Interpretation of long-term measurements of radiatively active trace gases and ozone depleting substances

Authors:
Alistair J. Manning, Maria Athanassiadou (Met Office),
Simon O'Doherty, Aoife Grant, Dickon Young (University of Bristol),
Richard G. Derwent (rdscientific),
Peter Simmonds

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1 Executive 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 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 is now being expanded to include three additional stations; Angus Tower near Dundee, Tacolneston near Norwich and Ridge Hill near Hereford. The latter two are under development and should be operational by early 2012. Angus Tower, run by Edinburgh University, has been making measurements since late 2005. This report will focus on the preliminary emission estimates from combining the methane (CH_4) data sets from both sites.

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 when the air is unpolluted at Mace Head, i.e. when the air has travelled across the 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 1990-2011 inclusive.

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. The estimates have been made using the NAME-inversion method. The estimates are presented as yearly averages and are compared to UNFCCC and other inventories where available.

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).

Using Mace Head observations only inversions for CH_4 have been performed over the entire dataset from 1990 onwards. This has been conducted using 2-hour air history maps and at the higher resolution of 25 km. Previously this analysis was performed at 3-hour and 40 km resolutions. The results are very consistent and show that there is significant disagreement between the inventory and the inversion estimates for the UK in the early 1990s. The agreement in the latter years, 2002 onwards, is good. This is under further investigation.

The inclusion of Angus Tower CH_4 observations into the inversion system along with the Mace Head observations is presented. The results are preliminary, but inversions have been performed using observations from Mace Head only, Angus Tower only and Mace Head and Angus Tower combined. For the UK the results are reasonably consistent. For Ireland the results are significantly different. These differences will be further explored when data from the two other stations become available and also as the Angus Tower observations are more fully examined for inter-comparability with Mace Head.

1.1 Publications

Rigby, M., Manning, A.J., Prinn, R. G. (2011) Inversion of long-lived trace gas emissions using combined Eulerian and lagrangian chemical transport models. Atmos. Chem. Phys., 11, 9887-9898.

Corazza M, P. Bergamaschi, A. T. Vermeulen, T. Aalto, L. Haszpra, F. Meinhardt, S. O'Doherty, R. Thompson, J. Moncrieff, E. Popa, M. Steinbacher, A. Jordan, E. Dlugokencky, C. Brühl, M. Krol, and F. Dentener, Inverse modelling of European N2O emissions: Assimilating observations from different networks, Atmos. Chem. Phys., 11, 2381-2398, 2011

Grant A, E. Yates, P.G. Simmonds, R.G. Derwent, A.J. Manning, D. Young, D.E. Shallcross, S. O'Doherty, A five year record of high-frequency in-situ measurements of hydrocarbons at Mace Head, Ireland, Atmos. Meas. Tech., 4, 955-964, 2011

Jones C.E, S. J. Andrews, L. J. Carpenter, C. Hogan, F. E. Hopkins, J. C. Laube, A. D. Robinson, T. G. Spain, S. D. Archer, N. R. P. Harris, P. D. Nightingale, S. J. O'Doherty, D. E. Oram, J. A. Pyle, J. H. Butler, and B. D. Hall, Results from the first national UK inter-laboratory calibration for very short-lived halocarbons, Atmos. Meas. Tech., 4, 865-874, 2011

Nevison, C.D, E. Dlugokencky, G. Dutton, J.W. Elkins, P. Fraser, B. Hall, P.B. Krummel, R.L. Langenfelds, S. O'Doherty, R.G. Prinn, L.P. Steele, R.F. Weiss, Exploring causes of interannual variability in the seasonal cycles of tropospheric nitrous oxide, Atmos. Chem. Phys., 11, 3713-3730, 2011

Skiba, U., S.K. Jones, U. Dragosits, J. Drewer, D. Fowler, R.M. Rees, V. Pappa, L. Cardenas, D. Chadwick, S. Yamulki, A. J. Manning (2011). UK emissions of the greenhouse gas nitrous oxide. *Accepted Royal Society.*

Logan, J.A., Staehelin, J., Megretskaia, A., Cammas, J. –P., Thouret, V., Claude, H., De Backer, H., Steinbacher, M., Scheel, H.E., Stubi, R., Frohlich, M., Derwent, R., 2011. Changes in ozone over Europe since 1990: analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites. *Submitted to JGR.*

Giostra, U, F. Furlani, J. Arduini, D. Cava, A.J. Manning, S. O'Doherty and M. Maione, The determination of a "European" atmospheric background mixing ratio for anthropogenic greenhouse gases: a comparison of two independent methods, submitted to Atmos., Environ.

Keller, C.A, D. Brunner, S. Henne, M.K. Vollmer, S. O'Doherty, S. Reimann, Evidence for under-reported Western European emissions of the potent greenhouse gas HFC-23, Geophys. Res. Lett., 38, L15808, doi:10.1029/2011GL047976, 2011

Simmonds, P.G., Manning, A.J., Athanassiadou, M., Scaife, A.A., Derwent, R.G., 2011. Impact of different hemispheric mixing mechanisms on nitrous oxide and chlorofluorocarbon seasonal cycles. *In preparation.*

Derwent, R.G., Simmonds, P.G., O'Doherty, Grant, A., Yates, E.L., Manning, A.J., Utembe, S.R., Jenkin, M.E., Shallcross, D.E., 2011. Seasonal cycles in short-lived hydrocarbons and halocarbons in baseline air masses arriving at Mace Head, Ireland. (*The trichloroethylene observations have been removed from the earlier drafts because of concerns about the reliability of these data. The paper is ready for submission but is awaiting discussions between Dickon Young and Peter Salameh concerning issues with the tetrachloroethylene blanks. When these are resolved, the manuscript will be submitted to Atmospheric Environment.*)

1.2 Meetings

AGAGE meeting (Bristol, May 2011) – new network and results from NitroEurope were presented.

ACCENT conference (Urbino, Italy, Sept. 2011) – CH_4 emission estimates presented.

EEA workshop on GMES (Copenhagen, Denmark, Oct 2011) – Inversion method presented.

Workshop on ozone trends (Toulouse, Spring 2011) A paper was presented on the baseline ozone trends at Mace Head up to the end of 2009. A contribution was made to a GAW report on ozone trends.

Nitrogen & Global Change, Edinburgh, April 11-14, 2011, "Inverse modelling of European N2O emissions: Assimilating Observations from different networks", poster presented.

Nitrogen & Global Change, Edinburgh, April 11-14, 2011, "Global and European scale N2O emissions estimated using a variational inversion approach", Nitrogen & Global Change, Edinburgh, April 11-14, 2011, poster presented.

Tyndall Conference, Dublin Castle, September 28-30, 2011, "Observations of Essential Climate Variables at the Mace Head Atmospheric Research Station", Tyndall Conference, Dublin Castle, September 28-30, 2011, poster presented.

2 Baseline analysis of Mace Head observations

The Mace Head observations of CH_4 have been analysed from February 1989 until August 2011 to estimate monthly and annual baseline (mid-latitude northern hemispheric) concentrations, baseline growth rates and seasonal cycles.

The raw Mace Head CH_4 data for 2008 is shown in Figure 1. By eye it is possible to discern a general baseline concentration, a dip in this value during the summer months and also periodic regional pollution events, such as the one around the 22nd January.
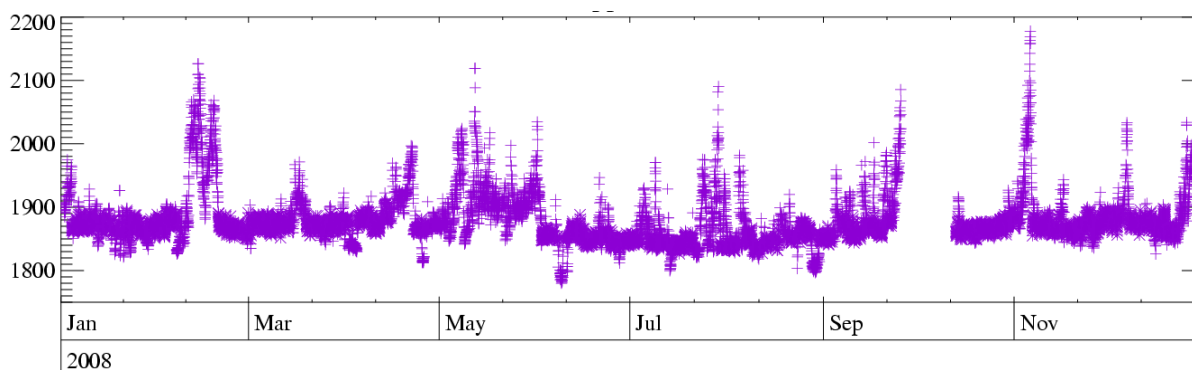

Figure 1: CH_4 observations (at 40 minute intervals) at Mace Head for 2008.

NAME, the Met Office Lagrangian atmospheric dispersion model, has been used to understand the recent (30 day) history of air before it reaches Mace Head for each 2-hour period from Feb. 1989 onwards. An example of a 2-hour air history map is shown in Figure 2.
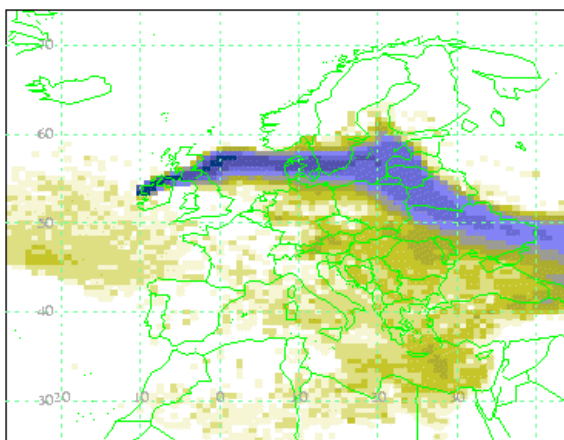

Figure 2: Example 2-hour NAME air history map

Using the NAME air history maps each 2-hour period has been categorised as either predominately baseline (from the mid to north Atlantic), polluted (from Europe), local (stagnant air over Mace Head), from southern latitudes or from a combination of these (Figure 3).
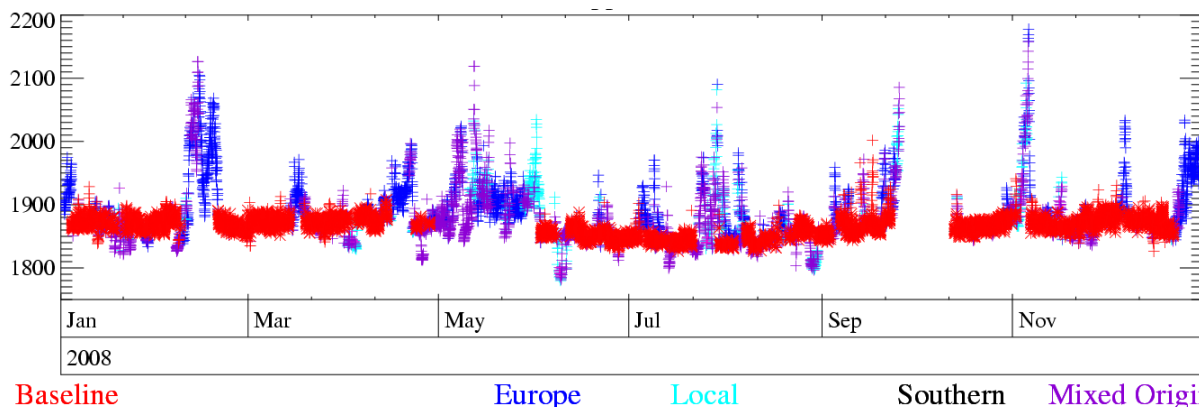
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Figure 3: CH_4 Mace Head observations categorised using the NAME air history maps. Those observations shown in red have been classified as baseline.

All non-baseline observations are temporarily removed from the dataset (Figure 4) in order for the mid-latitude northern hemisphere baseline concentration to be estimated.
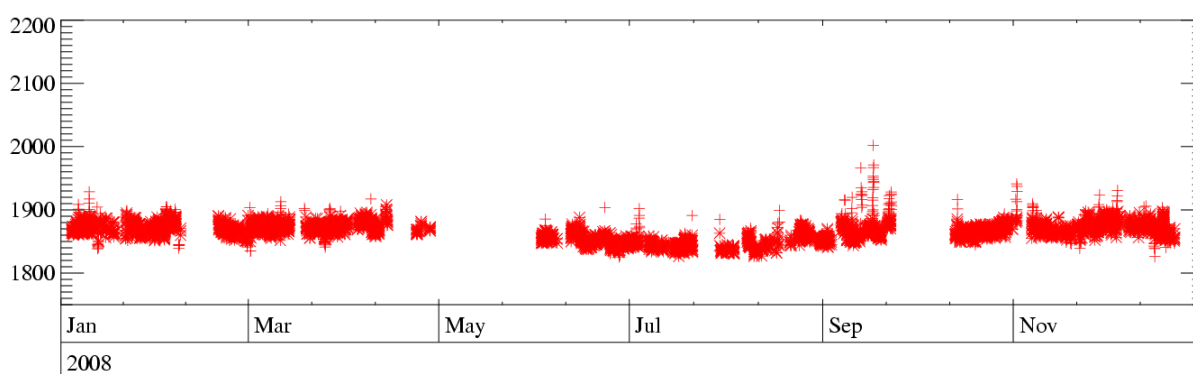

Figure 4: CH_4 observations classified as baseline.

The baseline observations are then filtered using a moving statistical algorithm to identify observations that have been classified as baseline but are more than 1.5 standard deviations (std) away from the surrounding baseline observations (Figure 5). Such observations are not thought to be baseline and may be due to the impact of shipping, the populated eastern seaboard of the North America or poorly resolved meteorology or dispersion.
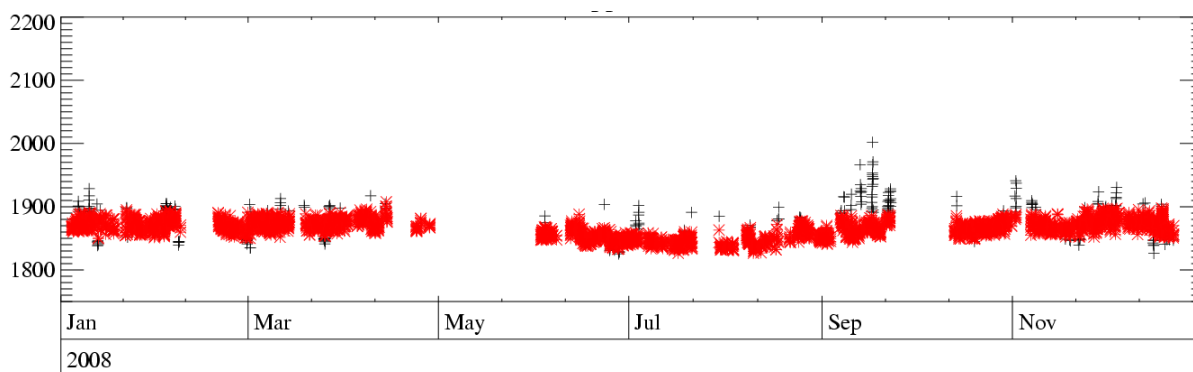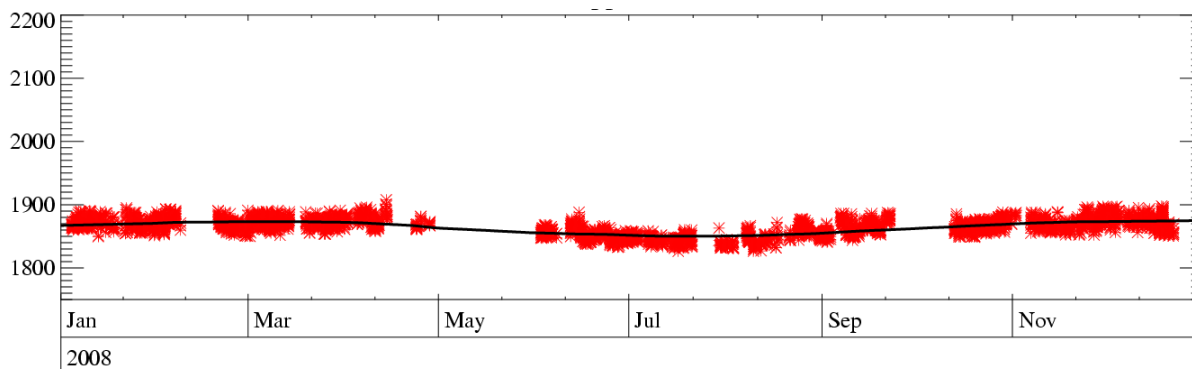

Baseline   Exc. Baseline

Figure 5: CH_4 observations classified as baseline (red) and those that have been identified by a statistical filter as being non-baseline (black).

A cubic line is then fitted to the baseline observations in a moving time window to estimate the baseline concentration for all time periods including those during 'pollution' events (Figure 6).

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Figure 6: CH$_4$ baseline observations (red) with a best-fit cubic fitted to the data (black).

The final baseline observations still have a degree of scatter as shown (on a greatly expanded y-scale) in Figure 7. This uncertainty in the baseline is captured by calculating the 1-std over the whole time-series of the deviation of the baseline observations from the estimated fitted baseline curve. The baseline uncertainty will be used in the emission estimate (inversion) calculation as the 'noise' in the observations.
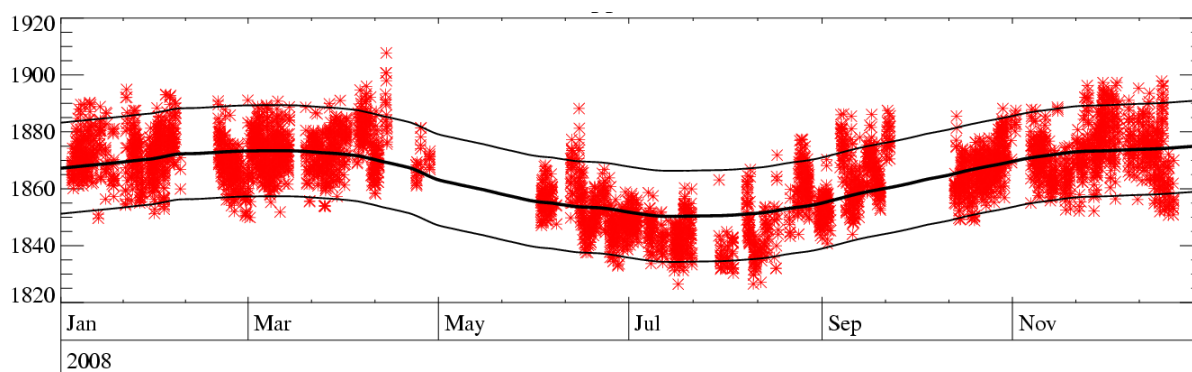
Figure 7: CH$_4$ baseline observations at Mace Head (red) and the estimated mid-latitude northern hemisphere concentration with 1-std uncertainty.

Figures 8 and 9 show the monthly and annual baseline concentrations, the annual baseline growth rates and the average seasonal cycles of CH$_4$ and nitrous oxide (N$_2$O) respectively. The atmospheric concentrations of both gases have risen significantly over the 22 year period. The growth shows significant year-to-year variability. For CH$_4$, this is largely the impact of changes to its natural sources such as the massive Indonesian fires in the late 1990s or increased wetland emissions in the Arctic and tropics (2007-08). For N$_2$O, this is the impact of the annual strength of the stratospheric – tropospheric exchange (STE), the stratosphere being its dominant sink. Both have definite seasonal cycles with maxima in the early spring and minima in summer. For CH$_4$, this is due to enhanced OH in summer, its major sink. For N$_2$O, the STE is at a maxima in the winter months, the impact of which takes approximately six months to reach the surface.
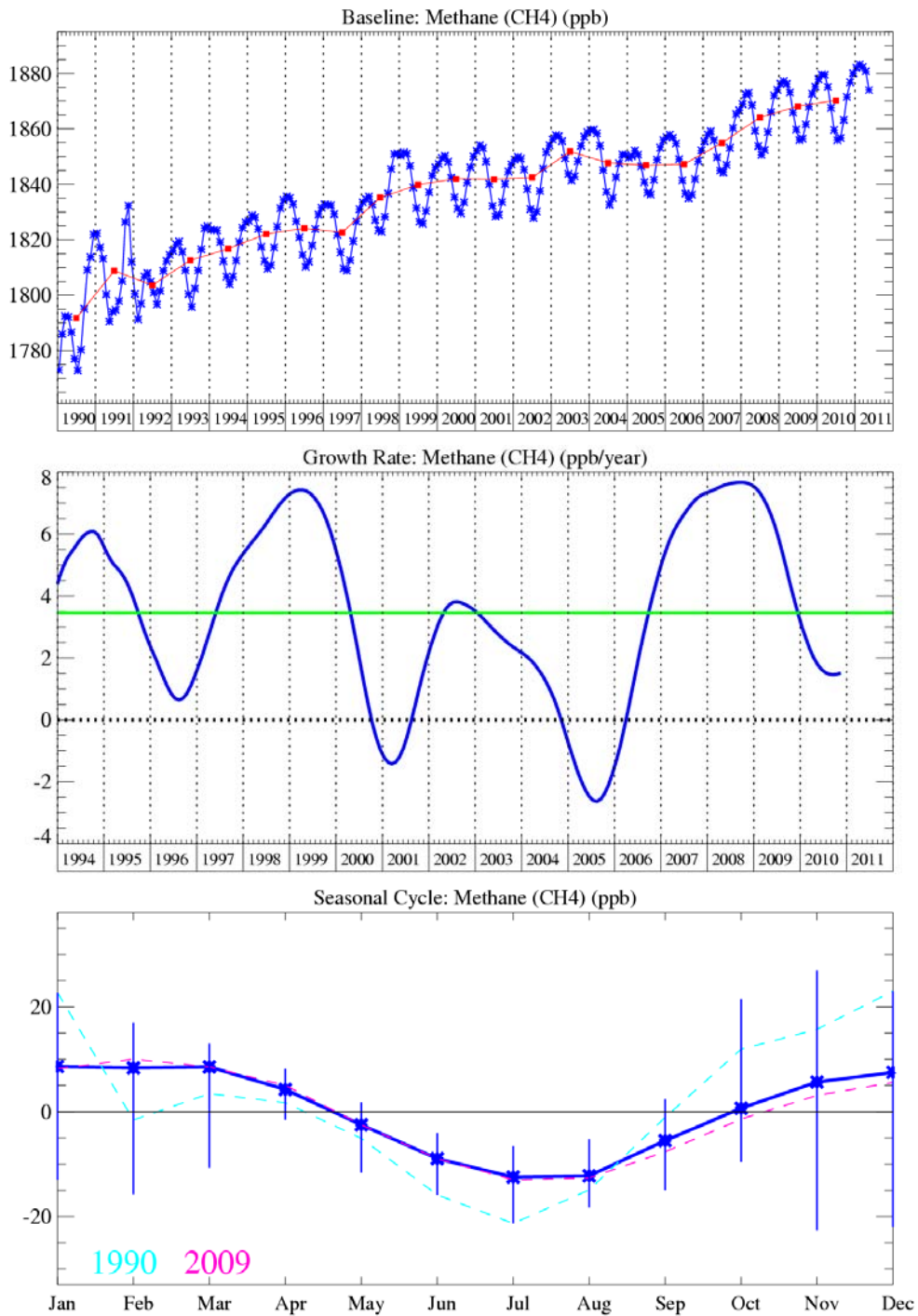
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Figure 8: CH$_4$ monthly (blue) and annual (red) baseline concentrations (top plot). Annual (blue) and overall average growth rate (green) (middle plot). Seasonal cycle (de-trended) with year to year variability (lower plot).

Figure 9: CH$_4$ monthly (blue) and annual (red) baseline concentrations (top plot). Annual (blue) and overall average growth rate (green) (middle plot). Seasonal cycle (de-trended) with year to year variability (lower plot).
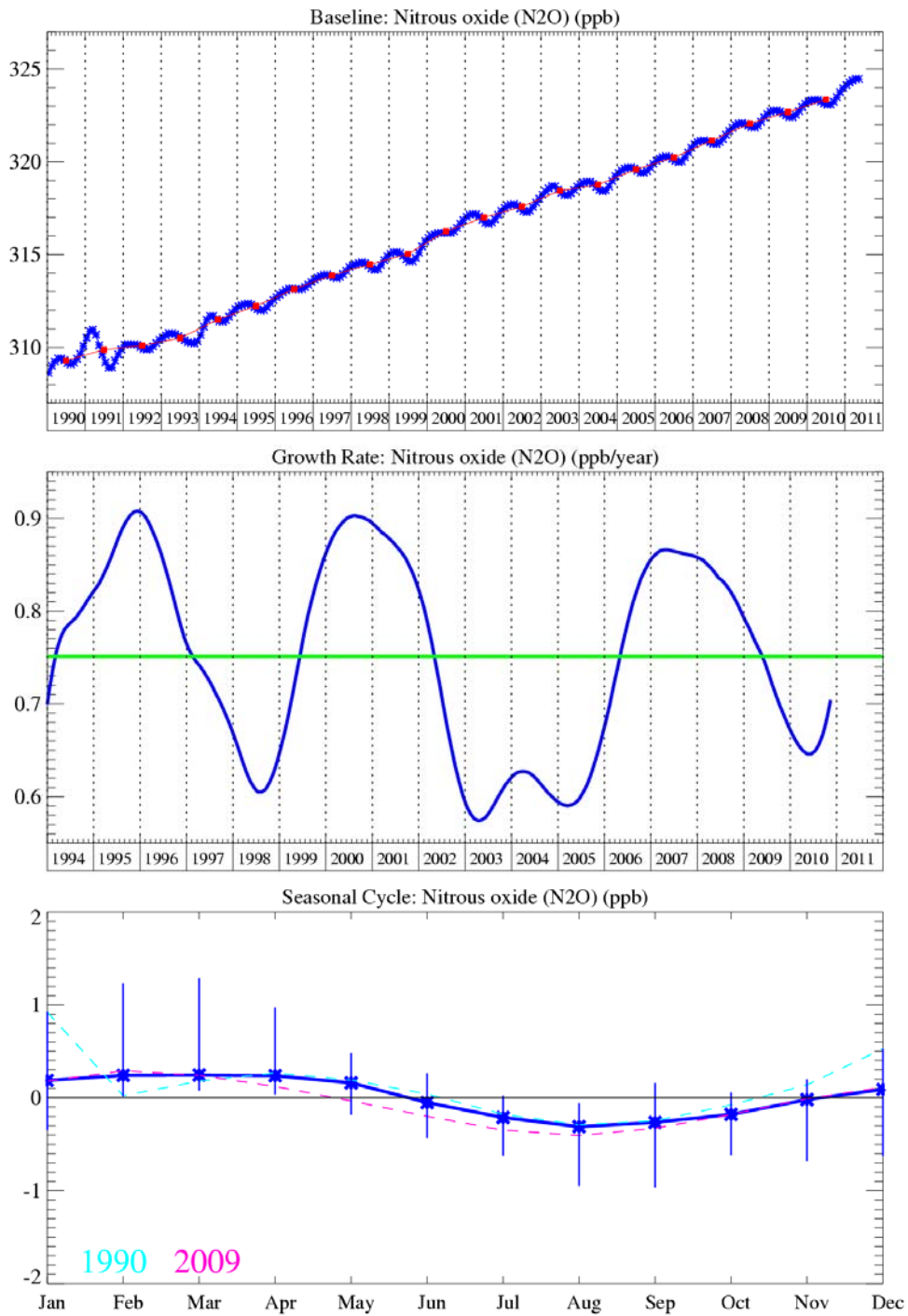
3 Regional Emission Estimates

By removing the time-varying baseline concentrations from the raw measurement data, a time-series of excursions from the baseline for each observed gas has been generated from 1989 onwards for CH_4 and N_2O. The observed deviations from baseline are averaged over each two-hour period. These perturbations are driven by emissions on regional scales that have yet to be fully mixed on the hemisphere scale. Henceforth these above-baseline measurements are referred to as simply the observations. The baseline concentration time-series estimated using the Mace Head observations is representative of the mid-latitude northern hemisphere. As such it is appropriate to use this baseline both at Mace Head and at Angus Tower. It is vital therefore that the observations at both stations are recorded on the same calibration scale and are directly inter-comparable. If this is not true then a bias will be manifest itself in the inversion results.

3.1 Inversion methodology

The observation time-series, together with the NAME model output predicting the recent history of the air, was used to estimate the emission distribution of each gas over NW Europe (NWEU). The iterative best-fit technique, simulated annealing (Press *et al* 1992), was used to derive these regional emission estimates based on a statistical skill score (cost function) comparing the observed and modelled time-series at Mace Head. The technique starts from a set of random emission maps, it then searches for the emission map that leads to a modelled time series at Mace Head that most accurately mimics the observations.

The aim of the inversion method is to estimate the spatial distribution of emissions across a defined geographical area. In the equation to solve ($D\ \underline{e} = \underline{o}$), the set of observations ($\underline{o}$) and the dilution matrix (D) as estimated using the NAME model are known. The observations are in volume mixing ratios. The dilution matrix has units (s/m) and is calculated from the time-integrated air concentrations produced by the NAME model. The dilution matrix has t rows equal to the number of 2-hour periods considered and has n columns equal to the number of grid points in the defined geographical domain. This matrix dilutes a continuous emission of 1 g/m^2s over a given grid to an air concentration [g/m^3] at the receptor during a 2-hour period. The observations are converted from volume mixing ratio [ppb] to air concentration [g/m^3] using the modelled temperature and pressure at the observation point.

The inversion domain is chosen to be a smaller subset of the full domain used for the air history maps. It covers XX 30^oW – 42^oE longitude and XX 29.3^oN – 77.3^oN latitude and is shown as the black box in Figure 10. The smaller domain covers all of Europe and extends a reasonable distance into the Atlantic. The inversion domain needs to be smaller to ensure re-circulating air masses are fully represented but also because emission sources very distant from where the observations are made have little discernible impact on the concentration at the station, i.e. the signal would be too weak to be seen. The inversion method assumes baseline concentration air enters the inversion domain regardless of direction. For the eastern and southern edges in particular this will be incorrect. Emissions in Russia and around the Black Sea would be expected to elevate the atmospheric concentrations along the eastern edge, and due to the latitudinal gradient it would be reasonable to assume below mid-latitudinal baseline concentration air enters from the south. This issue is overcome in the inversion by solving for but not analysing the estimated emissions in any grid on the edge of the inversion domain. It is assumed that the error of above or below baseline concentration air entering the domain will be absorbed into the solutions in these edge grids.
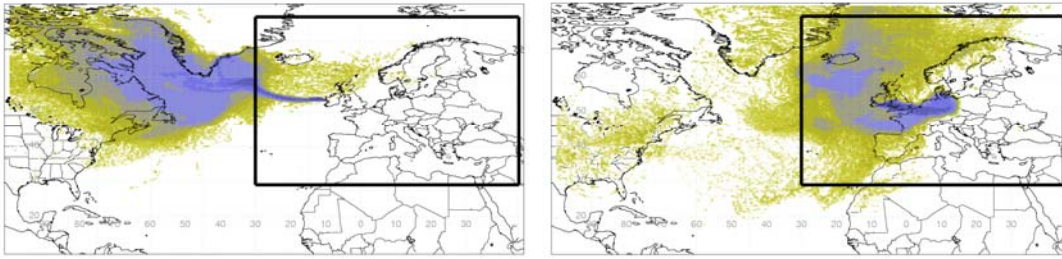
(a)   (b)

Figure 10: Examples of 2-hour air history maps derived from NAME (a) baseline period (b) regionally polluted period. The air-history maps describe which surface areas in the previous 12-days impact the observation point within a particular 2-hour period.

In order for the best-fit algorithm to provide robust solutions for every area within the domain, each region needs to significantly contribute to the air concentration at the observation stations on a reasonable number of time periods. If the signal from an area is only rarely or poorly seen at any observation station, then its impact on the cost function is minimal and the inversion method has little skill at determining its true emission.

The contribution that different grid boxes make to the air concentration observed varies from grid to grid. Grid boxes that are distant from the observation site contribute little to the observation, whereas those that are close have a large impact. In order to balance the contribution from different grid boxes, those that are more distant are grouped together into increasingly larger blocks. The grouping varies for each time period considered and between the different gases due to varying meteorology and the impact of missing observations respectively. The underlying horizontal grid resolution is 25 km ($= x$) and is equal to the resolution of the NAME output. The grouping creates blocks that have a resolution of x, $2x$, $4x$, $8x$, $16x$ and $32x$.

When observations from only one observation station are used in the inversion, the grid resolution is naturally coarser as there are fewer instances when each grid will contribute to the observations. Figure 11 shows an example inversion grid when only Mace Head data are used, Figure 12 when only Angus Tower data are used, and finally Figure 13 when the observations from both stations are used. By using both stations the resolution of the grid over Ireland, Northern Ireland, northern England and Scotland is much improved.
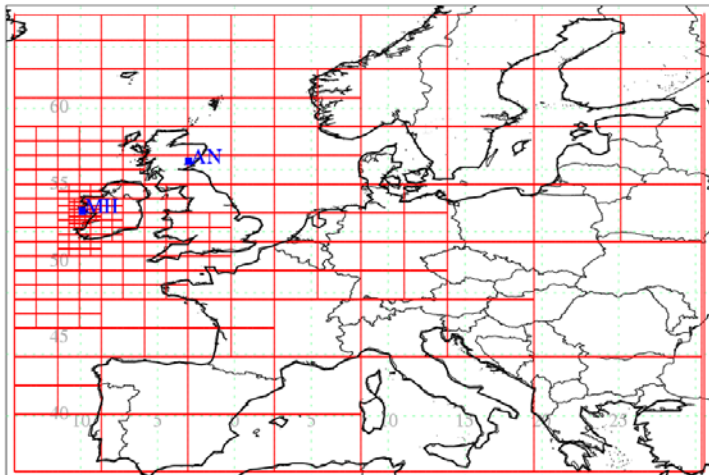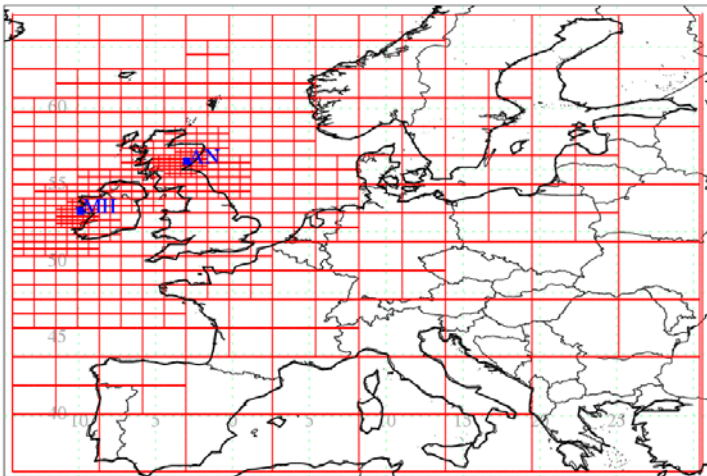

Max Grid Size = 32   Num Grids = 277

Figure 11: 3-year inversion grid when only Mace Head observations are used. The total number of grids is 277 in this example.
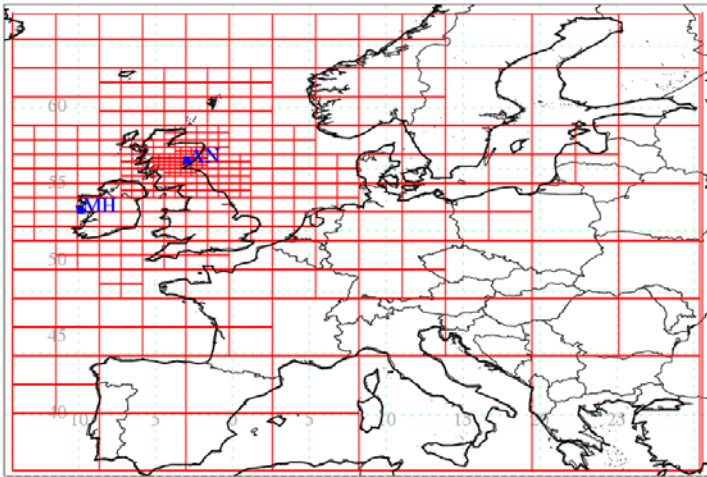
Max Grid Size = 32   Num Grids = 409

Figure 12: 3-year inversion grid when only Angus Tower observations are used. The total number of grids is 409 in this example.

Max Grid Size = 32   Num Grids = 598

Figure 13: 3-year inversion grid when the observations from both Mace Head and Angus Tower are used. The total number of grids is 598 in this example.

The inversion process works by iteratively choosing different emissions, varying the emission magnitudes and distributions, with the aim of minimising the mismatch between the observations and the modelled concentrations. No *a priori* conditions are set. The relative skill of a derived emission map is tested by comparing the modelled and observed time-series by using a cost function that combines four different statistics.

Cost function: $\left[5(1-r)\right]+\left[0.5\ NMSE\right]+\left[4(1-fac2)\right]+\left[20(1-facNoise)\right]$

where,
r = Pearson correlation coefficient

NMSE = Normalised Mean Square Error: $\left(\dfrac{Mean\ Square\ Error}{AvgObs\ x\ AvgModel}\right)$

fac2 = Fraction within a factor of 2 of observations

facNoise = Fraction of model values within *Noise* of the observations

Noise = std of baseline observations about the defined smoothed baseline value. Note observations below the *Noise* level are considered to have a magnitude equal to the *Noise* level with respect to the *fac2* calculation.

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The iteration process is repeated until the future potential improvement in skill in the emission map is estimated to be negligible.

To simulate uncertainties in the meteorology, dispersion and observations a time-series of random noise is applied to the observations. The random element is multiplicative and taken from a log-normal distribution with mean 1 and variance one fifth of the *Noise*. Any observations that are negative are considered to be zero.

Any periods that were classed as baseline but were removed by the statistical filtering are removed from the analysis as these are considered to be unrepresentative of air from that region. Times when the air is classed as 'local' are likewise removed from the analysis. The local times represent periods when the emissions from the local area (75 km x 75 km area centred on the observation station) would have a dominate effect on the observations. These are typically characterised by low wind speeds, low boundary layer heights and thus poor dispersion conditions. During such times the meteorological models used, with horizontal resolutions of between 25 and 80 km, are poor at correctly resolving the local flows as they are dominated by sub-grid scale processes, e.g. land-sea breezes. For reference, approximately 86% (87%) of the CH_4 (N_2O) Mace Head observations were retained for analysis.

For each time period solved for, the whole inversion process is repeated multiple times to give an indication of the potential uncertainty in the emission solution, each time with a different random starting point and a different time-series of random noise. Solutions are calculated for three-year periods covering the period when observations are available. After solutions have been estimated for a particular three-year period, the period is moved on by one month and the process repeated, e.g. Jan'95 – Dec'97, Feb'95 – Jan '98, etc.

An annual estimate of emission is calculated by averaging all of the solutions that contain a complete calendar year within the solved-for time period. The range for each year for each geographical region is calculated from the same sample of solutions and is taken as the 5th and 95th percentile solutions.

3.2 Impact of including Angus Tower CH4 data in the inversion system

Three different datasets were used in order to understand the impact of adding the CH4 observations:
- Only using Mace Head observations
- Only using Angus Tower observations
- Combining both data sets into a single inversion.

3.2.1 Mace Head only inversion

Figure 11 shows the grid resolution achievable for a 3-year inversion when only Mace Head data is used. 277 grids are resolved with the greatest resolution over Ireland.

Figure 14 is an example of the observed and modelled time series of air concentration for CH_4 for the first three months of 2008 at Mace Head. The magnitudes and patterns are similar and demonstrate that the inversion process is able to derive an emission map that produces a good match to the Mace Head observations.
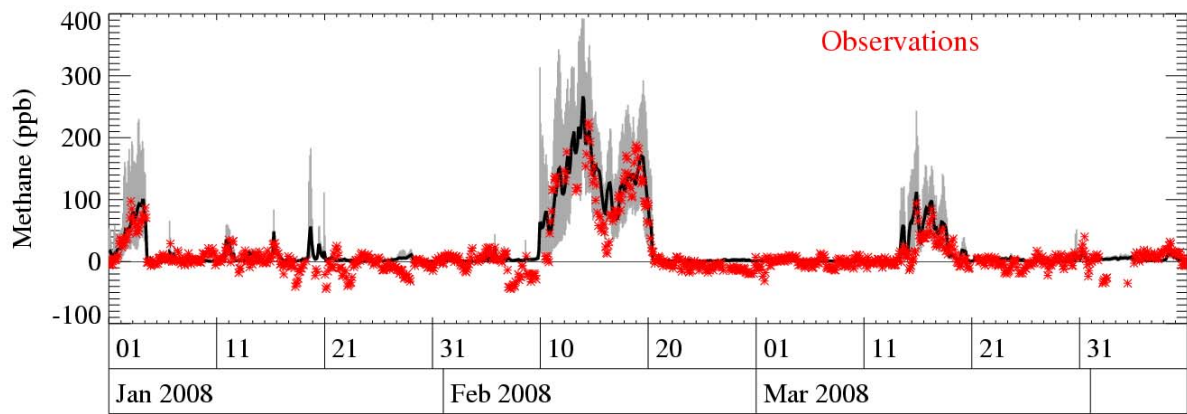
Figure 14: Time series of observed (deviation from baseline) and best-fit modelled CH_4 concentrations at Mace Head for the first three months of 2008 (solid line = median NAME-inversion solution, red crosses = Mace Head observations, grey shaded area = the range of individual solutions estimated by the inversion system).

Emission totals from specific geographical areas are calculated by summing the emissions from each 25 km grid box in that region (Fig. 15).
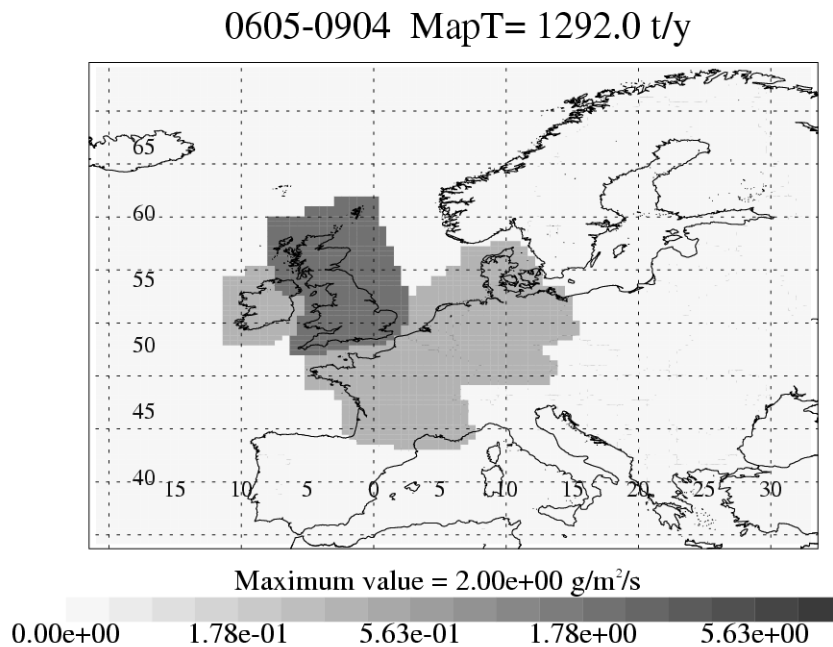

Figure 15: Shown are the geographical areas, UK and NWEU (north west Europe comprising of Ireland, UK, France, Germany, Belgium, Luxembourg, the Netherlands, Denmark) used to define regional totals.

The tabulated results (Mt/yr) for Ireland, the UK, Ire+UK and NWEU are shown in Table 1. The UK and NWEU estimates are also shown in Figures 16 and 17 respectively in comparison with the UNFCCC reported inventory. For the UK the agreement since 2002 between the inventory and the inversion estimates is good. However there is significant disagreement between the inventory estimates and the inversion estimates in the 1990s especially in the early years. Both methods have significant uncertainty. Also the inventory reports only the anthropogenic component whereas the inversion estimates show the combined impact of the biogenic and anthropogenic emissions. The latter would imply that the inversion estimates should be, if anything, larger than the inventory estimates, however the natural biogenic emissions for CH_4 in NWEU are thought to be small. The reasons for this discrepancy are currently under investigation.

Year	IRE	(5th-95th)	UK	(5th-95th)	UK+IRE	(5th-95th)	NWEU	(5th-95th)
1990	0.87	(0.54- 1.6)	2.6	(1.3- 4.4)	3.5	(2.1- 5.3)	10.9	(7.- 16.)
1991	0.86	(0.54- 1.5)	2.6	(1.3- 4.4)	3.5	(2.1- 5.2)	13.2	(8.- 19.)
1992	0.93	(0.55- 1.5)	2.7	(1.2- 4.4)	3.6	(2.1- 5.3)	14.9	(10.- 19.)
1993	1.04	(0.62- 1.6)	2.4	(1.1- 4.0)	3.5	(2.1- 5.0)	14.9	(10.- 20.)
1994	1.02	(0.60- 1.5)	2.1	(1.0- 3.4)	3.1	(1.9- 4.5)	13.3	(10.- 19.)
1995	0.9	(0.58- 1.4)	2.2	(1.1- 3.4)	3.1	(2.0- 4.4)	11.7	(9.- 15.)
1996	0.9	(0.59- 1.3)	2.3	(1.3- 3.6)	3.3	(2.2- 4.4)	10.4	(8.- 14.)
1997	1.03	(0.66- 1.7)	2.4	(1.3- 3.4)	3.5	(2.3- 4.6)	9.5	(7.- 13.)
1998	1.1	(0.70- 1.7)	2.4	(1.2- 3.7)	3.7	(2.3- 4.9)	10.1	(7.- 15.)
1999	1.04	(0.70- 1.5)	2.6	(1.3- 4.0)	3.6	(2.4- 5.1)	11.9	(8.- 17.)
2000	1.04	(0.70- 1.5)	2.6	(1.3- 4.0)	3.7	(2.4- 5.1)	11.9	(8.- 16.)
2001	1.04	(0.73- 1.5)	2.4	(1.3- 3.7)	3.5	(2.3- 4.7)	11.4	(8.- 15.)
2002	1.15	(0.80- 1.6)	2.2	(1.2- 3.4)	3.4	(2.3- 4.5)	11.9	(8.- 16.)
2003	1.25	(0.89- 1.7)	2.2	(1.2- 3.5)	3.4	(2.5- 4.8)	12.7	(8.- 17.)
2004	1.25	(0.89- 1.7)	2.4	(1.3- 3.9)	3.7	(2.6- 5.0)	12.6	(8.- 17.)
2005	1.25	(0.88- 1.7)	2.6	(1.5- 4.0)	3.9	(2.9- 5.2)	11.1	(7.- 16.)
2006	1.33	(0.93- 1.8)	2.5	(1.4- 3.9)	3.8	(2.7- 5.3)	11.1	(7.- 16.)
2007	1.39	(0.90- 1.9)	2.3	(1.3- 3.7)	3.7	(2.7- 5.1)	12.3	(9.- 17.)
2008	1.3	(0.80- 1.9)	2.2	(1.2- 3.5)	3.5	(2.4- 4.6)	12.7	(9.- 17.)
2009	1.19	(0.74- 1.8)	2.1	(1.1- 3.5)	3.3	(2.2- 4.6)	11.3	(6.- 16.)
2010	1.05	(0.70- 1.6)	2.2	(1.1- 3.5)	3.3	(2.2- 4.6)	8.9	(5.- 13.)

Table 1: Inversion emission estimates (Mt/yr) using Mace Head only observations.
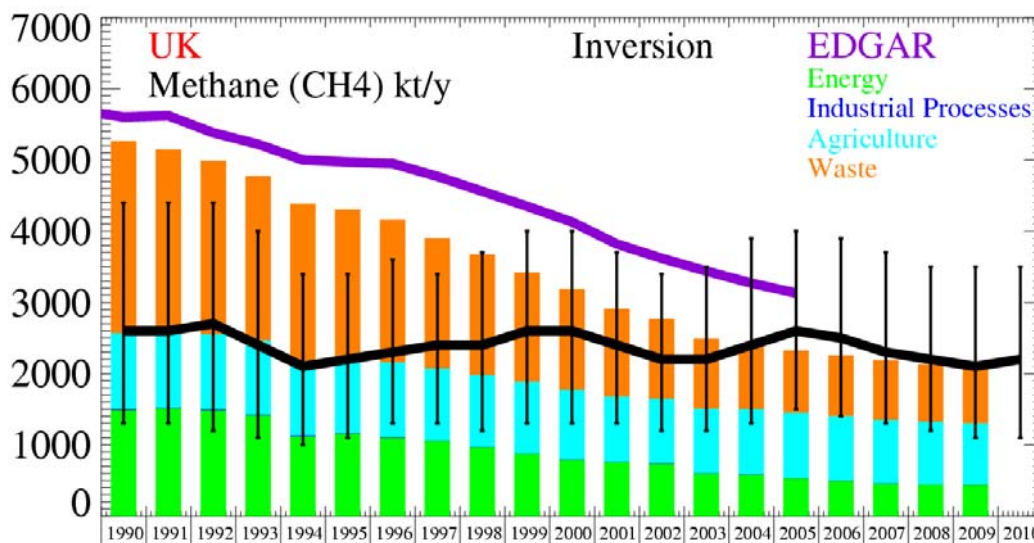

Figure 16: UK emission estimates comparing UNFCCC inventory and inversion estimates. The inversion results used only Mace Head observations. The base inversion period was 3-years with a base grid of 25 km and 2-hourly resolution.
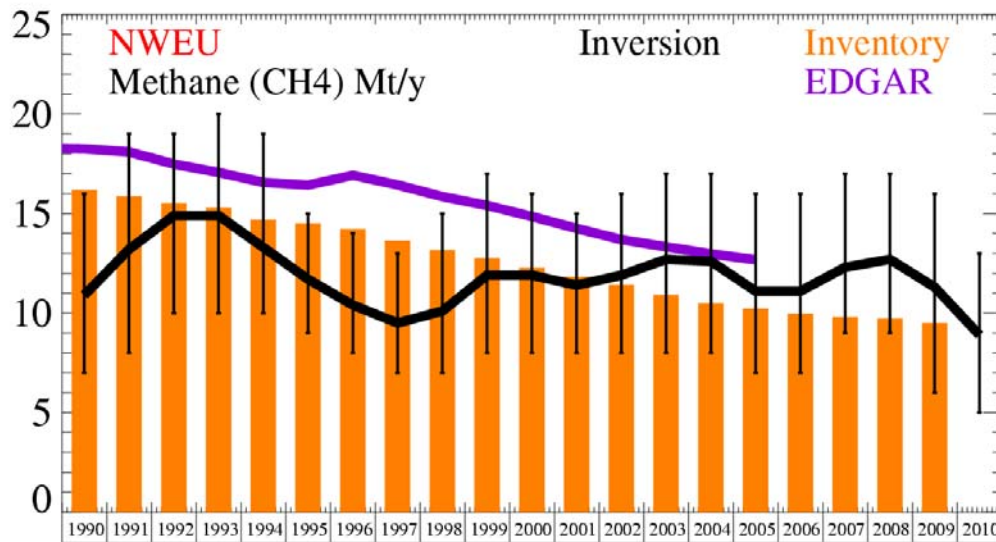
Figure 17: NWEU emission estimates comparing UNFCCC inventory and inversion estimates. The inversion results used only Mace Head observations. The base inversion period was 3-years with a base grid of 25 km and 2-hourly resolution.

3.2.2 Angus Tower only inversion

The experiment described above was repeated but this time only Angus Tower CH_4 observations were used. Figure 18 shows the modelled time series at Mace Head but using the only the Angus Tower data, the time period covered in the example is identical to that shown in Figure 14. The Angus Tower only inversion estimated emissions do not capture, in magnitude, the significant pollution peak seen at Mace Head between the 10th and 20th of February 2008. The emission estimates for the different geographical regions are given in Table 2.
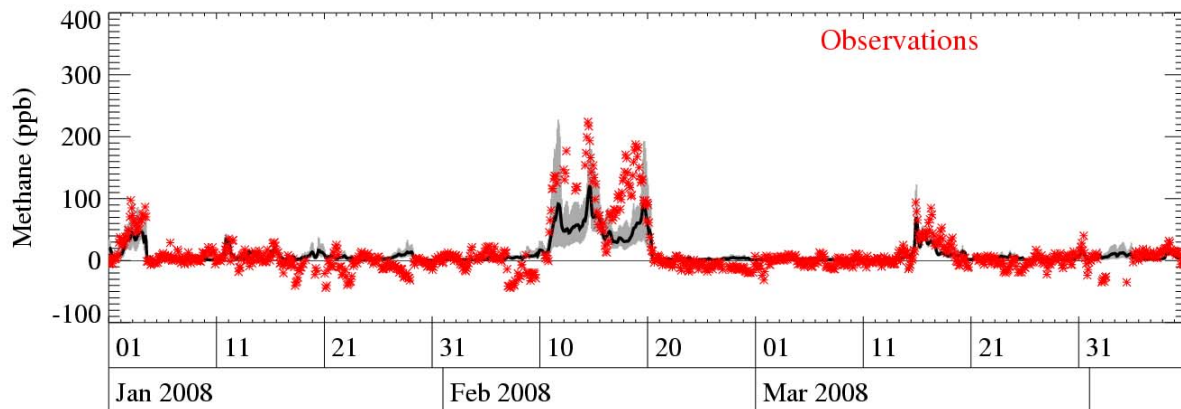

Figure 18: Time series of observed (deviation from baseline) and best-fit modelled CH_4 concentrations at Mace Head for the first three months of 2008. The inversion only uses Angus Tower data. (solid line = median NAME-inversion solution, red crosses = Mace Head observations, grey shaded area = the range of individual solutions estimated by the inversion system).

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Year	IRE	(5th-95th)	UK	(5th-95th)	UK+IRE	(5th-95th)	NWEU	(5th-95th)
2006	0.2	(0.19- 0.2)	1.91	(1.8- 2.1)	2.1	(2.0- 2.3)	7.4	(6.6- 8.)
2007	0.15	(0.12- 0.2)	1.84	(1.4- 2.5)	1.96	(1.6- 2.7)	8.2	(6.4- 12.)
2008	0.15	(0.12- 0.2)	1.94	(1.3- 2.8)	2.1	(1.5- 2.9)	8.8	(6.6- 13.)
2009	0.16	(0.11- 0.2)	1.72	(1.2- 2.5)	1.9	(1.4- 2.7)	8.8	(6.3- 13.)
2010	0.16	(0.12- 0.2)	1.42	(1.2- 1.8)	1.56	(1.4- 2.1)	8.2	(5.0- 12.)

Table 2: Emission estimates (Mt/yr) using Angus Tower only observations.

3.2.3 Combined Mace Head and Angus Tower inversion

The experiment described above was repeated but this time combining the CH_4 observations from Mace Head and Angus Tower. Figure 19 shows the modelled time series at Mace Head using the combined observation dataset, the time period covered in the example is identical to that shown in Figure 14. The combined inversion estimated emissions capture better the significant pollution peak seen at Mace Head between the 10th and 20th of February 2008 compared to the Angus Tower only inversion but not as well as the Mace Head only inversion. The emission estimates for the different geographical regions are given in Table 3.
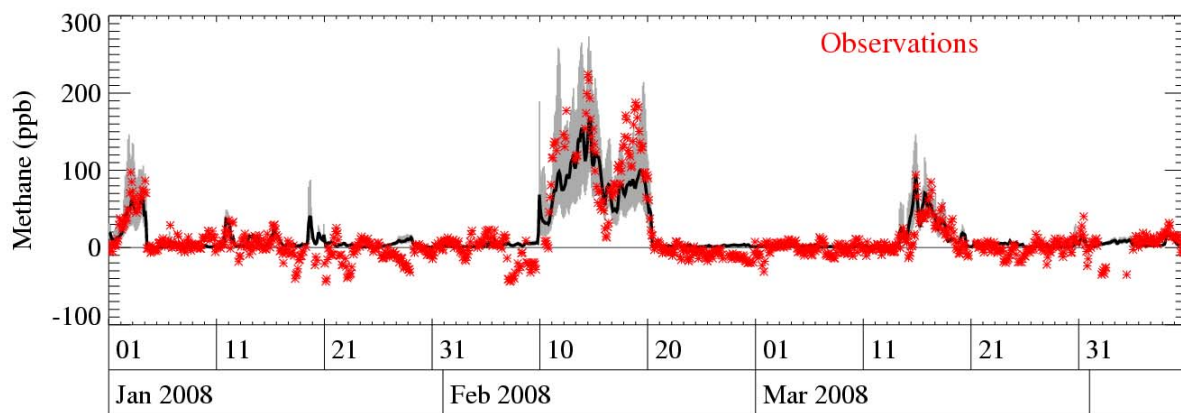

Figure 19: Time series of observed (deviation from baseline) and best-fit modelled CH_4 concentrations at Mace Head for the first three months of 2008. The inversion uses the combined Mace Head and Angus Tower data. (solid line = median NAME-inversion solution, red crosses = Mace Head observations, grey shaded area = the range of individual solutions estimated by the inversion system).

Year	IRE	(5th-95th)	UK	(5th-95th)	UK+IRE	(5th-95th)	NWEU	(5th-95th)
2006	0.44	(0.36- 0.5)	2.4	(1.9- 3.0)	2.9	(2.4- 3.4)	9.2	(7.0- 11.)
2007	0.47	(0.36- 0.6)	2.5	(1.8- 3.2)	2.9	(2.3- 3.6)	10	(7.5- 13.)
2008	0.46	(0.36- 0.6)	2.5	(1.7- 3.3)	3	(2.3- 3.7)	9.6	(7.5- 13.)
2009	0.46	(0.38- 0.6)	2.3	(1.5- 3.3)	2.8	(2.1- 3.8)	8.9	(7.3- 12.)
2010	0.45	(0.39- 0.5)	1.88	(1.4- 2.5)	2.3	(1.9- 2.9)	8.3	(6.2- 10.)

Table 3: Emission estimates (Mt/yr) using combined Mace Head and Angus Tower observations.

3.2.4 Discussion

The results presented above are preliminary. Also the data calibration of the Angus Tower data has yet to be directly inter-compared with the Mace Head observations. Therefore these results need to be considered carefully.

Looking at the tables above and comparing the UK inversion estimates for CH_4 the results are broadly consistent. This is shown more clearly in Figure 20. The uncertainty bars of the annual emission estimates using the different setups generally overlap. However the results for Ireland are significantly different (Figure 21). If the average inversion emission maps for 2008 for CH_4 using the three different datasets are considered, Figures 22 – 24, it is easy to see the reason for the difference in the estimated Irish emissions.

Clearly there is a significant issue with regards to the distribution and magnitude of emissions in Ireland between the different observational datasets. This will require further investigation. The observation systems currently under construction at Ridge Hill near Hereford and Tacolneston near Norwich will add considerably to our understanding of the Irish emissions. Further updates to the Angus Tower observational record in term of calibration and inter-comparability may also significantly alter the results.
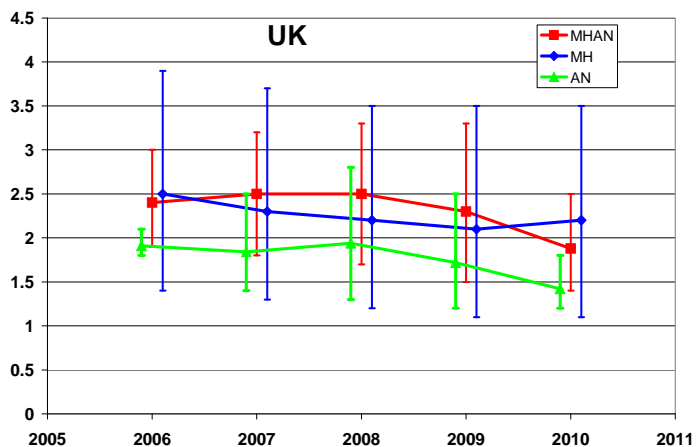

Figure 20: Comparing the inversion estimates (Mt/yr) for CH_4 for the UK using the three different observation datasets.
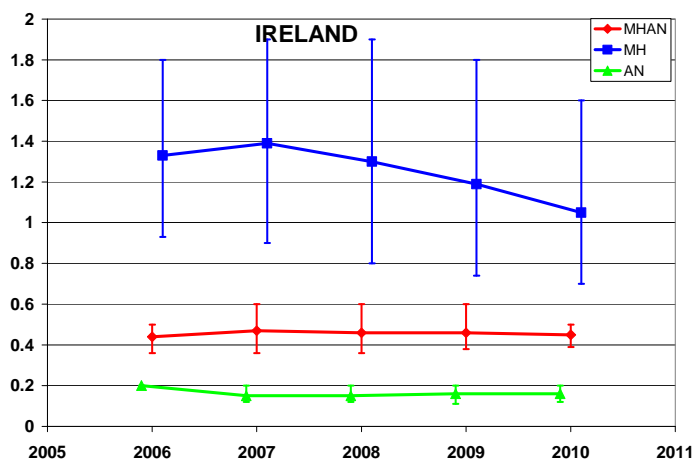

Figure 21: Comparing the inversion estimates (Mt/yr) for CH_4 for Ireland using the three different observation datasets.
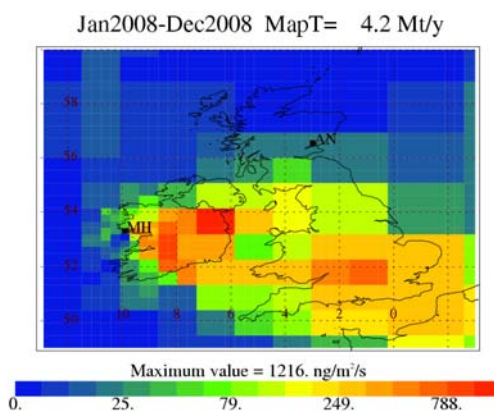

Figure 22: Average inversion emission map for CH_4 for 2008 using Mace Head only observations.
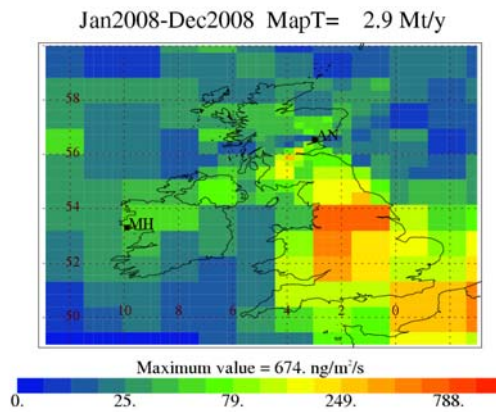
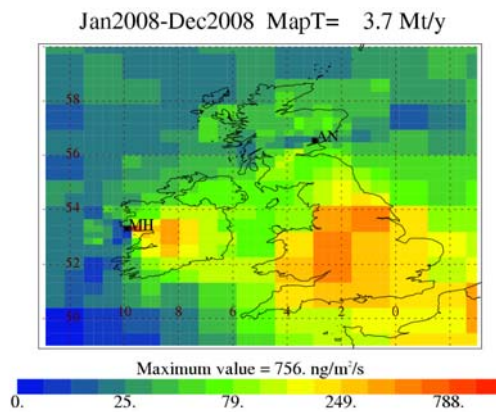Figure 23: Average inversion emission map for CH_4 for 2008 using Angus Tower only observations.

Figure 24: Average inversion emission map for CH_4 for 2008 using combined Mace Head and Angus Tower observations.

4 Update on Three UK sites

4.1 Angus Tower

The GC-ECD at Angus which measures N_2O and SF_6 is currently operating with some problems. This is primarily affecting the quality of N_2O data. A new ECD detector is being purchase and it is hoped that this will resolve the data issue. A comparison of Angus data and Mace Head data are shown in the Figure 25 below.
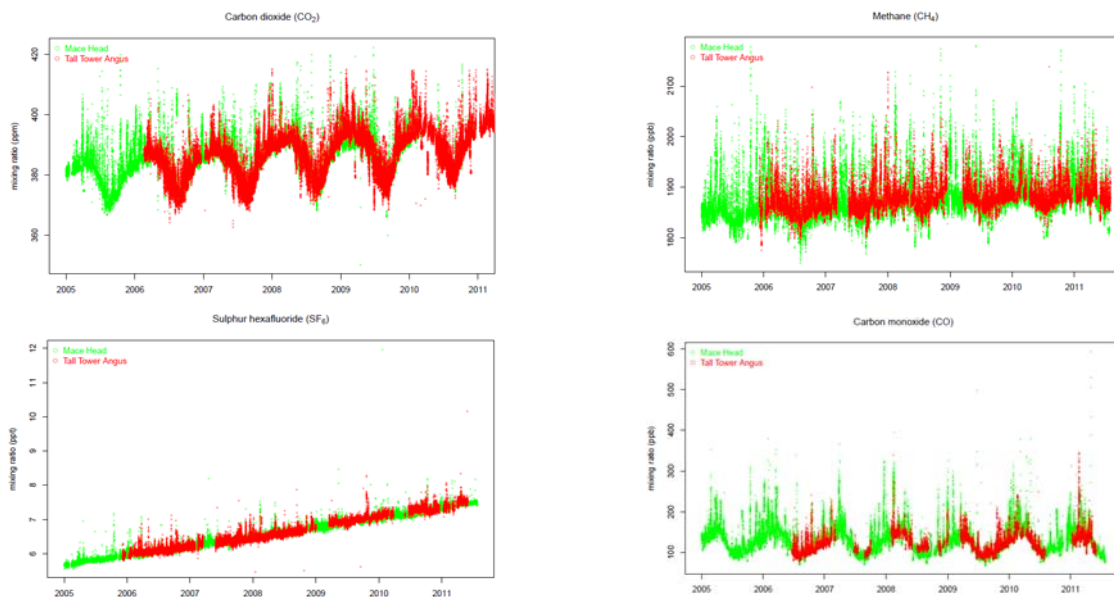

Figure 25: Plots of Angus data (red) with Mace Head data overlaid (green).

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4.2 Tacolneston

Instrumentation progress for Tacolneston is going well. The Tacolneston-MD which measures H_2 and CO, and was modified to measure N_2O and SF_6, is running well (Figure 26). Linearity testing was carried out on this instrument on the 12th of October and permanent data corrections applied. It will be moved into the Mobile Lab during the week starting the 17th of October.

Figure 26: The Tacolneston multiple detector which makes measurements of N_2O, SF_6, H_2 and CO.

The Tacolneston Picarro (purchased by NCAS) is being shipped to us from the University of East Anglia on Monday the 17th of October. It will then be installed in the mobile lab with the custom built sample module (Figure 27)

Figure 27: The sample module for delivering air from different tower heights and calibration standards to the Picarro.

The Medusa was running well until the 4th of October. An unknown error occurred most likely with the circuit board. This issue could not be resolved by our team at Bristol so an engineer has been called out to deal with this problem.

Training on instrumentation for the technician from University of East Anglia who will maintain instruments in the mobile lab at Tacolneston will be carried out on the 18th and 19th of October.

The tubing for the tall tower was ordered on 10th of October. It is due to arrive within four weeks. The first purchase order for the planning and design phase of the sample line installation at the tall tower has been raised. The next step is attending the project manager's site visit; the installation of the lines will follow this.

4.3 Ridge Hill

The Ridge Hill-MD which measures N_2O and SF_6 is now built and running standard samples successfully (Figure 28). However the chromatography is not optimal for SF_6. Currently SF_6 is not baseline separated from the O_2 peak. We believe this is because the post-column which was purchased from Thames Restek is not as tightly packed with adsorbent as the post-column (which we made ourselves) in the Tacolneston-MD. A new column will be made in the lab to resolve this issue.

Figure 28: The Ridge Hill instrument built to measure N_2O and SF_6.

The Picarro is running well, the sample module with nafion dryer for this instrument was built and finished in mid-September. This is now connected to the Picarro and running dried air samples through the instrument (Figure 29). Calibration standards purchased from MPI-Jena arrived in the second week of September. Specialised regulators for the unique cylinder type of the standards were purchased and arrived in mid-September.

Figure 29: The Picarro in the centre with sample module above and the monitor, showing real time urban measurements, at the top of the rack unit. The bottom three units is the uninterruptable power system which prevents instrument shutdown in case of a power cut.

The planning and design visit for Ridge Hill with the project manager will be on the 20th of October. After this we will receive and accurate build estimate and data for the installation of sampling lines up the tower.