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

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1 Executive Summary

1.1 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 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 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 1989-2013.

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).

2 Overview of Progress

The GC-MD at the Mace Head observation station continues to operate effectively and there are no data issues to report. The Medusa at Mace Head has had significant issues requiring significant effort to fix. Six weeks of data were lost during these issues.

Ridge Hill continues to operate well, no significant issues to report.

The Tacolneston Picarro and N_2O/SF_6 instruments have operated well with no significant issues to report. The Tacolneston Medusa has had significant issues and there have been several weeks of lost data.

Tall Tower Angus is now reporting methane and carbon dioxide observations. Work is ongoing to try to recover the CH_4 and CO_2 data collected prior to the transfer of the site to the University of Bristol.

Atmospheric baseline concentrations for each gas reported at Mace Head have been estimated through to the end of September 2013 and are presented through the website,

InTEM (**In**version **T**echnique for **E**mission **M**odelling) has been developed further. The Bayesian cost function, that allows for the use of *a priori* emissions data, has been further refined and comprehensively tested using the European INGOS CH_4 measurement network. Significant effort has been undertaken to further understand and incorporate the different strands of uncertainty into InTEM. For each observation there is now an observational uncertainty and a modelling uncertainty that is used directly within InTEM.

3 Operational sites and observed species

Sites -> Species	Mace Head MHD	Tacolneston TAC	Ridge Hill RGL	Angus TTA
CO_2	Picarro 2301*(1)*	Picarro 2301*(1)*	Picarro 2301*(1)*	LiCor 7000*(1)*
CH_4	Picarro 2301(1), GC-FID*(40)*	Picarro 2301*(1)*	Picarro 2301*(1)*	GC-FID*(40)*
N_2O	GC-ECD*(40)*	GC-ECD*(20)*	GC-ECD*(20)*	GC-ECD*(40)*
SF_6	Medusa*(120)*	GC-ECD*(20),* Medusa*(120)*	GC-ECD*(20)*	GC-ECD*(40)*
H_2	GC-RGA*(40)*	GC-RGA*(20)*	-	-
CO	GC-RGA*(40)*	GC-RGA*(20)*	-	-
CF_4	Medusa*(120)*	Medusa*(120)*	-	-
C_2F_6	Medusa*(120)*	Medusa*(120)*	-	-
C_3F_8	Medusa*(120)*	Medusa*(120)*	-	-
c-C_4F_8	Medusa*(120)*	-	-	-
HFC-23	Medusa*(120)*	Medusa*(120)*	-	-
HFC-32	Medusa*(120)*	Medusa*(120)*	-	-
HFC-134a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-152a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-125	Medusa*(120)*	Medusa*(120)*	-	-
HFC-143a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-227ea	Medusa*(120)*	Medusa*(120)*	-	-
HFC-236fa	Medusa*(120)*	Medusa*(120)*	-	-
HFC-43-10mee	Medusa*(120)*	-	-	-
HFC-365mfc	Medusa*(120)*	Medusa*(120)*	-	-
HFC-245fa	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-22	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-141b	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-142b	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-124	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-123	-	Medusa*(120)*	-	-
CFC-11	Medusa*(120)*	Medusa*(120)*	-	-
CFC-12	Medusa*(120)*	Medusa*(120)*	-	-
CFC-13	Medusa*(120)*	Medusa*(120)*	-	-
CFC-113	Medusa*(120)*	Medusa*(120)*	-	-
CFC-114	Medusa*(120*	Medusa*(120)*	-	-
CFC-115	Medusa*(120)*	Medusa*(120)*	-	-
H-1211	Medusa*(120)*	Medusa*(120)*	-	-
H-1301	Medusa*(120)*	Medusa*(120)*	-	-
H-2402	Medusa*(120)*	Medusa*(120)*	-	-
CH_3Cl	Medusa*(120)*	Medusa*(120)*	-	-
CH_3Br	Medusa*(120)*	Medusa*(120)*	-	-
CH_3I	Medusa*(120)*	Medusa*(120)*	-	-
CH_2Cl_2	Medusa*(120)*	Medusa*(120)*	-	-
CH_2Br_2	Medusa*(120)*	Medusa*(120)*	-	-
$CHCl_3$	Medusa*(120)*	Medusa*(120)*	-	-
$CHBr_3$	Medusa*(120)*	Medusa*(120)*	-	-
CCl_4	Medusa*(120)*	Medusa*(120)*	-	-
CH_3CCl_3	Medusa*(120)*	Medusa*(120)*	-	-
$CHCl=CCl_2$	Medusa*(120)*	Medusa*(120)*	-	-
$CCl_2=CCl_2$	Medusa*(120)*	Medusa*(120)*	-	-

Table 1: Operational sites, instrumentation and observed species. Number in brackets indicates frequency of calibrated air measurement in minutes.

4 Update on three UK 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.

4.2 Tacolneston

The Tacolneston site has experienced a number of problems since the last report. The Medusa-MS was not operational for an extended period from 23rd July to 19 August due to a failure of the Mass Spectrometer side-board. An alternative MS was installed by UoB on the 19th August and the equipment restarted. The Tacolneston MS was brought back to Bristol for repair. A number of days of data were also lost due to blown MS filaments, failure of the main site compressor and accidental shutdown of the Medusa oil diffusion pump.

The Tacolneston-MD also suffered a number of avoidable problems due to operator error. However, overall this instrument performed very well since the last report.

4.3 Angus

Operation of the Picarro-CRDS at Angus continued with no major issues to report.

4.4 Mace Head

The AGAGE-MD functioned with no major issues to report.. On the 23th July 2013 there was a GAW audit for O_3, CO_2, CH_4, N_2O, CO. High levels of H_2 in the audit tanks make CO analyses unreliable. For the first time, a travelling inter-comparison instrument is used as part of the audit. A Picarro G2401, measuring CO_2, CH_4 and CO, is set up to make ambient air measurements for a number of weeks. We are awaiting the results from the audit.

The AGAGE-Medusa experienced many more problems than usual On 1st August 2013 the Omega controller for trap 2 failed, causing trap 2 to overheat. A replacement Omega was supplied from another instrument in Bristol and installed. At this point it was determined that trap 2 had burned out and confirmed when the Medusa vacuum shell was opened by the smell and presence of a solid blob of Apezion grease on the bottom of the shell.

A spare trap was installed (# 081020A-E) however this did not heat properly, with the temperature overshooting significantly. Subsequent testing indicated the trap was shorting to the standoff. This trap had not been previously tested at Empa.

A further spare trap was sourced at EMPA (# 090226C-E) however that too did not heat properly and was diagnosed as being due to the temperature sensing thermocouple becoming detached. On investigation, the thermocouple did not have sufficient epoxy to maintain a secure mechanical connection to the standoff.

Numerous attempts were then made to fabricate a working combination of trap and standoff from the limited spare part available on-site at Mace Head, and in the course of all of this testing, a number of key issues arose:

1) The obvious question is what is an appropriate level of spare traps that should be kept on hand within the network an/or on individual sites;

2) All traps should be tested, at a minimum for continuity between the trap and the standoff. This test has subsequently been inserted in the trap change procedures by JM. However, given the effort involved in producing and replacing traps and consequences of a replacement trap not working, some functional testing would also be desirable;

3) The physical variation in traps is an issue for installation. Ideally, with the legs going straight through the feed-throughs, the standoff should line up exactly with the mounting hole on the baseplate. That was unfortunately not the case and trap legs had to be bent manually to allow installation without putting undue pressure on the trap to force the standoff into the position;

4) With older versions of the Medusa shell, it is not possible to install a trap and test that the 'live' leg is isolated from the shell as the other leg will always be grounded. 2 recommendations for those still using the older shells;

> a) Drill out the Ultratorr nut to ensure clear separation of the trap leg from the nut. Do it using a lathe or bench-drilling machine, as it's not possible to be neat and accurate with a hand held drill
> or
>
> b) Use a small insulating ferrule to centre the trap leg and isolate it from the nut
> e.g., a PTFE ferrule inserted backwards behind the PEEK ferrule (ion the nut side)

In this particular instance, both of the above were implemented.

Finally on the 11th Sept 2013, a trap # T2121228A-E-0 from EMPA was delivered and installed (using the recommendations above), testing on the following day indicated we finally had a working trap! There were some concerns about this trap as it utilised thicker walled tubing (off the shelf, as opposed to the custom made thinner walled tubing previously used) than the Miller/Greally design used heretofore however initial indications are the trap works as expected.

Throughout this period, various tests were carried out to try to eliminate other components as the source of the problem – Omega controllers were swapped whole, thermocouples were swapped between Omegas and torridal power supply's were swapped. Ultimately, the conclusion must be that if there had been a working trap available, this issue could have been resolved within days rather than weeks

4.5 NF_3 Measurements at Mace Head

Nitrogen trifluoride (NF_3) has potential to make a growing contribution to the Earth's radiative budget; however, our understanding of its atmospheric burden and emission rates has been limited. Atmospheric measurements of NF3 were started at Mace Head in June 2013, an example of the data record achieved thus far in comparison to measurements made using a similar Medusa-MS in California are shown in Figure 0. These measurements indicate similar atmospheric mole fractions at both sampling sites, as would be expected for two Northern Hemispheric sites, it is encouraging that these new measurements match so well, indicating both instruments are working well and the calibration of both instruments is linked to a common calibration scale.

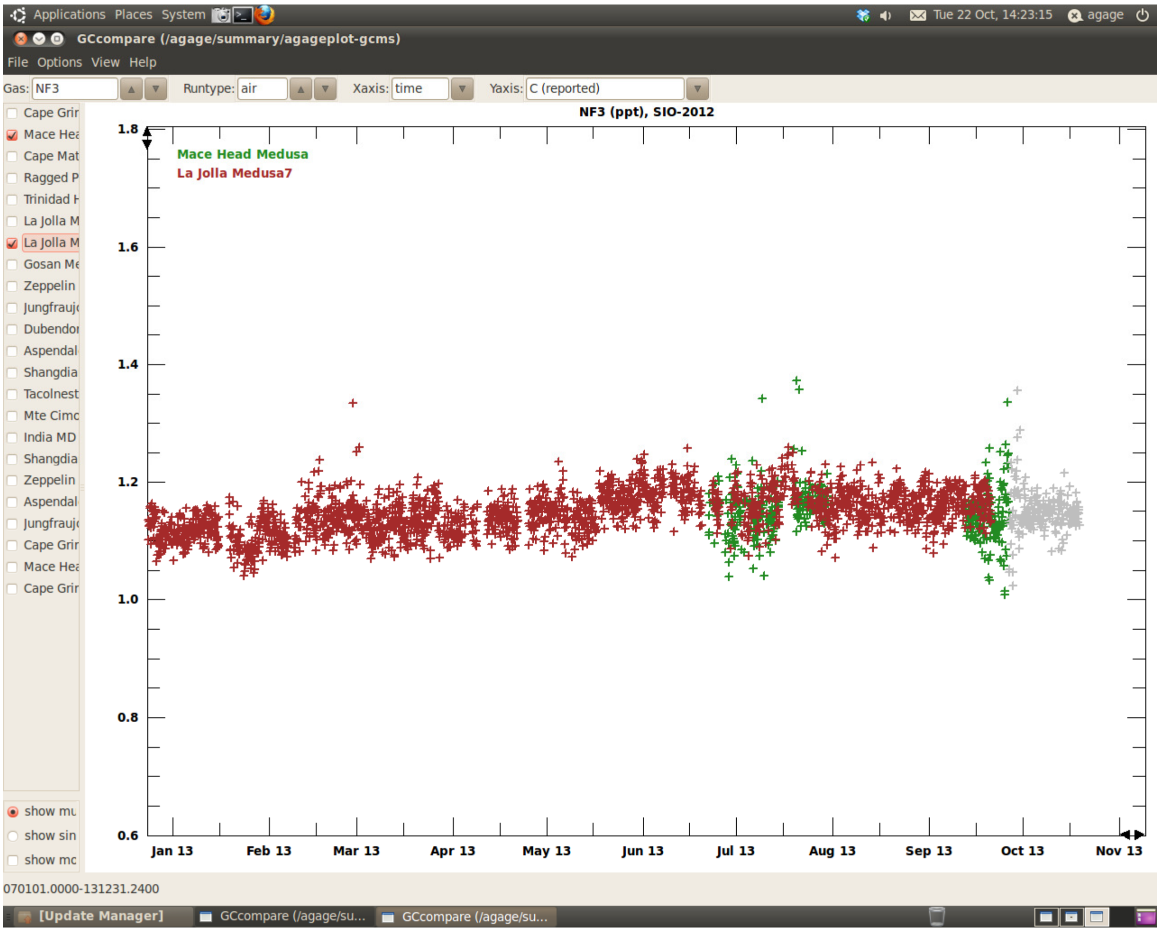

Figure 0. Comparison of Mace Head (green and grey points) and Californian (claret points) NF_3 measurements.

4.6 *Development of new CRDS software*

Work is on-going with software developers at SIO to formulate new GCWerks software to allow the easy importation of Picarro CRDS data. It is hoped that this software will enable data efficient data review of the very high frequency CRDS data (5Hz) in a similar manner to the AGAGE-MD and –Medusa systems. This will be a major advancement for the measurement of CO_2 and CH_4. The key software features are detailed below:

Same software interface as GCWerks for GC and GCMS.

Uniform acquisition, database, graphics and analysis regardless of CRDS model.

Uniform control of additional hardware such as sample box (Valco valves, inlet sample pressure and temperature etc.).

A single Linux system can control/acquire from all instruments at a remote site (CRDS, GC, GCMS).

Imported or acquired data stored as a binary strip-chart over 30 times smaller than the Picarro files (for fast data processing and copying over the internet).

Calculates the results based on periodic standard measurements.
Nonlinearity and other diagnostics.

Automatically rejects transient period (after inlet change) before averaging high-frequency.

Fast interactive graphics and data exportation.

Graphical data flagging (flagging and filtering applied to 1-minute averaged data.

5 Bayesian cost function applied to European INGOS CH_4 observation network

5.1 Introduction

In the previous quarterly report a new cost function (Bayesian) was incorporated into InTEM. This new method of deciding upon the best emission field takes into account *a priori* emission data and also clearly incorporates the different strands of uncertainty that are present within the system. There are three areas of uncertainty; modelling, measurement and *a priori*, these are now explicitly incorporated into InTEM and are discussed in this section. The new cost function has been applied to the European INGOS CH4 measurement network (12 high-frequency stations) for 2007 – 2011 using a combined natural / anthropogenic CH_4 prior emission field.

5.2 A Priori emissions

The anthropogenic prior emissions for CH_4 have been obtained from the EDGAR database. The anthropogenic emissions for the years 2007 – 2010 were explicitly available through INGOS and 2011 was assumed to have an identical prior to 2010. The (assumed) constant natural (biogenic) prior was taken from a combination of literature sources and combines estimates of the emissions from; the ocean, termites, wild animals and wetlands. The natural and anthropogenic priors for 2007 are shown in Figure 1, the combined prior is shown in Figure 2.

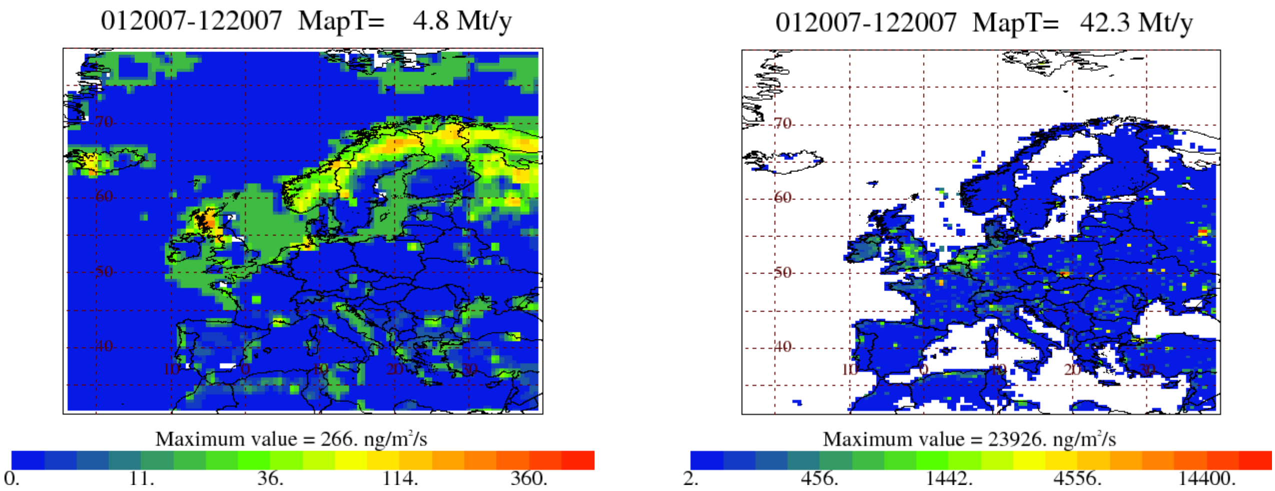

Figure 1: Natural (left) and anthropogenic (right) emission priors for CH_4 for 2007. Note the very different scales used on the two plots.

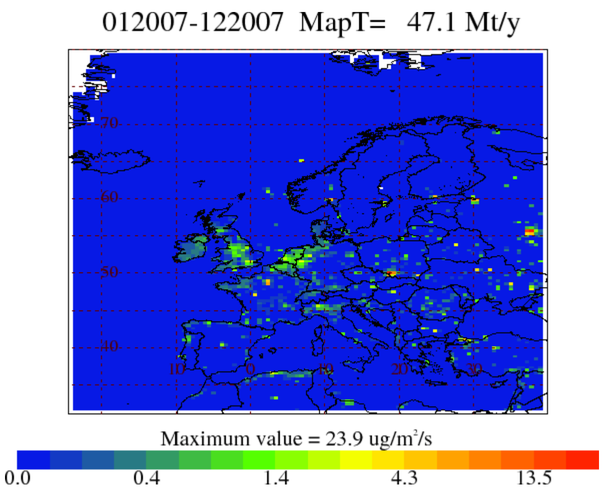

Figure 2: Total emission prior for CH_4 for 2007

5.3 Inversion grid and observations

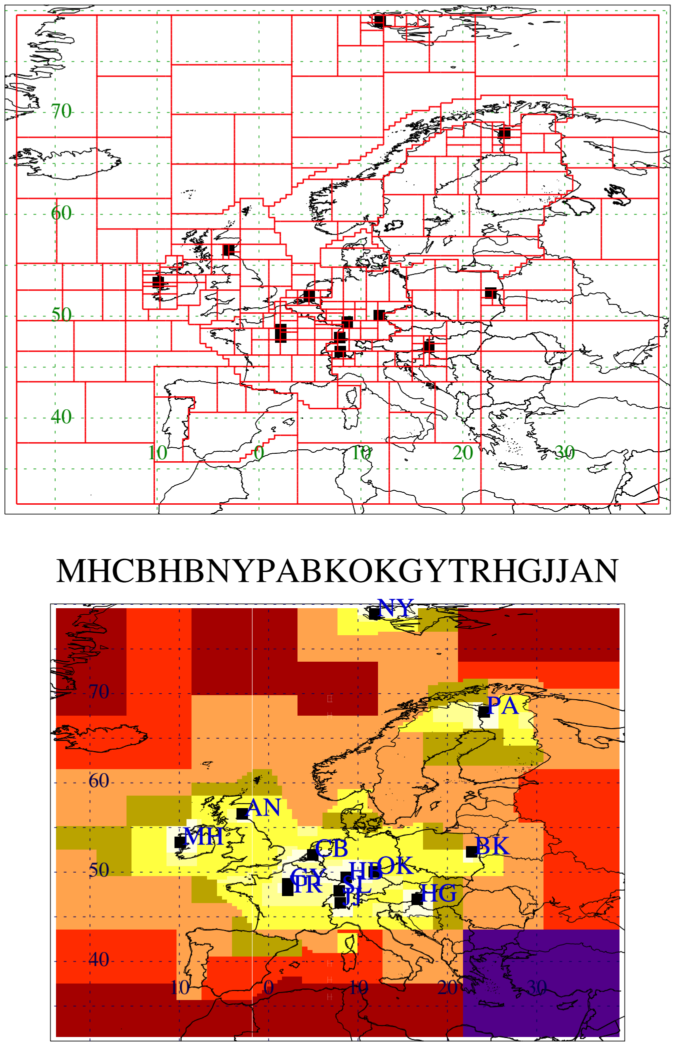

Figure 3: Inversion grid resolution used within InTEM for 2007 CH4 inversion using INGOS CH_4 observational network. The locations of the 12 measurement stations are shown.

CH4 observations from twelve high-frequency measurement stations were available through the INGOS observational network covering the period 2007 – 2011. The stations used were:

Station	ID	Latitude	Longitude	Altitude (masl)	Location
ZEP	NY	78.9	11.88	485	Ny-Alesund, Spitsbergen (475m+10m)
PAL	PA	67.97	24.12	572	Pallas, Finland (565m+7m)
TT1	AN	56.55	-2.98	535	Angus, UK (313m+222m)
MHD	MH	53.33	-9.9	40	Mace Head, Ireland (25m+15m)
BI5	BK	52.25	22.75	483	Bialystok, Poland (183m+300m)
CB4	CB	51.97	4.93	199	Cabauw, Netherlands (-1m+200m)
OX3	OK	50.05	11.82	1185	Ochsenkopf, Germany (1022m+163m)
HEI	HB	49.42	8.67	146	CM Heidelberg, Germany (116m+30m)
GIF	GY	48.71	2.15	167	Gif sur Yvette, France (165m+2m)
TR4	TR	47.96	2.11	311	Trainou, France (131m+180m)
HU1	HG	46.95	16.65	344	Hegyhatsal, Hungary (248m+96m)
JFJ	JJ	46.55	7.98	3590	Jungfraujoch, Switzerland (3580m+10m)

As described in previous reports, the resolution of the InTEM inversion grid decreases (larger grids) as the distance increases and the amount of information about sources decreases. The a priori emissions are interpolated onto the InTEM inversion grid, an example for 2007 is shown in Figure 4.

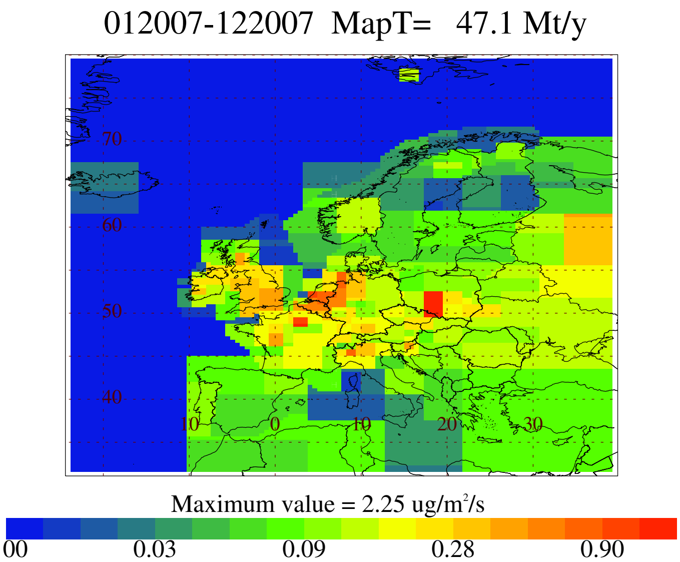

Figure 4: A priori CH_4 emissions for 2007 interpolated onto the InTEM inversion grid.

5.4 Bayesian cost function and uncertainty elements

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 whilst being 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 cost function implemented in InTEM is the standard Bayesian formulation used in many inversion studies and consists of 2 parts, J_1 and J_2. 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_2 represents the cost of moving away from the *a priori* emission distribution (x_{ap}), B is the uncertainty related to the *a priori* emissions. The overall cost is the sum of the two components.

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

$$J2 = (x - x_{ap})^T B^{-1} (x - x_{ap})$$

$$J = J_1 + J_2$$

The model and measurement elements are assumed uncorrelated and therefore only the diagonal elements of R are required. The emissions in the prior are also assumed to be uncorrelated with each other so B is also a diagonal matrix.

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

- Observation uncertainty ($\sigma_{precision}$ & $\sigma_{3h\ time\ period}$)

$\sigma_{precision}$ → 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 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.

$\sigma_{3h\ time\ period}$ → Uncertainty due to aggregating the observations over the time step of the air history maps, in this case 3-hours. All of the observations within each 3-hour period are averaged and the standard deviation of these observations is assumed to be the uncertainty in the measurements over this time window. At least three observations are required within each time window.

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

$\sigma_{baseline}$ → Uncertainty of the Mace Head baseline for each 3-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. At stations other than Mace Head this baseline is more uncertain, especially if the station is located in a meteorologically challenging area such as the Alps, therefore a multiple (2, 3 or 5) of this standard deviation is used to describe this uncertainty.

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 influence of the nine surrounding grid cells are known for each 3-hour period. These values are normalised (arbitrarily divided by 5e-9) 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.

$$R = (\sigma_{precision})^2 + (\sigma_{3h\ time\ period})^2 + (\sigma_{baseline})^2 + (\sigma_{local})^2$$

The Northern Hemisphere baseline estimated at Mace Head is used at all of the measurement stations. The uncertainty in the baseline is passed through to the inversion through the matrix R. The iterative solver simulated annealing is used to find the best fit (lowest cost) to the observations and the prior. By design simulated annealing cannot generate (impossible) negative emissions and is a key strength of this type of solver.

The B matrix is the uncertainty of the *a priori* emission data. Each grid across the *a priori* emission map is assumed to have the same percentage uncertainty. This has been calculated by assuming the UK emission of CH_4 has an uncertainty of ~24% (as reported to the UNFCCC). By implication therefore each 40km grid cell in the *a priori* has an uncorrelated uncertainty of 1000%, i.e. can range from zero to an emission ten times larger than reported in the prior.

5.5 Results of CH4 inversion using the INGOS network

Figure 5 shows the *a posteriori* solution for CH4 for 2007 using the observations from the INGOS network and constrained by the prior emissions (Figure 4). The difference between the *a posteriori* and the *a priori* (*a posteriori* – *a priori*) is shown in Figure 6. Over the UK the general trend is for the inversion to reduce the CH_4 emissions except around the central belt of Scotland. The overall map total emission has changed by only 10% but there has been some significant shifts in the location of the emissions with a significant elevation in Russia, although this grid will be significantly affected by edge effects due to any inaccuracies in the baseline along this edge of the inversion domain.

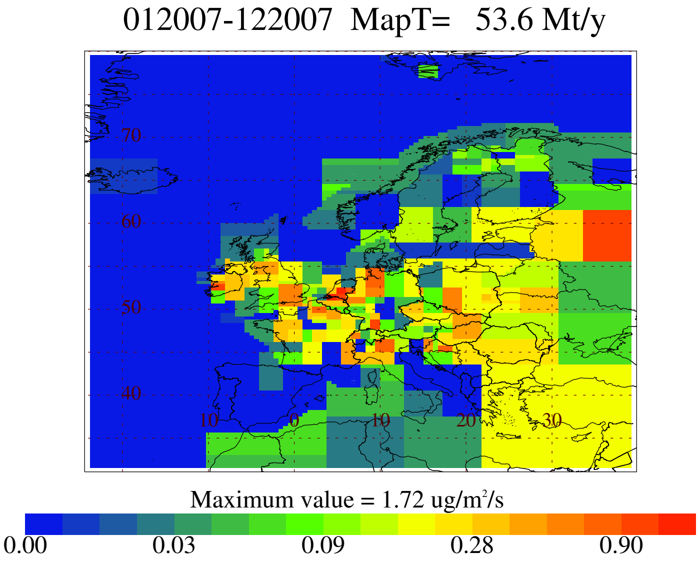

Figure 5: *A posteriori* solution for CH_4 for 2007 using the observations from the INGOS network

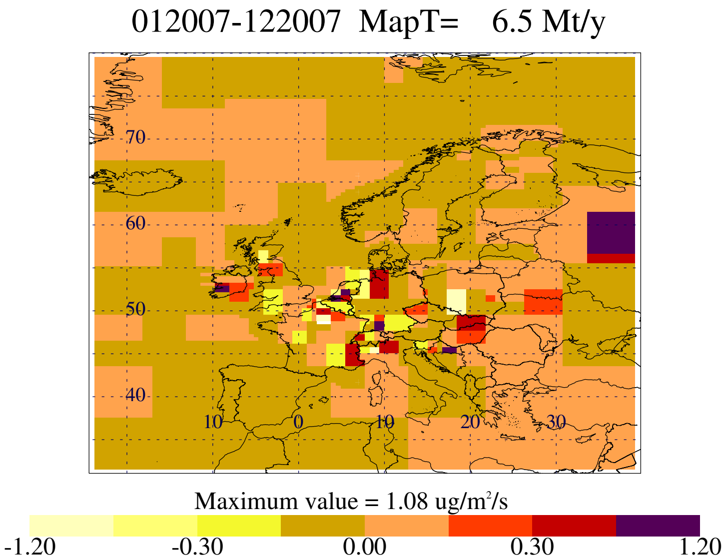

Figure 6: Difference between the *a posteriori* and the *a priori* (*a posteriori* – *a priori*) emissions for CH_4 for 2007.

The UK annual emissions 2007 – 2011 for CH4 are shown in Figure 7 comparing the emissions from those submitted to the UNFCCC in 2013, InTEM estimates from the last annual report (May 2013) using just Mace Head observations (3-year averages interpolated to annual estimates), *a priori* emissions combining EDGAR and natural emissions, and the InTEM *a posteriori* solution using the INGOS network (1-year averages) using the Bayesian cost function. The corresponding emissions from North West Europe (NWEU), comprising Ireland, UK, France, Germany, Denmark, the Netherlands, Belgium and Luxembourg, are shown in Figure 8. The *a priori* emissions are consistently larger in both regions across the time period. The UNFCCC estimates are generally lower than the InTEM estimates but the uncertainties consistently overlap across the years. The two InTEM solutions are broadly in agreement and certainly have strongly overlapping uncertainties. This latter result reveals some important points.

- The previous work using only Mace Head observations but with longer inversion time periods (3 years compared to 1 year) and a more simplistic cost function gives robust results for these two geographical regions. Note that the distribution of emissions within the NWEU has not been assessed.

- The cost function used within InTEM for the annual report (May 2013) that does not use *a priori* emissions gives comparable solutions and uncertainty estimates compared to the Bayesian with *a priori* estimates. This implies the impact of the *a priori* emissions is small.
- The EDGAR + natural *a priori* appears to be too high by a significant margin especially in the UK (1 – 1.5 Mt/y in the UK).
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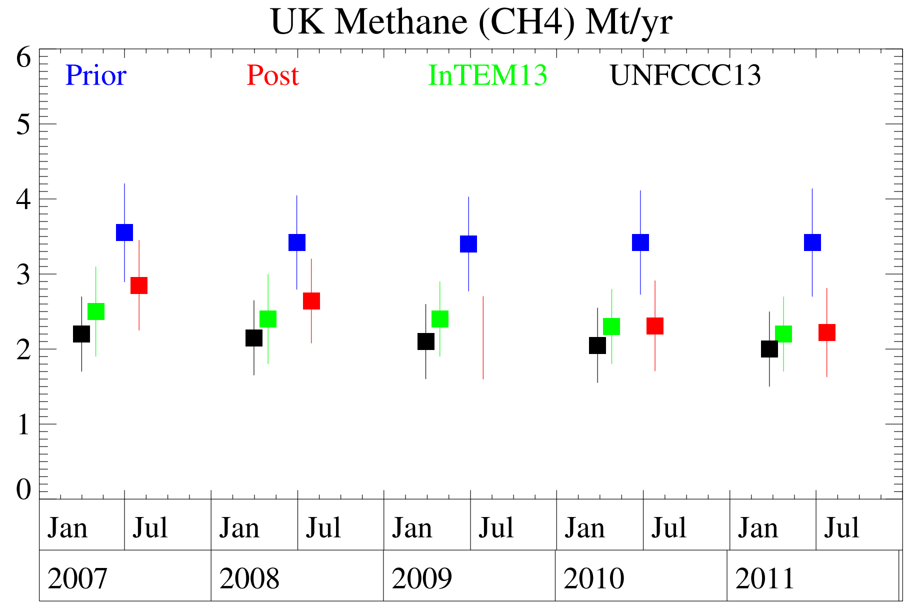

Figure 7: UK emission estimates for CH_4 comparing the UNFCCC inventory (black), InTEM estimate from the 2013 annual report (green), the EDGAR + natural *a priori* used and the *a posteriori* solution using the INGOS network.

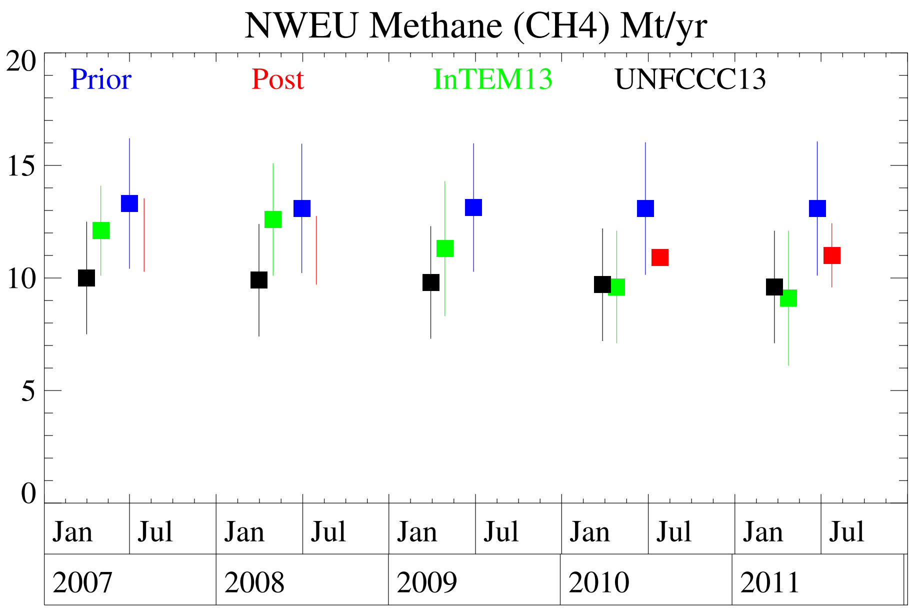

Figure 8: North West European emission estimates for CH_4 comparing the UNFCCC inventory (black), InTEM estimate from the 2013 annual report (green), the EDGAR + natural *a priori* used and the *a posteriori* solution using the INGOS network.

5.6 Future work

- Assess the impact of the new DECC network on the distribution of UK emissions
- Repeat the analysis presented here using N2O and the INGOS network.

- Repeat the analysis presented here using hydrofluorocarbons (HFCs) and the INGOS network (only Mace Head, Jungfraujoch, Ny Alesund and Monte Cimone).
- Incorporate an adjustment to the baseline per location and per month within the inversion framework.
- Assess the impact of simply using a population weighted *a priori* for the man-made gases.