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6.8 Are refill/penetration rates justified on the continent?

Provisional investigation has not provided any further details on refill/penetration assumptions for other North West EU nations. Further study is required, since only high-level documents (UNFCCC annual submission reports) are currently available. Access to continental equivalents of the RAC model would provide grounding for a more in depth inter-nation comparison of MAC assumptions (see further work).

6.9 Can this study be extended to other gases and are modifications effective?

The outcomes of this study will determine the likely compatibility of this method for other species. If future work is judged to effectively improve the accuracy of the HFC-134a inventory, such a methodology could be extended to other fluorinated species, including HFC-125 (used in refrigerant blends and fire suppressant equipment) and HFC-143a (used in refrigerant blends, as a propellant and for cleaning electrical equipment). Both are potent greenhouse gases.

6.10 Future work

In order to transfer the outcomes from this study into improvements to the UK's HFC-134a inventory estimates, we recommend that the next steps taken are:.

In collaboration with DECC (Julia Sussams), the relevant bodies from comparable nations (primarily focusing on Germany) will be contacted. The aim of this objective will be to gain an understanding of competing methodologies for calculation of refill and/or penetration rate parameters, ensuring (potential) modifications to the RAC model, made by the University of Bristol, reflect current understanding.

In direct response to provisional analysis of the RAC model, we (the University of Bristol) will assess the possibility of a modified refill parameter. This will involve the replacement of the YES/NO variable with a distribution type input/percentage value. If the modification is deemed feasible, (based on current in-house expertise) a copy of the RAC model will be altered to incorporate an updated refill input system. A range of scenarios will then be tested (based on the new input system and using similar methodology to that presented above) and results presented to assess the likely success of the modification.

Further research is needed to determine the accuracy of the penetration rate estimates, and to assess the uncertainty introduced via interpolation of 1990 and 2008 data points. Initially, efforts will be made to trace the source of the input parameters, through relevant contacts at Ricardo-AEA and ICF international. The likely accuracy of these input values will be assessed, and if deemed necessary, new values calculated via collaboration with the relevant bodies. Where possible, estimated penetration rates will also be calculated for the complete range of years; these values will be compared with interpolated estimates to determine the likely accuracy of such methods. If interpolation is deemed not to be an appropriate means of penetration rate calculation, using experience gained through modification of the refill parameter, the RAC model will be altered to accept annual penetration rates via manual entry. The results of this modification will be compared with original inventory figures to quantify any improvements made.

References

SPATZ, M., MINOR, B. & DUPONT, H. HFO-1234yf. A low GWP refrigerant for MAC, Honeywell/DuPont joint collaboration, VDA Alternative Refrigerant Winter Meeting, 2008.

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7 Estimating emissions of nitrogen trifluoride through inversion modelling

7.1 Introduction

Production of nitrogen trifluoride (NF_3) has been increasing rapidly to meet demand in end use applications (the manufacture of semiconductor devices, flat panel displays and photovoltaic cells). The first ambient air measurements from the Advanced Global Atmospheric Gases Experiment showed the rapidly rising global atmospheric abundance due to this market expansion. Although the current contribution of NF_3 to radiative forcing is small, its potential to impact climate is significant (the 100-year global warming potential is 17,885 from IPCC AR5, Chapter 8, Supplementary Material, Table 8.SM.16), and is thus now included in the Kyoto Protocol.

Adaptation of the Mace Head Medusa in June 2013 allowed measurement of NF_3 on a 130-minute frequency, alongside all the other important halogenated gases. This new capability allows us to use InTEM to calculate the UK and European contribution to global NF_3 emissions.

7.2 Measurements and general observations

The general trend observed in the observations at Mace Head corresponds well with other measurement series made elsewhere, which show a rise in the Northern Hemisphere over 2013-2014 period of ~0.1 ppt (Fig 21). Given the relatively poor precsion of measurements, significant deviation from the well mixed atmosphere is difficult to observe. However, one pollution episode in June 2013 stands out well beyond the precision of the baseline measurements. This episode coincides with a unique meteorological period of air masses arriving at Mace Head from the East Coast USA and Canada (Fig 22, left). Given the significant activity in manufacture (Air Products in Allentown, PA) and end-use of NF_3 (probably several semiconductor plants) in this region it is therefore highly probable that emissions from North America are responsible for this atypical pollution episode. Smaller pollution episodes are also observed due to long range transport of air masses from the west.

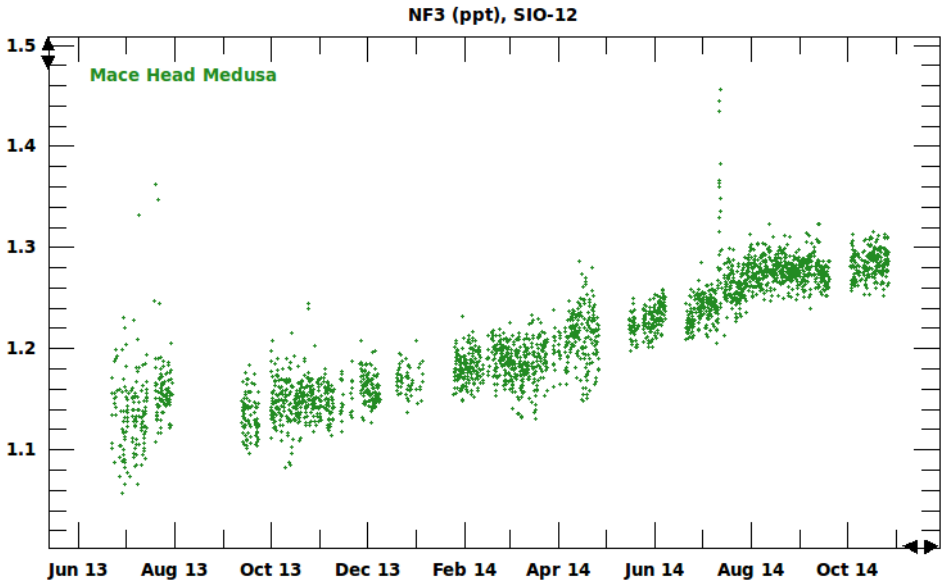

Fig 21: Full atmospheric NF_3 measurement record for Mace Head

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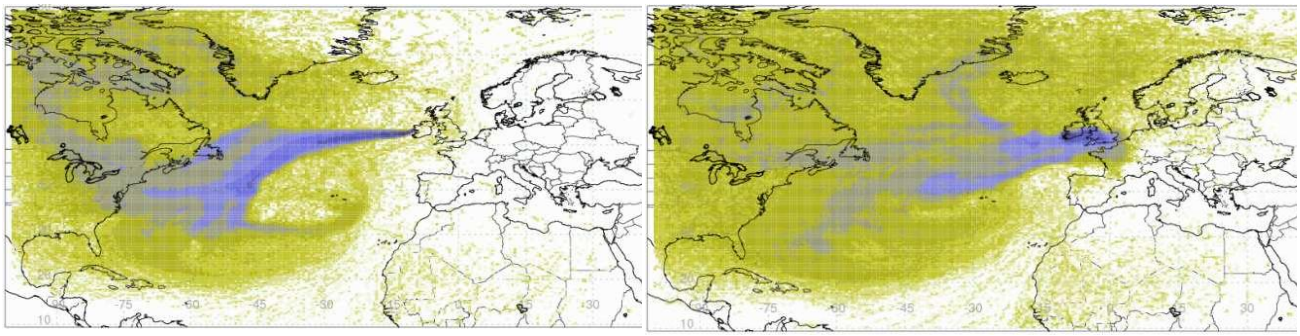

Fig 22: Air history maps representative of the air masses arriving at Mace Head for the significant pollution episode in June 2014 (left) and for a measurement within the baseline during same month (right).

7.3 Modelled emissions

We used InTEM to make the first regional emissions estimate for NF_3. As expected given the insignificant deviation of measurements from baseline, emissions from Europe were small, totalling less than 0.4 metric tons $year^{-1}$ – less than 0.04% of the global total. This inversion calculation also provided a range of possible UK emissions of between 2×10^{-5} and 4×10^{-2} metric tons $year^{-1}$.

The poor precision on our emission estimates originates from the fact emissions are small relative to their detectability at Mace Head (i.e. uncertainties in our baseline are large). Nonetheless our calculations provide a good estimate for upper emission bounds which should highlight if inventory estimates are too large.

7.4 Future work

Measurements are currently only made at Mace Head and the advantages of extending an NF_3 measurement capability to the Tacolneston site should be investigated. Given the short timeseries of measurements at Mace Head, continued measurements over the coming months and years will allow us to monitor potential changes in NF_3 usage in the UK and Europe and emission estimates will be become routine.

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8 Usefulness of $\delta^{13}C_{CH4}$ measurements in the DECC network – separating CH_4 gas leaks from coal and biogenic emissions, and their value in modelling.

Measurement of CH_4 isotopes in ambient air samples provides a powerful discriminator between source inputs. Atmospheric CH_4 comes from many sources. Broadly, biological sources are 'light' – i.e. have relatively less carbon-13 and deuterium, while combustion and fossil-fuel sources are relatively 'heavy', i.e. richer in C-13 and deuterium. The $^{13}C/^{12}C$ and D/H ratios are expressed as $\delta^{13}C$ and δD, respectively, which express parts-per-thousand deviation from a standard. UK gas leaks, for example, typically have $\delta^{13}C_{CH4}$ around -35‰, while coal mines vary and emissions from landfills and cows may be around -55‰. Thus by measuring air from a source, and subtracting the background, the CH_4 increment from that source can be determined. This can be done at any distance, depending on the emissions, from a few hundred metres downwind of a local landfill or gas leak, to the study in New Zealand air of CH_4 emissions from grassfires in SE Africa. In practice, isotopes can be measured either to low precision (about 1‰) by a variety of optical methods (e.g. Picarro CRDS), or to high precision (about 0.05‰ or better) by mass spectrometry with pre-concentration methods, and investigations are also under way to combine optical methods with pre-concentration technology. Low precision work is useful very close to known sources such as wetlands, but not when the local CH_4 has been more diluted by mixing into ambient air.

To be useful on a wider scale downwind of sources in ambient air, the measurement needs to be at *high precision* (about 20 times better than attained by portable optical methods), but although this is challenging, analysis is routine once established. Sampling is extremely easy, in Tedlar bags (plastic bags: stable for CH_4 for 6-9 months, but not for CO or CO_2), or in metal or glass flasks if multi-gas studies are needed. The 'Keeling plot' technique is widely used: if several samples have a varying mix of background air and source input, then a plot or calculation of 1/CH4 vs. $\delta^{13}C$ will identify the source isotopic ratio of the source to good precision (Fig 23). Back-trajectory analysis then confirms its location. For example, in London the bulk of the CH_4 emission source mix can be tracked as it varies diurnally and seasonally, from 'light' dominant biological emissions on warm afternoons to 'heavy' gas leaks in cold winter nights. Globally, isotopic trajectory analysis shows, for example, that Arctic emissions are mainly from wetlands and gas leaks, and that China has large coal sources in winter.

There are a handful of labs worldwide that carry out this high-precision work: in Europe, most isotopic measurements are made by Royal Holloway, University of London ($\delta^{13}C$) and Utrecht University ($\delta^{13}C$ and δD); in the USA by INSTAAR/ University of Colorado (mainly on glass flask samples); and in New Zealand by NIWA-NZ. Royal Holloway currently carries out ~300-500 analyses per year for various external partners, in addition to NERC work. Although the method is difficult to initialise and demands skilful personnel, the technique is routine once set up. It is also quick, for example, in the Elgin Gas leak in the North Sea, CH_4 isotopes in air samples taken by the FAAM plane rapidly suggested that the source of the leak was likely to be a pocket in the Cretaceous Hod Formation (i.e. limited in size), and not in the main gas reservoir. In UK terms, for the DECC network, regular (e.g. weekly or bi-weekly) bag sampling for $\delta^{13}C_{CH4}$ from tall tower stations is feasible at modest analysis cost of ~£50/sample, which would equate to approximately £6,000/year/site (including shipping costs).

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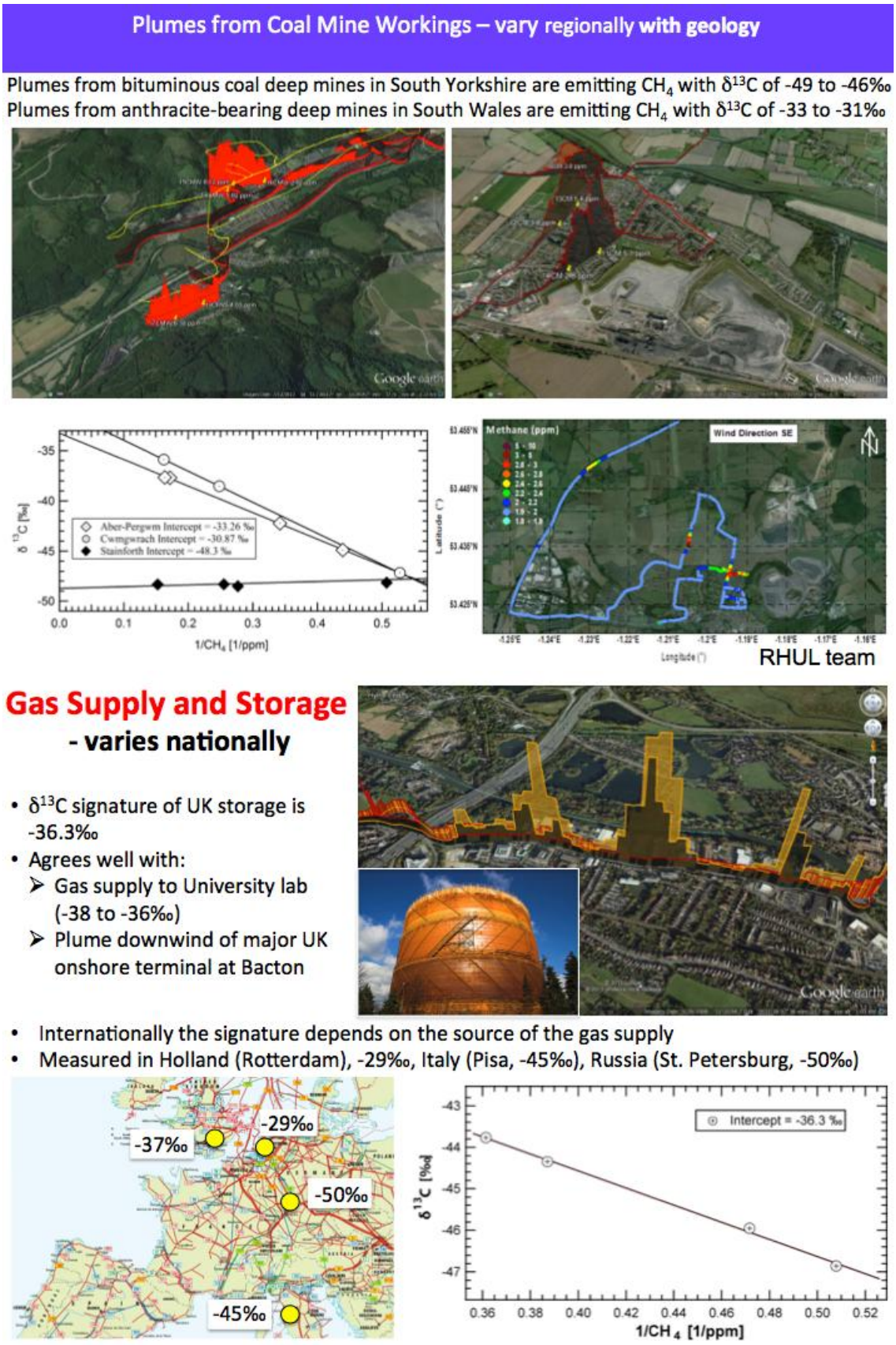

Fig 23: Examples of Keeling plot studies of emissions from gas (top) and coal mines (bottom)

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9 Separating natural from anthropogenic influences on CO_2 using isotopic CO_2 measurements in the DECC network

Isotopic measurements of CO_2 provide valuable information on the causes of observed variation in atmospheric CO_2 concentration that cannot be obtained from CO_2 measurements alone. CO_2 measured over the UK by the DECC network is sensitive to both natural exchanges of CO_2 with vegetation and soils and anthropogenic sources of CO_2 from fossil fuel combustion and other human activities.

Isotopic measurements help to distinguish natural from anthropogenic influences because they impart different isotopic signatures on CO_2 (Fig 24, left). The radiocarbon (^{14}C) content of CO_2 is an excellent tracer of combustion because fossil fuels have undergone millions of years of radioactive decay that has removed all radiocarbon atoms. Thus only stable isotopes of carbon are added by combustion and atmospheric $^{14}CO_2$ is diluted in urban areas (lower right panel of figure). Conversely, the addition of CO_2 by respiration has little impact on atmospheric $^{14}CO_2$ content (upper right panel of figure). Isotopic measurements are reported in delta notation as the per mille (‰, or 0.1 %) deviation from a standard ratio, such that an isotopic value of 0 ‰ is the same as the standard ratio and a positive value implies the sample is enriched in the heavy isotope whereas a negative value implies the sample is depleted in the heavy isotope. Standard ratios are defined by international metrology groups.

The ^{18}O content of CO_2 can also be used to differentiate combustion from respiration sources of CO_2 because combustion imparts the isotopic composition of atmospheric O_2 while respiration is generally enriched in ^{18}O. A complication of using $\delta^{18}O$ is that the composition of leaf and soil water, and thus respiration, can be highly variable (Fig 24, left). There are also challenges associated with using ^{14}C, namely the higher cost of measurement and the confounding influence of ^{14}C emissions from nuclear power plants that are particularly strong from reactor types used in the UK. The ^{13}C content of CO_2 can differentiate natural gas vs. gasoline combustion sources if the influence of combustion has been determined separately (e.g. using radiocarbon), but $\delta^{13}C$ cannot differentiate combustion from respiration since gasoline and respiration have similar $\delta^{13}C$ signatures. Observations of $\delta^{13}C$ and $\delta^{18}O$ in CO_2 are also used to study plant physiology and water cycling in forests and other terrestrial ecosystems.

Cost of stable isotope analysis of atmospheric CO_2 samples ($\delta^{13}C$ and $\delta^{18}O$) is relatively cheap while radiocarbon analysis is approximately £200-400 per sample. These costs are in addition to sampling module construction and the purchase and shipping costs of glass flasks to the analysis facility. The application of this type of isotopic measurement is currently being studied as part of the NERC funded GAUGE project.

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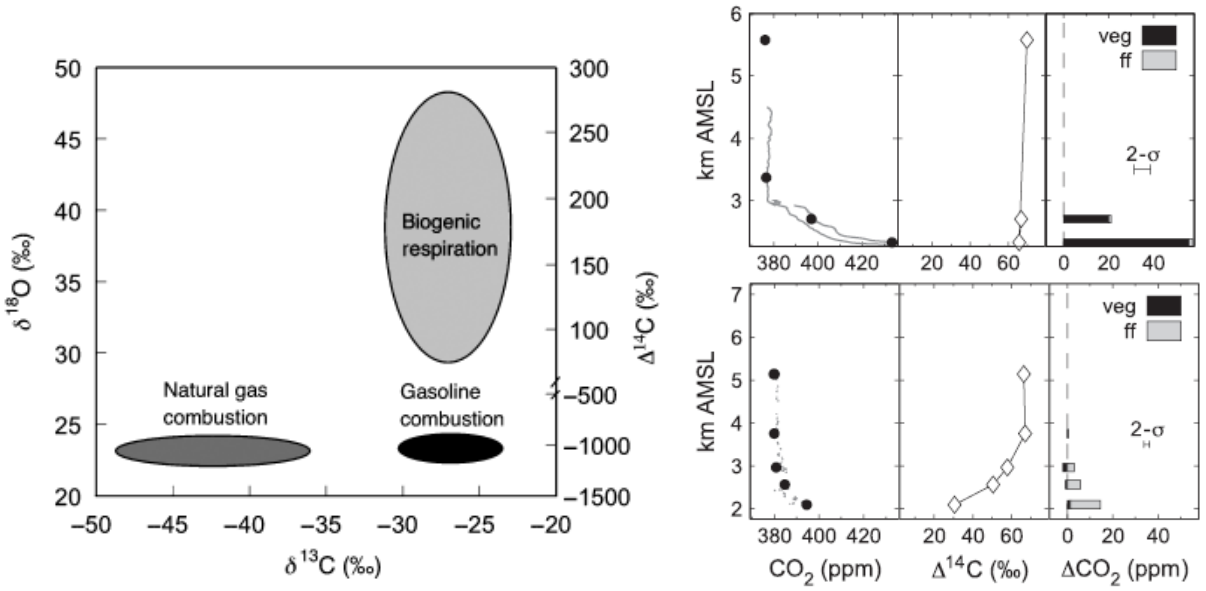

Fig 24: Left: Common ranges of the stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope composition and radiocarbon composition ($\Delta^{14}C$) of continental CO_2 sources. From Pataki et al. Global Change Biology 2006. Right: Vertical profiles of CO_2, $\Delta^{14}C$ and the components of CO_2 from fossil fuel combustion and vegetation exchange calculated from CO_2 and $\Delta^{14}C$. Measurements in a rural location showed respiration greatly enriched surface-level CO_2 (top); measurements in an urban location showed fossil fuel combustion increased CO_2 and decreased $\Delta^{14}C$ at surface levels. From aircraft data over Colorado USA, Graven et al. Tellus 2009.

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