



University of
BRISTOL

Methodology Report
Verification of Emissions using
Atmospheric Observations

BEIS

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1. Executive Summary

This document describes the method used to estimate UK emissions of greenhouse gases from atmospheric measurements. The project falls naturally into two distinct components: making high quality measurements of each greenhouse gas, some having very low atmospheric concentrations of the order of parts per trillion, i.e. 1 part gas to 1 trillion parts air; and modelling, where the atmospheric mixing and movement of the gases emitted are simulated and combined with the measurements to estimate UK emissions of each gas. This project provides the Department of Business, Energy and Industrial Strategy (BEIS) with an independent verification of its inventory programme, a key part of the UK's National and International commitments related to climate change, e.g. UK Climate Change Act and United Nations Framework Convention on Climate Change (UNFCCC).

Atmospheric measurements are made at four locations around the British Isles, referred to as the UK Deriving Emissions related to Climate Change network (UK DECC network). It comprises of a coastal site on the west coast of Ireland (Mace Head; MHD) and three sites on telecommunications masts at strategic locations in the UK. The MHD station has been operating since 1987 and is part of a global network of stations (Advanced Global Atmospheric Gases Experiment – AGAGE) that has pioneered the development of in situ high frequency measurements of ozone-depleting and greenhouse gases. All four stations measure the three key greenhouse gases; carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O), in addition, two stations measure all of the principle gases reported to the UNFCCC; hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulphur hexafluoride (SF₆), along with important ozone-depleting gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Nitrogen trifluoride (NF₃) is only measured at Mace Head. The measurements are made on-site, at high frequency (two-hourly or better) and to very high precision.

The atmospheric measurements are a vital input into the modelling that ultimately estimates UK emissions of each principle greenhouse gas. The movement and dispersion of emissions is simulated in an atmospheric transport model called NAME (Numerical Atmospheric dispersion Modelling Environment) that is driven by the UK Met Office's weather prediction model. A mathematical tool, InTEM (Inversion Technique for Emission Modelling), has been developed to calculate the magnitude and distribution of emissions of each gas that has the best statistical match between the measurements and the modelled values. The estimated UK emissions are directly comparable to the UK

estimates produced for BEIS by the inventory team and thereby provide an independent check of the inventory estimates, a process considered best practice by the signatories of UNFCCC.

2. Atmospheric Observations

Real-time, high-frequency measurement networks are essential for investigating climate change and ozone depletion, and for verifying Kyoto (climate) and Montreal (ozone) Protocol driven emission targets. Greenhouse gas (GHG) observation stations exist within the UK and Ireland at Tacolneston (TAC), Norfolk; Ridge Hill (RGL), Herefordshire; MHD, Ireland; Bilsdale (BSD), North Yorkshire; as the UK DECC Network. An additional observation station, Heathfield (HFD), Sussex, is operated by the National Physics Laboratory (NPL). Sites in the UK DECC network have measured the composition of the atmosphere continuously since 1987 (at MHD only), and 2012 at TAC and RGL and 2014 at BSD and HFD. Angus station (TTA) in Scotland was decommissioned in Sept 2015. The UK DECC Network is distinguished by its capacity to take high frequency measurements of all of the important GHG species in the Kyoto Protocol and the ozone depleting substances (ODS) in the Montreal Protocol within the UK.

This document sets out the methods used for the measurement of GHGs and ODSs, and their interpretation for inventory verification. An overview of the UK DECC network and the instrumentation used within the network is described in section 2.1 and 2.2, with methods used for the interpretation of data presented in section 3.

2.1 UK DECC Network

GHGs and ODSs have been measured continuously by the University of Bristol since 1987 at MHD, a coastal research station located in County Galway in the west of Ireland (53.33° N, 9.90° W). In 2012, three regional tall tower sites were added to create the UK DECC network: TAC, Norfolk (52.52° N, 1.14° E); RGL, Herefordshire (52.00° N, 2.54° W) and TTA, Dundee (56.56° N 2.99° W). TTA was replaced by BSD, North Yorkshire (54.36° N, 1.15° W) in September 2015. In addition NPL operate a station at HFD, Sussex. This extended network was created to better quantify and spatially resolve the emissions of GHGs and ODSs originating from the UK and northern Europe (Figure 1).

MHD (Figure 1) is part of the UK DECC Network, and also the Advanced Global Atmospheric Gases Experiment (AGAGE: 1993-2015; <https://agage.mit.edu/>). AGAGE and its predecessors (Atmospheric Lifetime Experiment, ALE: 1978-1981; Global Atmospheric Gases Experiment, GAGE: 1981-1993) have measured the composition of the global atmosphere continuously since 1978 using the following sites: (a) MHD (53°N, 10°W, 1987 to present), prior to this at Adrigole (52°N, 10°W, 1978-1983); (b) on the U.S. west coast, first at Cape Meares, Oregon (45°N, 124°W, 1979-1989), then at

Trinidad Head, California (41°N, 124°W, 1995 to present); (c) Ragged Point, Barbados (13°N, 59°W, 1978 to present); (d) Cape Matatula, American Samoa (14°S, 171°W, 1978 to present); (e) Cape Grim, Tasmania, Australia (41°S, 145°E, 1978 to present); (f) Jungfrauoch (Switzerland, 47°N, 8°E, 2008 to present); (g) Zeppelinfjellet (Ny-Ålesund, Norway 79°N, 12°E, 2010 to present), (h) Gosan, Jeju Island, Korea (33°N, 126°E, 2007 to present), with co-operative sites also at Hateruma Island, Japan (24°N, 123°E, 2004 to present), and Monte Cimone (Italy, 44°N, 11°E, 2003 to present). MHD is on the west coast of Ireland and is ideally situated to sample air from the Atlantic Ocean and is used to estimate the mid-latitude northern hemisphere background concentrations of GHGs and ODSs, as shown in Figure 15a. The DECC network also receives air that has travelled over the UK and Europe and is therefore polluted with emissions from those areas, as shown in Figure 15b. The magnitude of the increase in the atmospheric concentration over the background level gives an indication of areas of high emission and can be used with modelling techniques (section 3) to estimate the strength and geographical distribution of the emissions over the UK and northern Europe. A wide range of gases (Table 1 and Table 2) are measured at this station using a Gas Chromatography – Multi-Detector (GC-MD) instrument with dual Electron Capture Detection (ECD; section 2.2.3.), Flame Ionisation Detection (FID) and mercuric oxide Reduction Gas Analyser (RGA; section 2.2.4.) and Medusa Gas Chromatography – Mass Spectrometry (GC-MS; section 2.2.5.). CO₂ and CH₄ data is also obtained from Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Paris, quantified using Cavity Ring-Down Spectroscopy (CRDS; section 2.2.1.), from the same mast at MHD as the GC-MD and Medusa GC-MS.

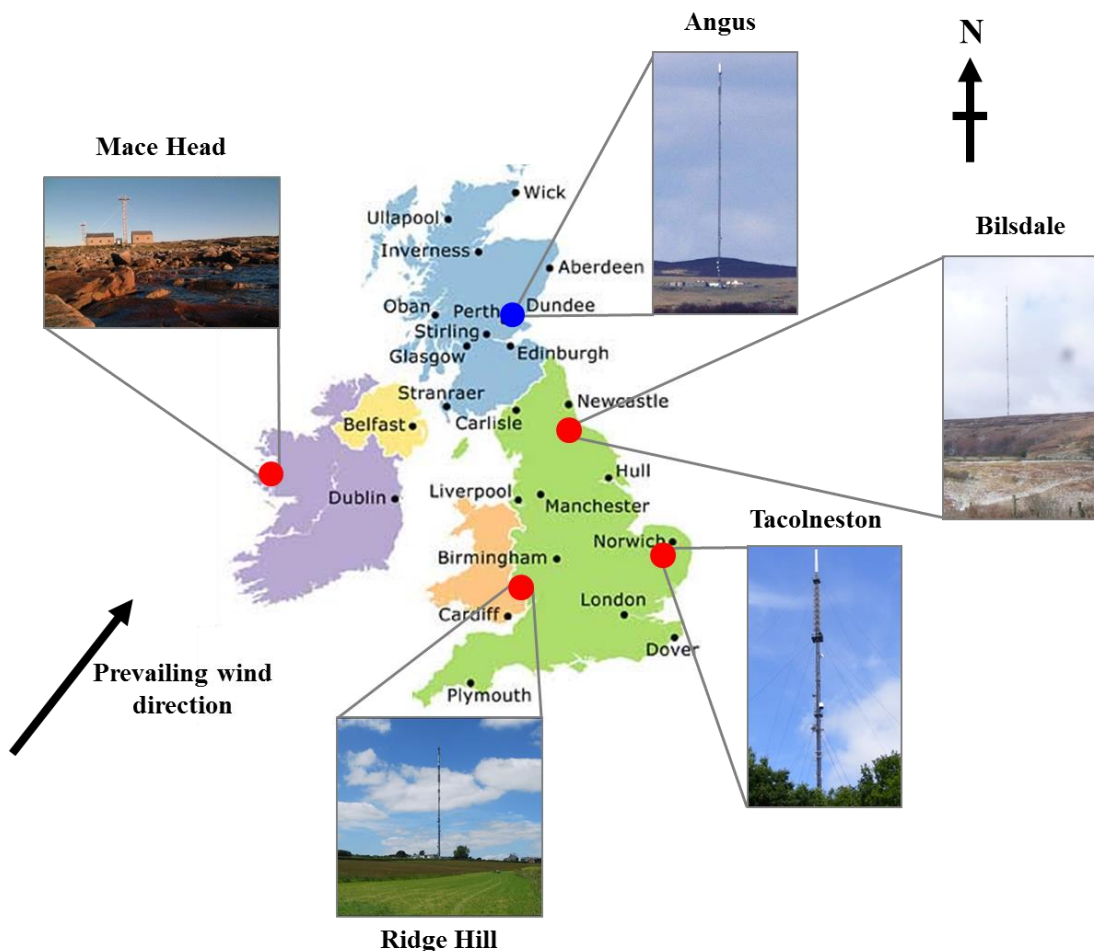


Figure 1: UK DECC network tall tower sampling stations. All UK sites are based at telecommunication tower sites. Red points represent current UK DECC sites, whilst blue points represent former UK DECC sites.

The TAC mast is 11 km from Norwich, ~140 km from central London, and stands 206 m tall. A wide range of gases (Table 1 and Table 2) are measured at this station using CRDS (section 2.2.1.), GC-MD with dual ECD (section 2.2.3.) and RGA (section 2.2.4.), and Medusa GC-MS (section 2.2.5.) in the University of Bristol (UoB) custom, purpose-built mobile laboratory. The GC-MD will be replaced by an Off-Axis Integrated Cavity Output Spectrometer (OA-ICOS; section 2.2.2.) at the station to measure N₂O and CO. This site was chosen to measure the whole suite of the Kyoto basket of greenhouse gases due to its easterly location, as it receives a strong emission signal from London, the South East and the Midlands and, to a lesser but still important extent, from the rest of the UK. It also provides vital information on the composition of the in-flow of air to the UK from Continental Europe.

Site	Start date	Intake height (m)	CRDS	OA-ICOS	GC-ECD/MD	Medusa (GC-MS)
Mace Head	1987	10	CO ₂ /CH ₄ ^a	-	CH ₄ /CO/H ₂ /N ₂ O/CFC-11/ CFC-12/CFC-113/CHCl ₃ / CH ₃ CCl ₃ /CCl ₄	Halocarbons and other trace gases
Tacolneston	January 2013	54	CO ₂ /CH ₄	N ₂ O/CO	-	-
		100	CO ₂ /CH ₄	N ₂ O/CO	N ₂ O/SF ₆ /CO/H ₂	Halocarbons and other trace gases
		185	CO ₂ /CH ₄	N ₂ O/CO	-	-
Ridge Hill	January 2013	45	CO ₂ /CH ₄	-	-	-
		90	CO ₂ /CH ₄	-	N ₂ O/SF ₆	-
Bilsdale	January 2014	42	CO ₂ /CH ₄ /CO	-	-	-
		108	CO ₂ /CH ₄	-	N ₂ O/SF ₆	-
		248	CO ₂ /CH ₄ /CO	-	-	-

Table 1: UK DECC network tall tower sampling stations and instrumentation.

^a data obtained from Laboratoire des Science du Climat et de l'Environnement, Paris.

Compound	[2014] (ppt)	Typical % precision	Compound	[2014] (ppt)	Typical % precision	Compound	[2014] (ppt)	Typical % precision
CF ₄	81.8	0.11	HFC-365mfc	1.03	1.82	CH ₃ Br	7.61	0.26
PFC-116	4.10	0.31	HFC-4310mee	0.26	2.13	CH ₃ I	0.58	0.64
PFC-218	0.61	1.22	HCFC-22	241.5	0.17	CH ₂ Cl ₂	49.1	0.31
PFC-318	1.48	0.60	HCFC-124	1.27	1.57	CHCl ₃ ^{§a}	11.6	0.22
C ₆ F ₁₄	0.30	1.51	HCFC-141b	25.4	0.19	CCl ₄ ^{§a}	82.8	0.30
SF ₆ ^{§b}	8.45	0.17	HCFC-142b	23.4	0.21	CH ₂ Br ₂	1.55	0.51
SO ₂ F ₂	2.14	0.64	CFC-11 ^{§a}	233.9	0.11	CHBr ₃	4.24	0.35
HFC-23	27.8	0.39	CFC-12 ^{§a}	523.4	0.07	CH ₃ CCl ₃ ^{§a}	3.73	1.24
HFC-32	11.6	0.69	CFC-13	3.01	0.82	CHClCCl ₂	0.36	1.28
HFC-125	18.1	0.54	CFC-113 ^{§a}	72.8	0.12	COS	446.5	0.13
HFC-134a	84.2	0.19	CFC-114	16.3	0.23	CH ₄ ^{ac}	1898 (ppb)	0.07
HFC-143a	17.4	0.40	CFC-115	8.40	0.31	N ₂ O ^{ab}	327 (ppb)	0.04
HFC-152a	10.0	0.41	H-1211	3.87	0.31	CO ^{ab}	140 (ppb)	0.70
HFC-227ea	1.10	0.83	H-1301	3.41	0.72	H ₂ ^{ab}	500 (ppb)	0.30
HFC-236fa	0.14	3.28	H-2402	0.43	0.75	CO ₂ ^c	400 (ppm)	0.02
HFC-245fa	2.40	0.75	CH ₃ Cl	532.9	0.16			

Table 2: Species measured at Mace Head and Tacolneston. Compounds are measured on the Medusa (GC-MS) unless otherwise stated. § denotes where compounds are measured both on the Medusa GC-MS and GC-MD. ^a denotes compounds measured via GC-MD at MHD, ^b denotes compounds measured by GC-MD at TAC, ^c denotes compounds measured by CRDS. (ppt = parts per trillion, ppb = parts per billion, ppm = parts per million)

The RGL mast is located in Herefordshire, 8 km south-east of Hereford and 20 km south-west of Worcester. The mast is 164 m tall and the station is currently equipped with a Picarro G2301 CRDS for the measurement of CO₂ and CH₄ (section 2.2.1.) and a GC-ECD (section 2.2.3.) for N₂O and SF₆ measurements.

The BSD mast, located at Bilsdale West Moor, close to Helmsley, North Yorkshire is 314 m tall. The station is equipped with a Picarro G2401 CRDS (section 2.2.1.) for CO₂, CH₄, and CO measurements and a GC-ECD (section 2.2.3.) for N₂O and SF₆ measurements.

2.2 Measurement Methods

A number of methods are used to measure GHGs and ODSs within the UK DECC network. These are described in further detail here and consist of CRDS (section 2.2.1.), OA-ICOS (section 2.2.2.), GC-ECD (section 2.2.3.), GC-MD (section 2.2.4.) and Medusa

GC-MS (section 2.2.5.) as the main measurement techniques. Section 2.2.6. outlines the methods for reviewing data and quality assurance of data. Table 1 shows the GHGs and ODSs measured by each instrument at each site.

The setup at each station is outlined in Table 1 and Figure 2. Air is sampled through tubing at different heights (outlined in Table 1). An inverted stainless steel cup shields the inlet to prevent water entering the tubing. Perspex water decanting bowls are installed at the bottom of the towers to ensure that any liquid water that has condensed in the line is removed before entering the laboratory and instruments. The air is filtered for particulates after entry into the station laboratory, before branching into secondary sample lines to the CRDS (section 2.2.1.), GC-ECD/MD (section 2.2.3./2.2.4.) and Medusa GC-MS (section 2.2.5.) at each site (Figure 2). The CRDS samples each height sequentially for 20 or 30 minutes; determined by the number of inlet heights and a desire to sample from each one at least hourly.

2.2.1. Cavity Ring-down Spectroscopy

In situ wavelength-scanned CRDS (Picarro G2301 and G2401) is used to make high frequency (~three second measurements) CO₂, CH₄, H₂O and CO ambient air measurements over a number of different sampling heights (Table 1). CRDS measurements are made over a number of different heights to enable investigation of the extent of vertical mixing within 100-250 m of the ground. The gases (CO₂, CH₄, H₂O and CO) to be analysed absorb near-infrared light uniquely at different wavelengths. CRDS works by passing a laser through a cavity filled with gas (Figure 3) and allowing the intensity to build up. The laser is then switched off and the decay in the light intensity is measured using a specific detector. As the absorption wavelengths of CO₂, CH₄, CO, and H₂O are well known, the concentration of each gas can be determined by alterations in the time it takes the light intensity to decay. To increase the accuracy of the instrument, the cavity optical path is increased to 15-20 km using multiple reflections within the 34 cm³ optical cell (Figure 3A). The increase in the optical path results in greater absorption by gases within the cavity and thus a greater decay in light intensity, improving the accuracy of the instrument. Both the G2301 and G2401 series scan specific and unique wavelengths to determine the differing gas concentrations.

The sampling scheme shown in Figure 2 consists of branched secondary lines pulling from the primary intake line. Filters are used to prevent airborne particles from entering the analyser. For sites with multiple sample inlets (TAC and BSD have three inlets each, and RGL has two inlets), each height is sampled sequentially for 20 or 30 minutes,

depending on the number of inlets and ensuring that each height is sampled every hour. The CRDS operating at MHD (funded by the LSCE) continuously samples from the 10 m inlet.

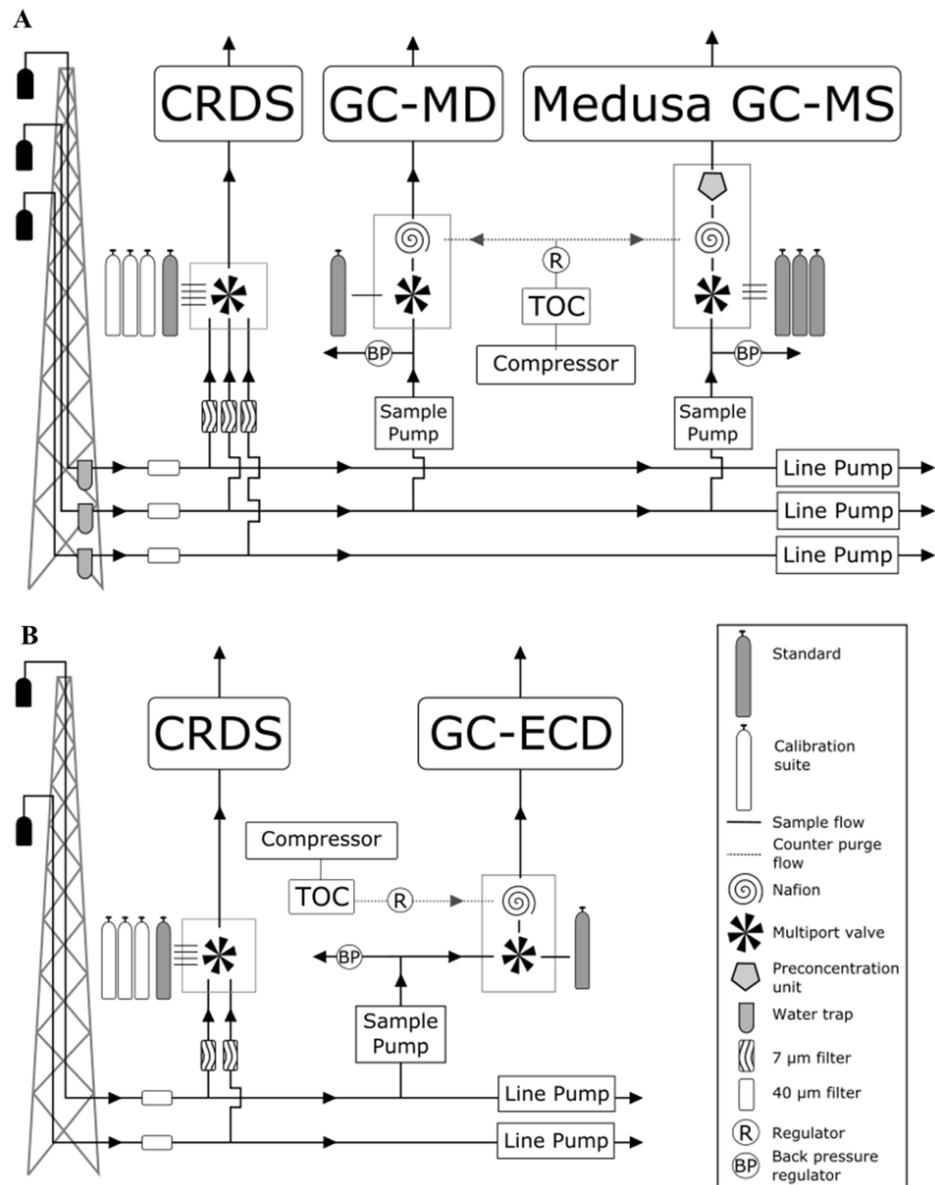


Figure 2: Station set up for A. Tacolneston and Mace Head (one inlet only), and B. Ridge Hill and Bilsdale (three inlets).

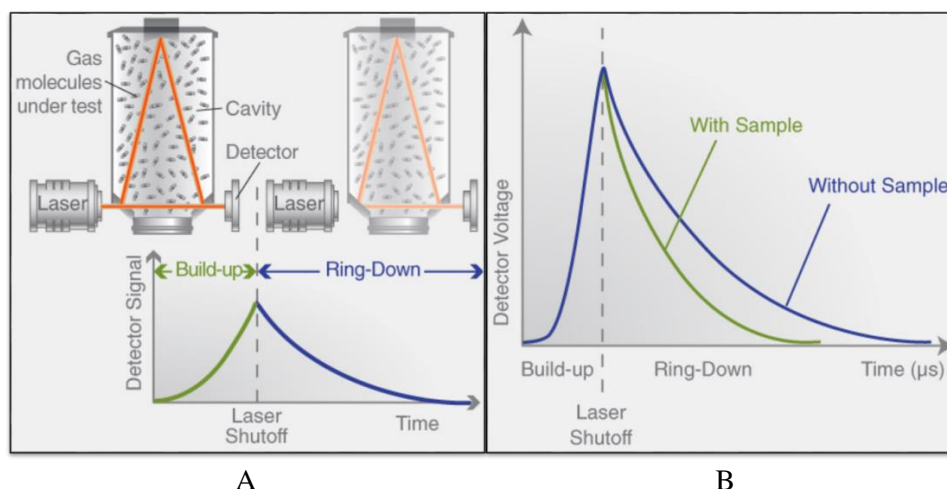


Figure 3: A. Schematic of Cavity Ring-down Spectroscopy between beam emittance and detection, and B. the difference in detector voltage between with and without sample (Picarro Inc., 2015).

Measurements of water vapour (H_2O) are necessary on CRDS instruments as measurements are made on wet ambient air, yet CO_2 , CH_4 , and CO are reported as dry air mole fractions. Corrections are applied to CO_2 , CH_4 , and CO data to account for the effects of differing amounts of H_2O in the atmosphere. A water test is undertaken annually to assess the response between H_2O and CO_2 , CH_4 , and CO on each individual instrument. A steady stream of a known concentration of gas is analysed on the CRDS instruments. Ultrapure H_2O is injected into the sample stream to humidify the air. The differing response between H_2O and CO_2 , CH_4 and CO is assessed (Figure 4) to create a correction factor, which is applied to the ambient CO_2 , CH_4 , and CO data.

To ensure that measurements made by the CRDS instruments are accurate, a standard gas of near atmospheric concentration of CO_2 , CH_4 , and CO is run daily for 20 minutes. This standard gas is used to correct for linear changes between the daily measurements; also known as instrumental drift. Precision, a measure of the repeatability of the daily standard is shown in Table 3. To ensure the measurements are accurate across the whole range of CO_2 , CH_4 , and CO concentrations observed in the atmosphere, a suite of gases at different concentrations covering more than the expected atmospheric range are used to characterise instrumental changes over varying gas concentrations. This is also referred to as instrumental non-linearity. The standard and calibration gases have been given certified values for CO_2 , CH_4 , and CO at the World Calibration Centre, Empa (Swiss Federal Laboratories for Materials Science and Technology; <https://empa.ch/web/s503/wcc-empa>). Empa uses the WMO calibration scale, signifying that the CRDS instrument at Empa was calibrated with calibration gases from the National Oceanic and Atmospheric Administration (NOAA; <http://www.esrl.noaa.gov/gmd/ccl/>; shown in Figure 5), the institution that created the

scale. The assignment of standard and calibrant gas values to the WMO calibration scales means that CO₂, CH₄ and CO measurements on the CRDS are comparable to other sites linked to the WMO scales. Instrumental “non-linearity correction” along with the instrumental drift correction are applied through the GCWerks software (<http://gcwerks.com>). Both the standards and calibration gases are linked to WMO scales for CO₂ (x2007), CH₄ (x2004A), and CO (x2014A).

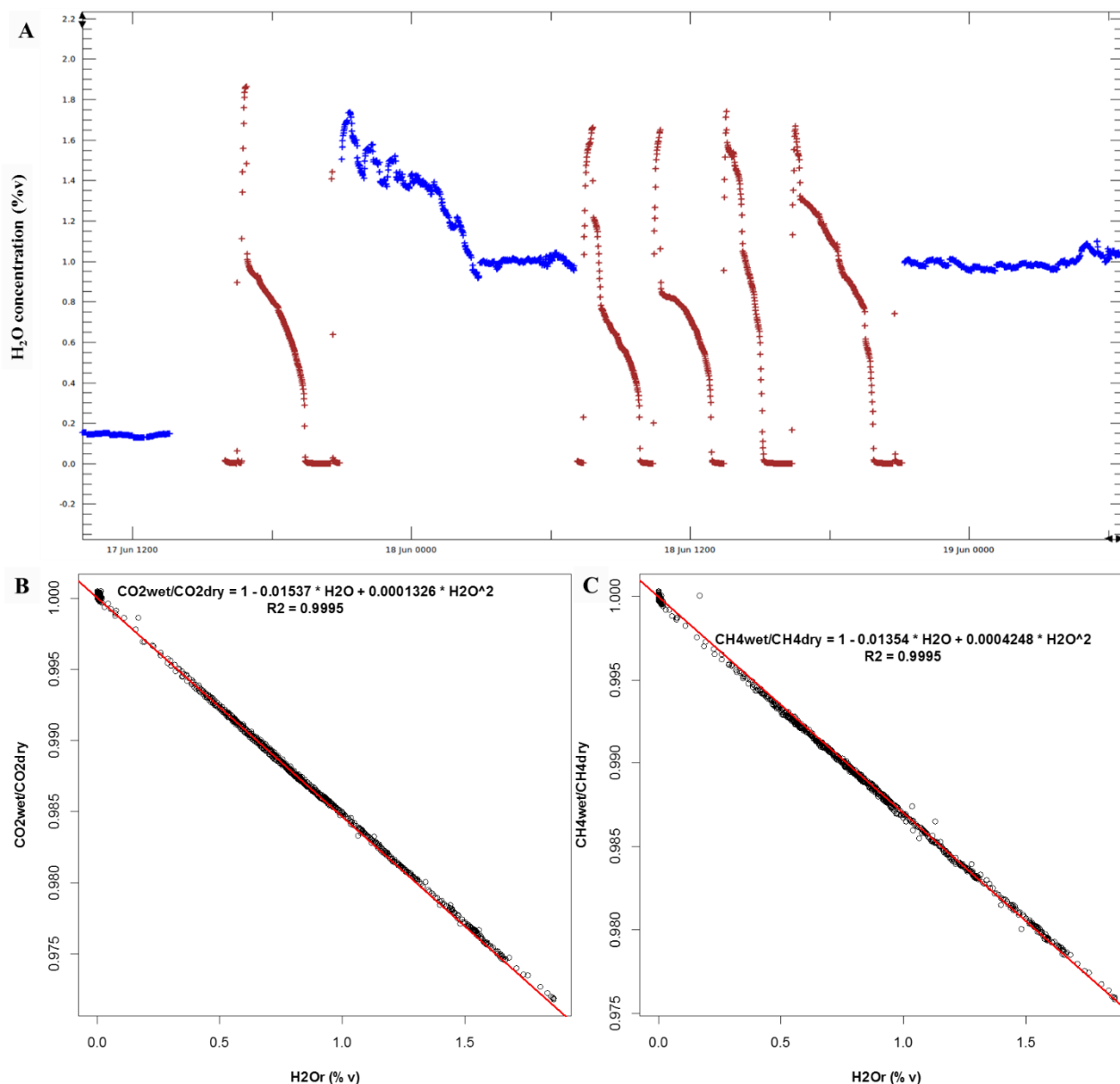


Figure 4: A) Water droplet tests undertaken at Tacolneston (blue points represent air sampled from the multiple inlets and red points are the dry standard used for the test) and the water correction applied at the station for B) CO₂ and C) CH₄.

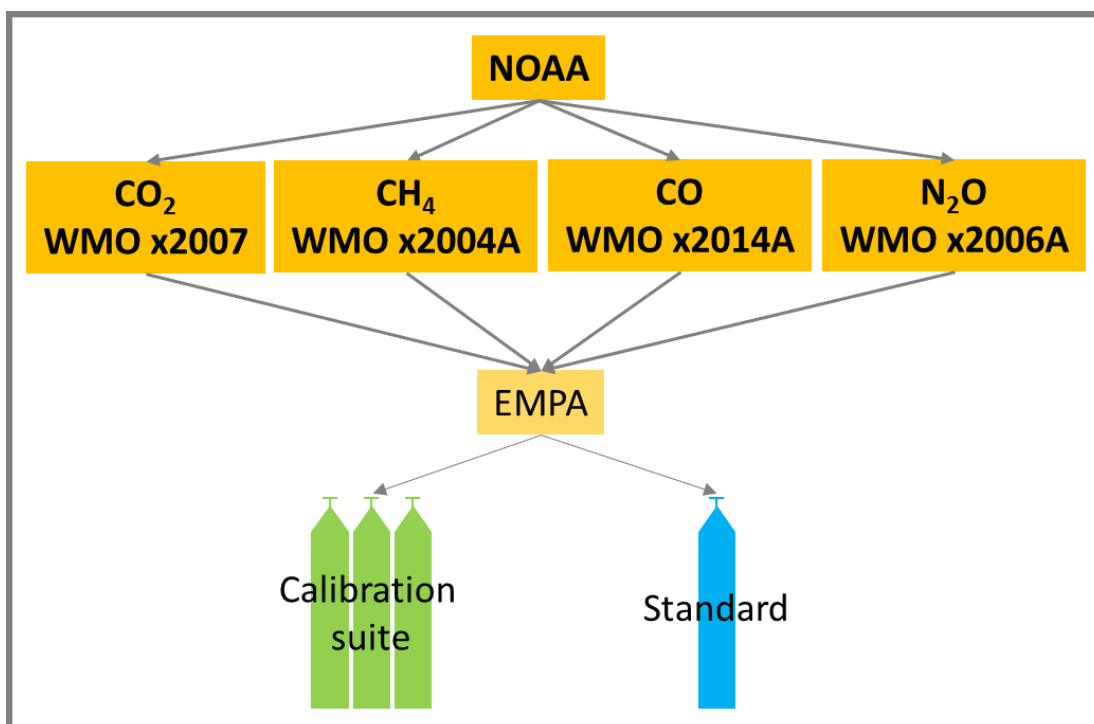


Figure 5: Schematic of certification of CO₂, CH₄, CO, and N₂O values for standard and calibration gases for CRDS instruments. The primary scale was created by the National Oceanic and Atmospheric Administration (NOAA).

	CO ₂	CH ₄	CO
Tacolneston ¹	0.03 ppm	0.13 ppb	GC-MD
Ridge Hill ¹	0.01 ppm	0.13 ppb	-
Bilsdale ²	0.01 ppm	0.13 ppb	1.3 ppb

Table 3: CRDS precision, based on the standard deviation of repeated measurements of standard gas, run for 20 minutes daily.¹ Uses a G2301 (CO₂ and CH₄); ² Uses a G2401 (CO₂, CH₄ and CO).

Good comparability between measurements within the UK DECC network is essential. To help assess this comparability in CO₂, CH₄, and CO, CRDS systems within the UK DECC network take part in the GAUGE intercomparison programme. This involves measuring three cylinders on the CRDS at each site without knowing the concentrations of the gas within the cylinders and reporting values to the programme. The station CO₂, CH₄ and CO values are then compared to the certified values given by the calibration laboratory, with the aim of achieving the WMO compatibility goals for CO₂ (± 0.1 ppm), CH₄ (± 2 ppb), and CO (± 2 ppb) (World Meteorological Organization, 2012).

2.2.2. Off-Axis Integrated Cavity Output Spectroscopy

In situ OA-ICOS (Los Gatos Research (LGR) N₂O-CO 30-EP Analyser) is used to measure high frequency (~1 second) CO and N₂O concentrations over a number of differing sampling heights (TAC: Table 1). As per the CRDS instruments (section 2.2.1.), N₂O, CO, and H₂O gases absorb near-infrared light uniquely at different wavelengths. OA-ICOS works by sweeping a laser through a cavity filled with gas (Figure 6) off-axis to

a detector. Highly reflective mirrors (Figure 6) provide a long optical pathway within the 408 cm³ cavity. Unlike CRDS (section 2.2.1.), OA-ICOS measures absorption of the laser light rather than the decay in light intensity within the cavity.

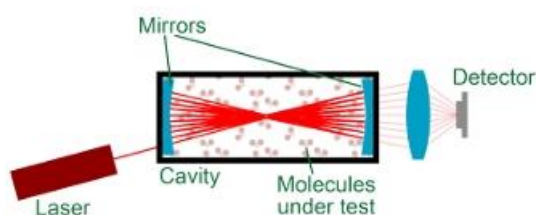


Figure 6: Schematic of Off-Axis Integrated Cavity Output Spectroscopy (American Laboratory, 2012).

The OA-ICOS sampling scheme is similar to the CRDS, including a branched secondary line from the primary inlet and filters to prevent airborne particles from entering the analyser (Figure 2). An automated sample module (Earth Networks) is used to switch between each inlet height sequentially for 20 minutes, resulting in all three inlet heights being sampled each hour. N₂O and CO are reported as dry concentrations and so the wet whole air samples require drying using a Nafion drier (Figure 7). Air is dried in the Nafion using two concentric tubes (Figure 7) with the sample gas passing through the central tube, made of a membrane that allows H₂O to pass through it, in one direction, whilst a counter-purge gas of the sample gas at a lower pressure is passed through the outer tube in the opposite direction. Due to the counter purge gas being at a lower pressure than the sample it creates a H₂O concentration gradient; thus, H₂O passes through the membrane into the counter-purge gas and the sample is dried (Figure 7).

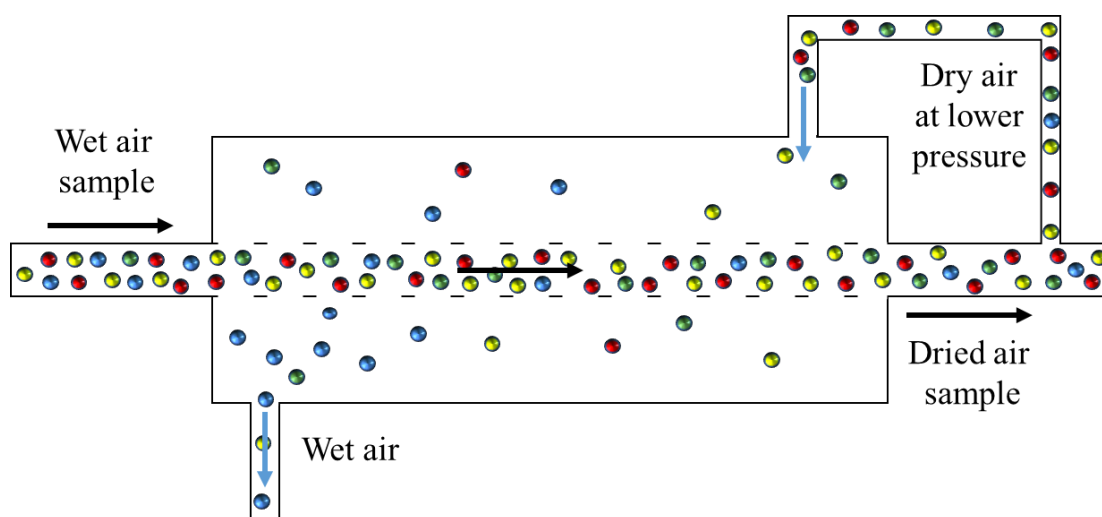


Figure 7: Schematic of a Nafion drier used to dry whole air samples using dry sample air at a lower pressure.

Standard and calibration gases are used to correct for linear and nonlinear drift in the same manner as the CRDS (see section 2.2.1. for more information), using cylinders

calibrated at the World Calibration Centre, Empa (<https://empa.ch/web/s503/wcc-empa>) for CO and N₂O. The OA-ICOS will take part in the GAUGE intercomparison programme to help assess this comparability in N₂O and CO, with the aim of achieving the WMO compatibility goals for N₂O (± 0.1 ppb), and CO (± 2 ppb) (World Meteorological Organization, 2012).

2.2.3. Gas Chromatography-Electron Capture Detection

In situ GC-ECD (Agilent 7890A GC) is used to measure the biogenic/anthropogenic gas N₂O, and anthropogenic gas SF₆ in ambient air 72 times per day from dried whole-air samples. GC-ECD air samples are obtained from one specific inlet (Table 1), generally ~100 m above ground surface, apart from at MHD (10 m). Multiple inlets at different heights are not sampled on this instrument because the sampling frequency is too low. The sample module for the GC-ECD (Figure 8) is custom-made for each instrument and comprises of a multi-position valve, a sample loop held within a temperature controlled box and a sample pump. As GC-ECD systems do not deal well with H₂O, air samples need to be dried. A Nafion drier is used to achieve this using dried zero-air (atmospheric air with H₂O, CO₂, CH₄ and CO removed) as the counter-purge gas (Figure 9).



Figure 8: GC-ECD sample module (left), containing Nafion drier, valves and electronics, and the GC oven and ECD detector (right) (Met Office, 2012).

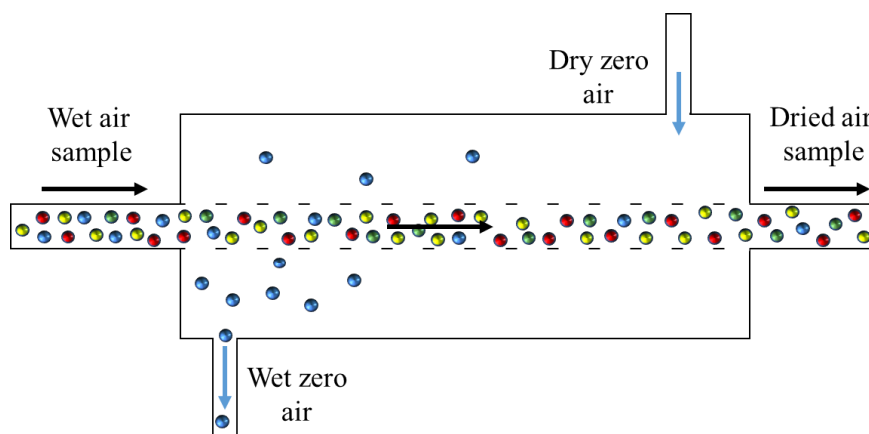


Figure 9: Schematic of a Nafion drier used to dry whole air samples using dry zero air.

The multi-position valve within the sample module (Figure 8) directs air or calibration gas (see below) through a Nafion drier (Figure 9), with a zero-air counter purge, to the sample loop. The sample loop (8 ml) is continuously flushed (volumetrically a minimum of 5 times) before the sample flow is stopped and the sample pressure in the loop is allowed to decay to ambient pressure before being injected into the columns of the GC using a carrier gas. The columns within the GC-ECD system are used to separate N_2O and SF_6 chromatographically, whilst allowing other interfering atmospheric gases to be removed. N_2O and SF_6 detection occurs in the micro-ECD when the analytes pass between a radioactive beta-emitter (^{63}Ni) and reduce the current at the anode by absorbing the electron emissions (Figure 10).

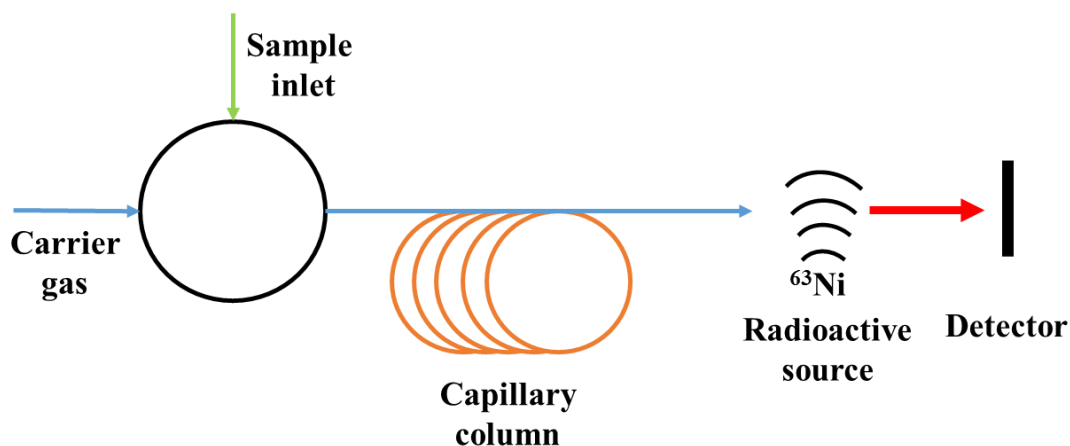


Figure 10: Schematic of an electron capture detector (ECD).

Air measurements are calibrated by ratio comparison to an average of two bracketing calibration standards. Samples (air and standard) are automatically injected by a computer-controlled sampling module at 10 minute intervals – giving a fully calibrated ambient air measurement every 20 minutes. The calibration standard, of near atmospheric concentration, is used to correct for short term instrumental drift. Standard

gases have been given certified values for N₂O and SF₆ at MHD (Figure 11) using the Scripps Institute of Oceanography calibration scales as part of AGAGE (<https://agage.mit.edu>). Precision, a measure of the repeatability of the standard on the GC-ECD, is shown in Table 4. To correct for changes in a larger span in concentrations of N₂O and SF₆, a dynamic dilution test is conducted annually. This involves using a high concentration calibration gas diluted down using zero-air to produce varying concentrations of N₂O and SF₆. The response from this test can be used to characterise instrumental non-linearity and correct for this within the GCWerks software used to control and interpret data.

	CO	N ₂ O	SF ₆	H ₂
Mace Head	0.2 %	0.05 %	0.17 %	0.6 %
Tacolneston	0.7 %	0.05 %	0.3 %	0.3 %
Ridge Hill	-	0.04 %	0.5 %	-
Bilsdale	CRDS	0.06 %	0.5 %	-

Table 4: Precision the GC-ECD/MD systems in the UK DECC network sites, calculated from the standard-standard ratios of concurrent standard analysis.

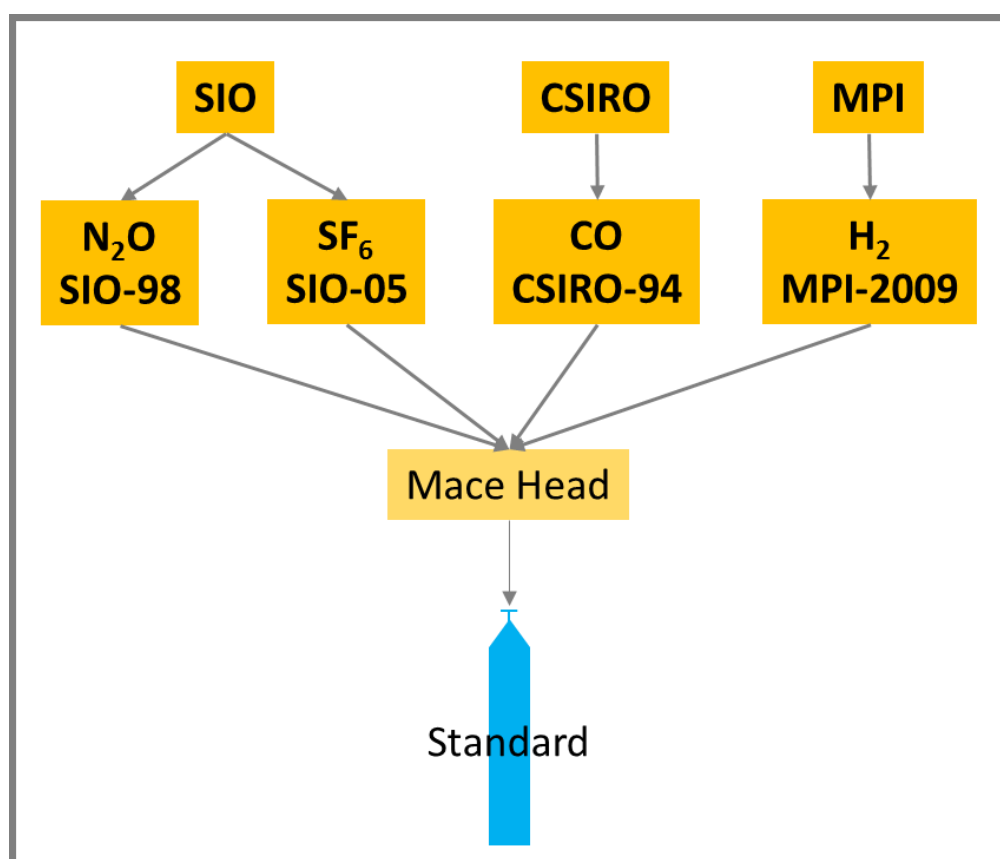


Figure 11: Schematic of GC-ECD/MD standards calibration for N₂O, SF₆, CO, and H₂. Creators of primary scales include Scripps Institute of Oceanography (SIO), Commonwealth Scientific and Industrial Research Organisation (CSIRO), and the Max Planck Institute (MPI).

As for the CRDS, the GC-ECDs within UK DECC Network also take part in the GAUGE intercomparison programme to assess the comparability between the sites and establish

if the sites are within the WMO guidelines for N₂O (±0.01 ppb) and SF₆ (±0.02 ppt) (World Meteorological Organization, 2012).

2.2.4. Gas Chromatography-Multi Detection

In situ GC-MD is comprised of two analytical systems: A GC-ECD (already described in section 2.2.3.) and a Reduction Gas Analyser (RGA, Anagas Peak Performer 1) described below. One sampling module is used with two sampling loops, directing air or calibration samples into each analytical system simultaneously. The RGA analytical system is used to measure the biogenic/anthropogenic gases CO and H₂ in ambient air 72 times per day from dried whole-air samples. RGA air samples are taken from a single inlet (Table 1); 100 m above ground surface at TAC and 10 m at MHD. As the RGA shares the front end system with the GC-ECD system, air samples are dried using a Nafion drier, using dried zero-air as the counter-purge gas (Figure 9).

After samples have been injected, they pass through a heated column to separate the two gases from other abundant atmospheric gases (Figure 12). The sample then travels over a heated mercuric oxide bed, which transforms CO and H₂ into CO₂ and H₂O, as well as producing mercury vapour. This vapour is then determined using ultraviolet photometry downstream of the reaction bed (Figure 12). As per the GC-ECD instruments, air samples are calibrated using bracketing standards. Standards are calibrated through MHD under the AGAGE programme (Figure 11). RGA precision is shown in Table 4. Dynamic dilution tests are performed yearly to account for instrumental non-linearity (see section 2.2.3.).

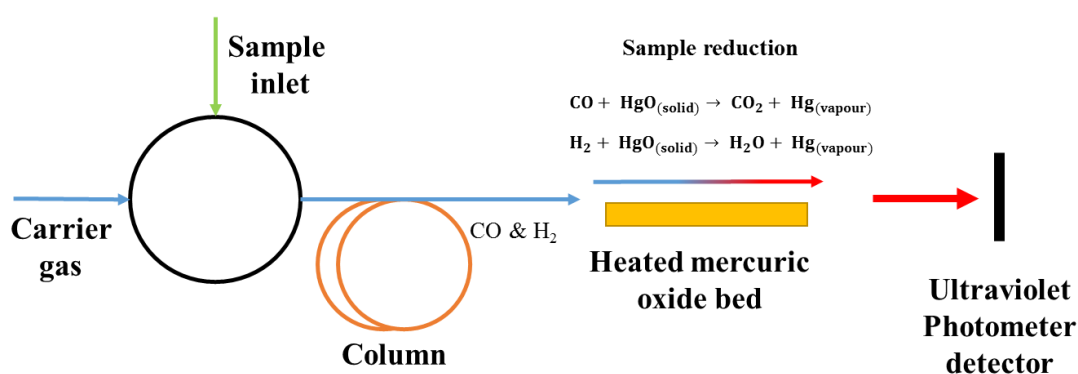


Figure 12: Schematic of a reduction gas analyser (RGA).

The GC-MD at TAC is part of the GAUGE intercomparison programme to assess the comparability between the sites and establish if the sites are within the WMO guidelines for CO (±2 ppb) and H₂ (±2 ppb) (World Meteorological Organization, 2012).

2.2.5. Medusa Gas Chromatograph-Mass Spectrometer

In situ Medusa GC-MS is used to measure HCFCs and HFCs, which are interim or long-term alternatives to CFCs now restricted by the Montreal Protocol, along with other hydro/halocarbons, halons, PFCs, SF₆, NF₃ and trace CFCs; the majority of which are regulated under the Montreal or Kyoto Protocols. These measurements are carried out at TAC, UK and MHD, Ireland. Table 2 lists the major gases being measured at TAC and MHD by the Medusa GC-MS.

The Medusa GC-MS system is a sampling and pre-concentration system. Briefly, the system comprises of six valves, two Nafion driers (Figure 9; zero-air counter-purge), two adsorption traps that are cooled and heated between -150 and 100 °C and three chromatographic columns. The traps and columns are used to remove the most abundant atmospheric gases (i.e. N₂, O₂, H₂O, CO₂ and CH₄) and pre-concentrate the lesser abundant atmospheric gases to detectable levels (Figure 13). The gas sample is then passed to the GC-MS for detection. Within the MS, the analyte is ionised by electron impact to produce positive ion fragments. The ions are accelerated by a statically charged plate before being deflected by rapidly varying (scanning) the electric and magnetic fields of a quadrupole (two positively and two negatively charged magnets in sequence). The resultant beam of ions is detected by an electron multiplier which enables detection of compounds according to their fragment ion masses. The lighter the ion, the more it is deflected. The amount of deflection also depends on the number of positive charges on the ion, resulting from the ionisation process with more highly charged ions being deflected more. Different compounds exhibit different fragmentation patterns which allows for more selective analysis of the chromatograms.

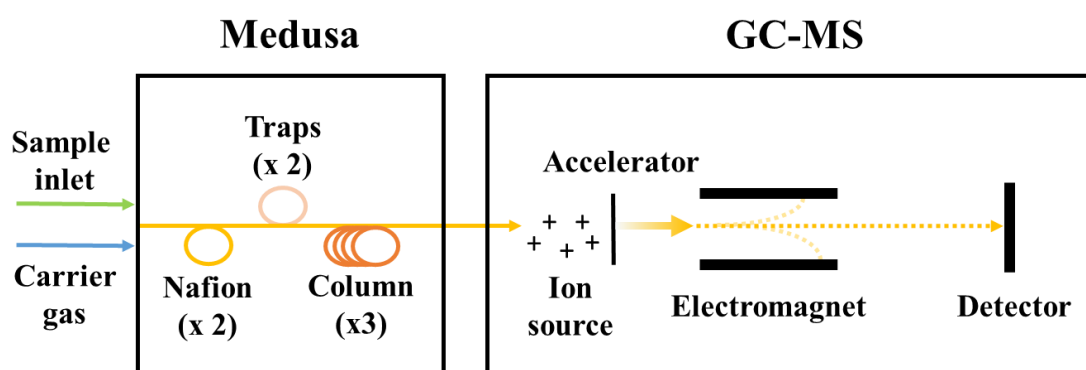


Figure 13: Schematic of a Medusa Gas Chromatograph-Mass Spectrometry (Medusa GC-MS).

Calibration of the Medusa GC-MS is achieved using two different gas standards: tertiary standards (J-tanks) and quaternary standards (H-tanks). J-tanks are cylinders filled with whole air at Trinidad Head, California, USA and calibrated at Scripps Institute of Oceanography (SIO), the primary calibration centre. These cylinders are measured

weekly on site by the Medusa GC-MS to assign values to the H-tanks, or the working standards. H-tanks are cylinders filled with whole air at the MHD research station (Figure 1). H-tanks are measured every second run on the Medusa GC-MS to ensure accurate calibration of all species, giving calibrated air samples every two hours. Medusa GC-MS precisions for each compound are given in Table 2.

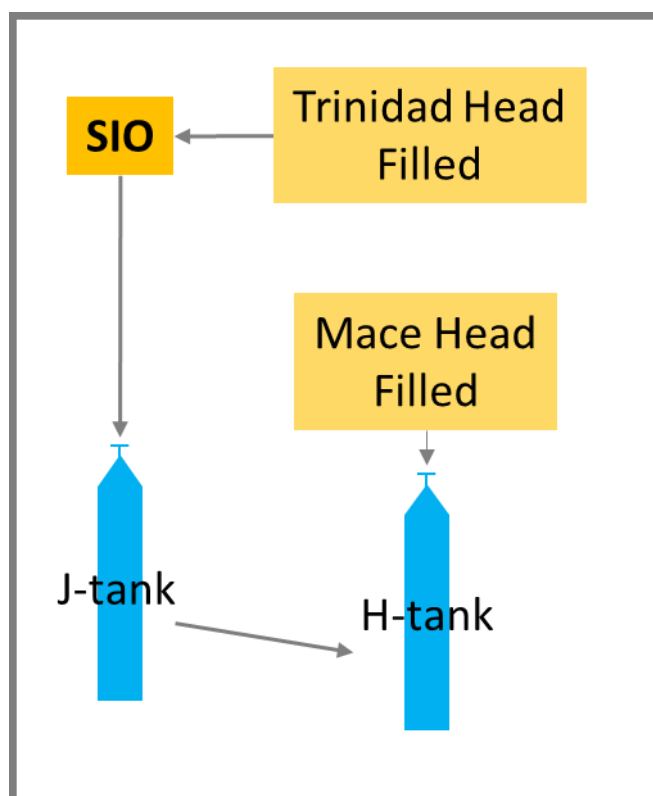


Figure 14: Schematic of Medusa GC-MS standards (H- and J-tank) calibration. Creators of primary scale are Scripps Institute of Oceanography (SIO).

The Medusa GC-MS are involved with the NOAA/GMD intercomparison programme, involving exchanges of tanks (checking absolute calibration) and examination of differences between the AGAGE and GMD in situ instruments at common sites. MHD undergoes a regular ‘system and performance’ audit by the World Calibration Centre-Empa in agreement with the WMO/GAW quality assurance system [WMO, 2007]. MHD has a dual status as a WMO/GAW research and monitoring ‘global’ station and as an EMEP supersite. At the end of each assessment period a report is produced that summarises the assessment of the MHD GAW station in general, as well as the surface CH₄, CO₂, N₂O, CO and O₃ in particular. This report is distributed to all involved institutes, the Irish GAW Country Contact and the World Meteorological Organization in Geneva. MHD was audited in 1996, 1998, 2002, 2005, 2009 and 2013.

2.2.6. Data review: quality assurance and control

Data from the network are reviewed over two different time periods for quality assurance and control purposes: daily to weekly reviewing of individual site data by the member of staff responsible for the site and monthly overall network data review by all members of the network group. Daily to weekly reviewing of data is done on raw or one-minute mean data and follows well documented protocols. Firstly, chromatograms and instrumental parameters measured during sampling on individual instruments are reviewed to look for systematic biases and anomalous results. This process allows the elucidation of issues with the data, as well as potential issue that may be developing (e.g. the aging of a filament or ion source in the GC-MS or changes in the Picarro critical orifice, which can be a sign of imminent pump failure). Instrument precision is initially reviewed over time by monitoring the standard gas concentrations for anomalies. Air data are then reviewed, looking at different ancillary and instrumental parameters in conjunction with gas concentrations to check for further anomalous data.

On a monthly basis, the data from the entire network are reviewed by members of the network group to compare sites within the network with the baseline station (MHD) and to look to differences between sites. Potential issues not previously noted can be investigated using ancillary and instrumental parameters, as well as air history maps produced on a two-hourly basis using the atmospheric transport model outlined in section 3.2.

3. Atmospheric Modelling

This section describes how we understand and estimate emissions (model) by investigation of where the air has come from, and where it has passed over, as it travels to the observation station where the atmospheric measurements are recorded. We use the same three-dimensional time-varying description of the meteorology that is used by the UK Met Office to understand our current weather and from which weather forecasts are produced. Wind speed and wind direction that vary in time, location and height, along with other important weather variables such as ‘boundary-layer height’, surface heating, atmospheric temperature and pressure, are extracted from this model and are used as input to the Met Office’s Atmospheric Transport Model, called NAME. This model describes how pollution moves and dilutes in the atmosphere.

3.1 Meteorological Model

The time-varying three-dimensional weather data comes from the Met Office operational weather forecast called the Unified Model (UM). The UM is run every six hours and it predicts the weather globally. It is a grid-based model and currently it has a global horizontal resolution of 12 km and a UK resolution of 1.5 km and has a vertical resolution of tens of metres near to the ground and then increasing with height. It is under constant review and improvement and is one of the world’s leading weather forecast models.

3.2 Atmospheric Transport Model

NAME (Numerical Atmospheric dispersion Modelling Environment) is the UK Met Office’s particle atmospheric transport model [Jones *et al.*, 2007]. It is a world leading model that is operationally employed by the UK government to respond to a very wide range of atmospheric dispersion applications including volcanic ash, dust, fire plumes, nuclear accidents and biological diseases such as foot and mouth virus [Gloster *et al.*, 2007; Leadbetter *et al.*, 2011, Ryall *et al.*, 1998, Witham and Manning, 2007]. It is actively developed and improved and is widely used across the UK research community. It principally uses the Met Office UM time-varying, three-dimensional meteorology, but it can also use three-dimensional weather information from other meteorological centres such as the ECMWF (European Centre for Medium Range Weather Forecasting). NAME follows theoretical particles in the modelled three-dimensional meteorology, by following many thousands of such particles you gain an understanding of the likely spread and dilution of pollution in the atmosphere from different emission sources.

NAME is run backwards in time to estimate the previous 30-day history of the air before it arrives at *each measurement height at each observation station* in the UK DECC

network (currently; Mace Head [MHD], Tacolneston [TAC], Ridge Hill [RGL], Bilsdale [BSD]) for each 2-hour period from 1989 to the current day (see Figure 15 for two examples). Global resolution time-varying three-dimensional meteorology is used to drive NAME. UK Met Office Unified Model (UM) data are used from Aug 2002 – current day, its global horizontal resolution has improved from 40 km in 2002 to 12 km in 2017 (and 1.5 km over the UK from 2013), the vertical resolution has also increased from 31 levels in 2002 to 59 levels in 2015. From 1989 to Aug 2002 ECMWF (European Centre for Medium range Weather Forecasting) ERA-Interim (Re-Analysis) data, with a ~80 km horizontal resolution and 37 vertical levels, are used. The ERA-Interim data are preferred over older UK Met Office data (pre-Aug 2002) as it uses more up-to-date physics, is run at a higher resolution and, as it is a re-analysis, it does not change over time. The horizontal resolution of the NAME output is set at 25 km throughout (the Lagrangian nature of NAME means that this is independent of the resolution of the meteorology, higher resolution meteorology simply improves the description the flow) and estimates the surface (0-40 m) impact of a large regional domain stretching from North America to Russia (-98° to 40° longitude) and North Africa to the Arctic circle (10° to 79° latitude) and extends from the ground to more than 19 km vertically. The three-dimensional locations and times when the model particles leave this regional domain are also recorded and used in the emission estimation process to improve the background (baseline) estimate.

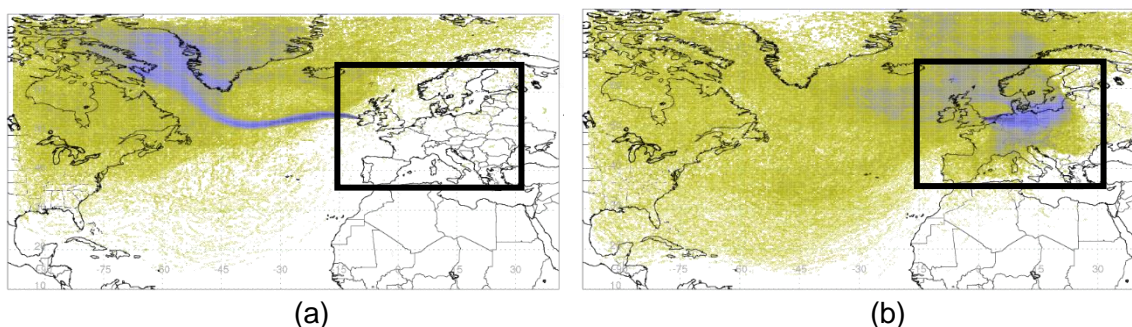


Figure 15: Examples of 2-hour air history maps derived from NAME (a) for MHD, baseline period (b) for TAC, regionally polluted period. The air-history maps describe which surface areas (0-40m) in the previous 30-days impact the observation point within a particular 2-hour period. The black box indicates the geographical domain used for the emission estimates.

The NAME model is three-dimensional, therefore it is not just surface to surface transport that is modelled. The NAME particles are released in a 20 m vertical line centred on the height of the observation. An air particle can travel from the surface to a high altitude and then back to the surface. However only those times when an air particle is within the lowest 40 m above the ground will it be recorded in the ‘air-history’ maps. Particles leaving the regional domain (shown above) at all elevations are recorded to

help improve the background (baseline) estimate. For each 2-hour period thousands of inert model particles are used to describe the atmospheric dispersion. Running NAME backwards is very computationally efficient as every modelled particle has a direct impact on the air history maps produced.

3.3 Estimating Greenhouse Gas Emissions using Observations

The UK and European emission estimates are calculated using a sophisticated inversion methodology referred to as InTEM (Inversion Technique for Emission Modelling) and described in detail in *Manning et al.*, [2011], and previously in *Manning et al.* [2003]. InTEM finds the geographical emission distribution map that, when diluted through atmospheric mixing produces modelled time-series' at each of the observation stations that best matches the actual observations recorded. The uncertainties in the observations and the modelling are taken into consideration when matching the modelled and observed time-series. Times when the model or the observations are more uncertain are less important, through being de-weighted in the inversion, compared to those times when both the model and the observations are considered to be more certain.

The InTEM methodology is flexible in that where observations (and uncertainties) are available from other additional monitoring stations they can be readily incorporated into the inversion system to better quantify, spatially and temporally, the estimated emissions. This flexibility has been readily demonstrated in our work within the EU project, InGOS (using data from more than twenty stations across Europe), and in the NERC (University) project, GAUGE (using data from two additional UK towers, observations from a ferry and an aircraft, and five surface stations across East Anglia). The Met Office is one of the five inversion modelling groups involved in InGOS. The work within GAUGE and InGOS clearly demonstrates the need for measurements that are robust and comparable. Any biases in any of the measurement systems leads to errors in the emission estimation results. One of the key points is that all observations from across the UK DECC network are regularly and systematically inter-compared to ensure an un-biased robust data set of observations.

The observations from each station are averaged (where the frequency of observation is greater than two hours) over each two-hour period and the standard deviation of the observations over the two hours is used as part of the observational uncertainty. If there are fewer than three observations from a station within a two-hour period, the two time periods either side of this time period are considered in determining the observational

uncertainty. At frequent intervals, the observation systems measure specific tanks of air ('standards') to assess how the raw instrument signal is changing over time. We also use these multiple measurements of the standard to calculate individual measurement precision, which can then be applied to the air measurements (and makes up part of the observational uncertainty).

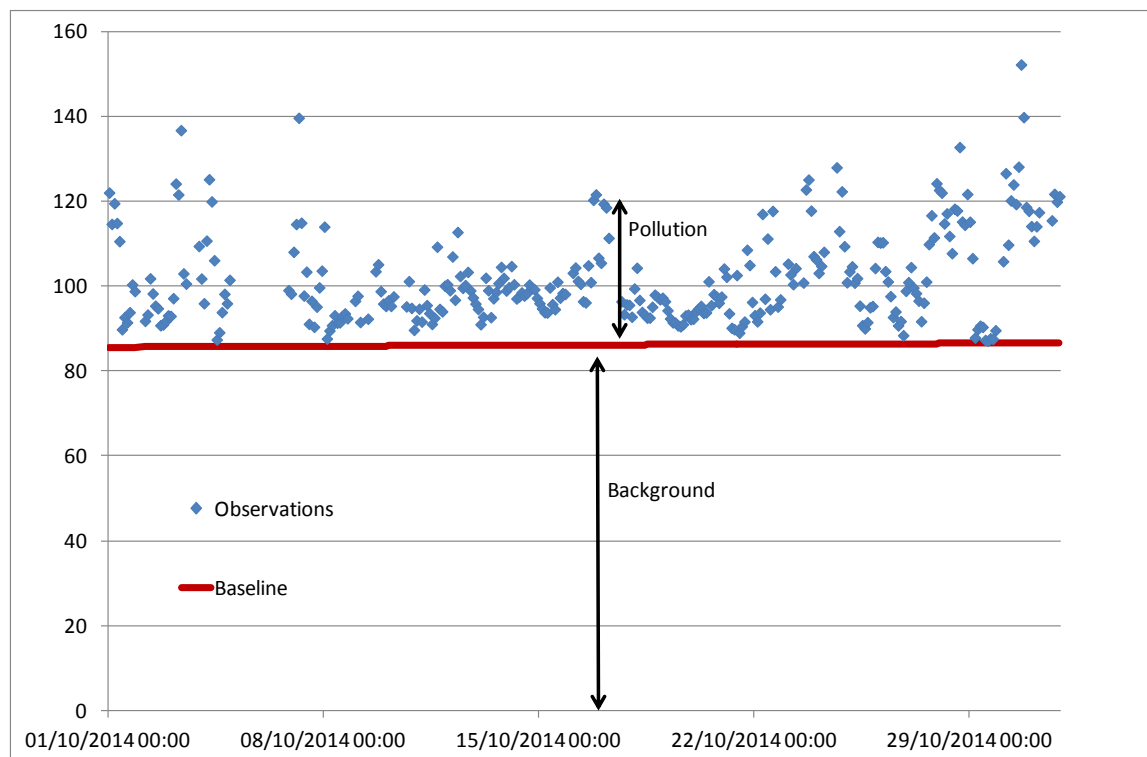


Figure 16: Time-series of observations of HFC-134a (greenhouse gas used in car air-conditioning) at a measurement site in the UK. The blue dots are the actual observations (in ppt). The red line is the estimated Northern Hemisphere background concentration (baseline). The difference between the measured concentration and the background concentration reflects the amount of regional pollution at this point in time.

The observed concentrations are comprised of two distinct components; (a) the Northern Hemisphere background concentration, referred to as the baseline, that changes only slowly over time, and (b) rapidly varying perturbations above the baseline (see Figure 16). These observed deviations above background (baseline) are assumed to be caused by emissions on regional (European) scales that have yet to be fully mixed on the hemisphere scale. The magnitude of these deviations from baseline and, crucially, how they change as the air arriving at the stations travel over different areas, is the key to understanding where the emissions have occurred. The inversion system considers all of these changes in the magnitude of the deviations from baseline as it searches for the best match between the observations and the modelled time-series. The best match will occur when the actual emissions most closely match the estimated modelled emissions.

The observation time-series, together with the NAME model output predicting the recent history and dilution of the air, are used to estimate the geographic map of emissions. The minimisation technique, Non-Negative Least Squares Fit [Lawson and Hanson, 1974], is used to derive these regional emission estimates based on a statistical skill score (cost function) comparing (best-fitting) the observed and modelled time-series at each observation site. The cost function is 'Bayesian' (i.e. improving a prior emission distribution through additional knowledge provided by the observations) and all of the uncertainties are defined as Gaussian (the statistical distributions are symmetric about the mean value, with an equal likelihood of being above or below the mean (truncated at zero)). The mathematical equation is given below.

$$C = (M'e' - y)^T R^{-1} (M'e' - y) + (e' - e'_p)^T B^{-1} (e' - e'_p)$$

Or

$$C = \left(\begin{array}{c} \textit{Mismatch between} \\ \textit{Modelled timeseries and} \\ \textit{Observations} \end{array} \right) + \left(\begin{array}{c} \textit{Mismatch between} \\ \textit{Emission solution and} \\ \textit{Prior estimate} \end{array} \right)$$

Where,

C = Cost function score (the aim is to minimise this score)

M' = Dilution matrix from NAME

e' = Estimated emission map

y = Measurements

R = Observation – Model uncertainty matrix

e'_p = Prior estimate of the map of emissions

B = Uncertainty of the prior estimate.

This equation is in two parts. The left hand part describes the mismatch (fit) between the modelled time-series and the observed time-series at each observation station. The right hand part describes the mismatch (fit) between the estimated emissions and any prior estimated emissions that might be available. In this work, because we want to estimate emissions that are independent of the inventory process, we routinely remove this second part of the equation (by making the uncertainty of the prior extremely large). If we did not do this then the emissions we estimated may not be independent of the current inventory estimates (if the inventory, or any information used to derive the inventory, helped inform the prior) and therefore this would not be an independent verification process, rather a process to estimate the emissions given all available

knowledge. In theory an independent prior could be used, however in practice all of the inventories available use similar statistics, e.g. population, and so they are not totally independent of the UNFCCC estimates. In specific circumstances we can include the right hand part of the equation to investigate the impact of using all of the available knowledge. The uncertainty matrix, R , is a critical part of the equation. It describes, per two-hour time period, the uncertainty of the model and the observation at each time. The different components of the uncertainty matrix are described in a later section.

The aim of the inversion method is to estimate the spatial distribution of emissions across a defined geographical area. The emissions are assumed to be constant in time over the inversion time period. The inversion time period depends on the number of measurements that are available. If there are only measurements from the MHD station (1989 – 2011), then the inversion time window is set to be three years. If there are measurements from two or more stations, then the inversion window is set to one year (from Aug 2012 onwards). In order for InTEM to estimate robust emissions of the UK it needs to be informed by sufficient information from the UK. Since MHD, on the west coast of Ireland, only sees the UK 20-30% of the time, it takes several years worth of data to build up sufficient information, hence the three-year window. More stations, especially those based in the UK, add significant quantities of information about UK emissions to enable shorter time periods to be used. For the special case of methane (CH_4 , N_2O and SF_6), where there are measurements available from four or more stations (2012 onwards), the inversion time period is set to 6 months. Assuming the emissions are invariant over long periods of time is a simplification, but is necessary given the scarcity of the observations available. In order to compare the measurements and the model time-series, the latter are converted from air concentration [g m^{-3}] to the measured mole fraction (e.g. parts per billion [ppb]) 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 $14^\circ \text{ W} - 31^\circ \text{ E}$ longitude and $36^\circ \text{ N} - 66^\circ \text{ N}$ latitude and is shown as the black box in Figure 15. The smaller inversion domain covers all of Europe and extends a reasonable distance into the Atlantic. It is good for the inversion domain to be smaller to ensure re-circulating air masses (air that leaves the domain but then re-enters at a later time) are properly represented. It is also computationally efficient to do so and also it has little impact on the UK estimates because emission sources very distant from the UK have little discernible impact on the concentrations measured at the UK DECC network stations, i.e. the observed signal is too weak to be seen.

Monthly and annual estimates of emissions per gas per geographical region (UK, Irish, North-West Europe [NWEU]) are reported by calculating the mean of all of the solutions that contain that month or year within the solved-for time period (e.g. any three-year inversion period that encompasses the year in question are included in the statistics for that year). An uncertainty range is estimated for each month or year for each gas and geographical region by calculating the maximum (therefore a conservative estimate) of the corresponding uncertainties. The inversion results will be compared to available inventories. Figure 17 shows an example of the time-series of emission output for the UK that is generated for methane.

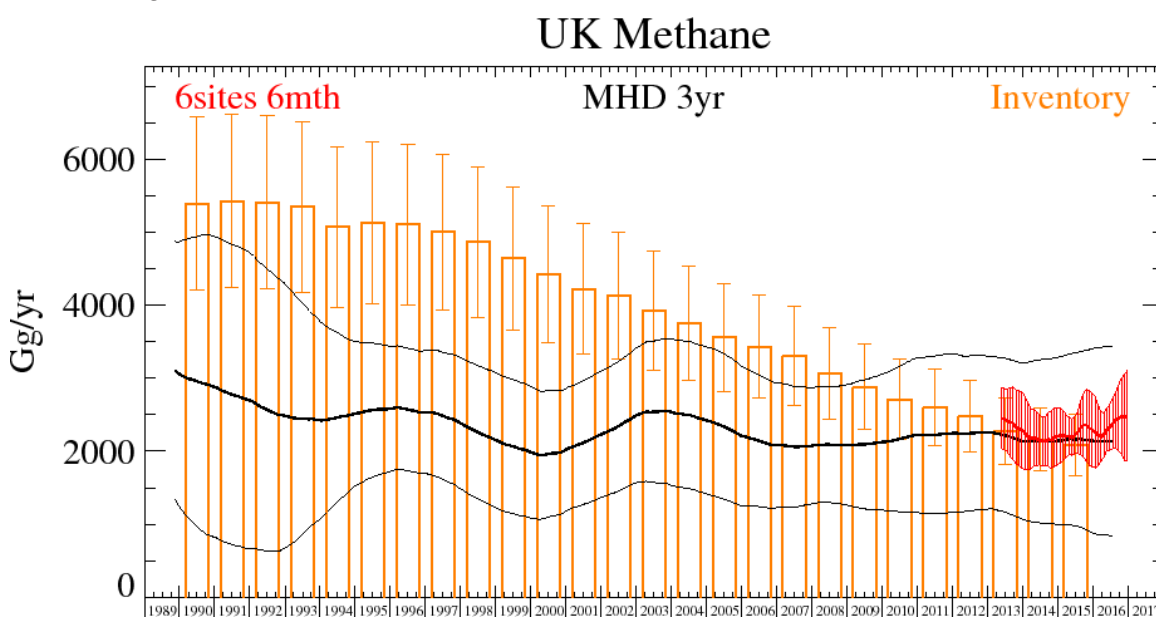


Figure 17: CH₄ emission estimates for UK (Giga gram per year). Orange columns are the UK UNFCCC submissions with uncertainty. The black line is the inversion median value for MHD-only 3-year inversions and associated uncertainty. The red line is the median value for 6-month inversions using the full UK DECC network (and HFD) and associated uncertainty.

3.3.1. Atmospheric ‘Baseline’ Northern Hemisphere Concentration

Baseline concentrations are defined as those that have not been influenced by significant emissions within the regional domain (Figure 15a) as the air travels to MHD on the west coast of Ireland. These times are when the atmospheric concentrations are well mixed and therefore are representative of the mid-latitude Northern Hemisphere background concentrations. The analysis considers the long-term trend of the monthly and annual baseline mole fractions, their rate of growth and their seasonal cycle.

A two-hour period will be classed as ‘baseline’ if it meets certain criteria assessed using the NAME air history output:

- Local emissions particularly over land do not significantly contribute.

- Populated regions do not significantly contribute.
- The US, African and Eastern European areas (see Figure 18) do not significantly contribute.
- The air mass has a dominant contribution from the north-west sector (chosen because southerly and south-westerly trajectories can be depleted in trace gas concentrations or influenced by the east coast of the USA, and easterly trajectories are influenced by Europe).

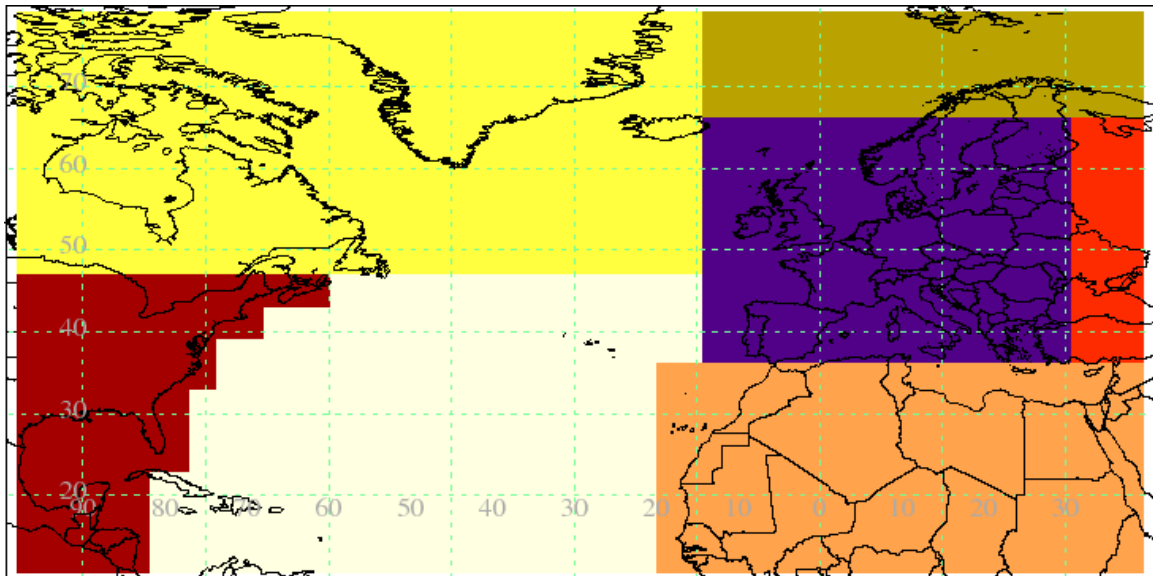


Figure 18: Purple area is the inversion domain. For baseline assessment the US is defined as the brown area, Africa the area coloured tan and Eastern Europe is red.

As an example, Figure 19 shows a three-month extract of the CH₄ observations measured at MHD. The observations have been colour coded to indicate whether, using the above classification, the air mass they were sampled from was considered baseline. For the baseline analysis all non-baseline observations are removed.

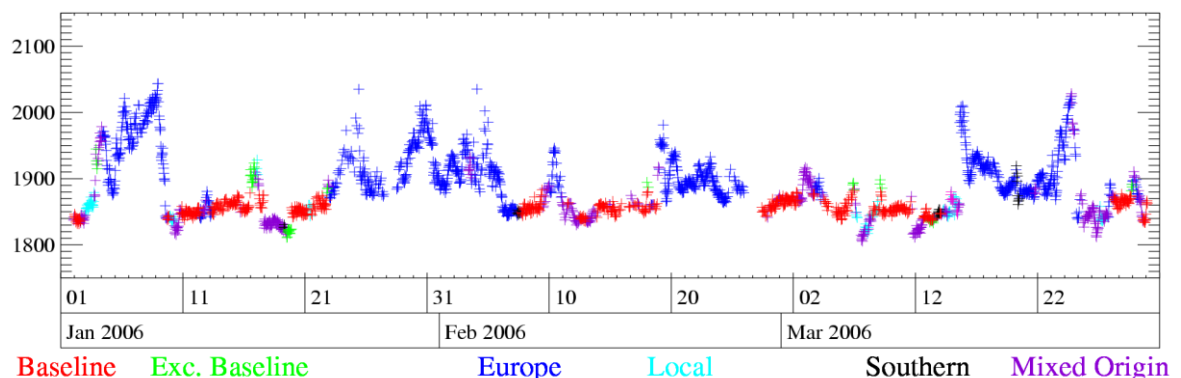
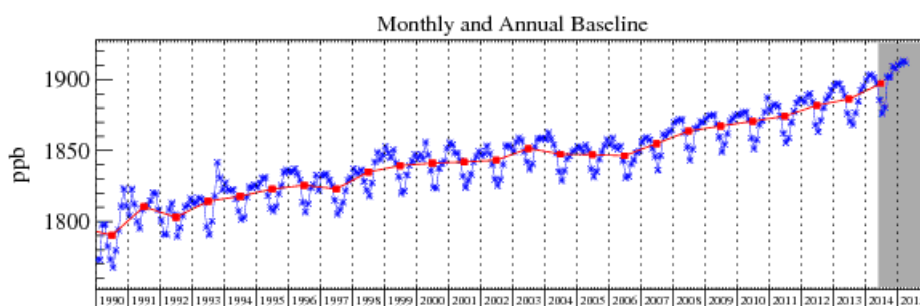


Figure 19: Example three-month time-series of Mace Head CH₄ observations (ppb) showing the impact of the baseline and non-baseline classification. The baseline observations are shown in red.

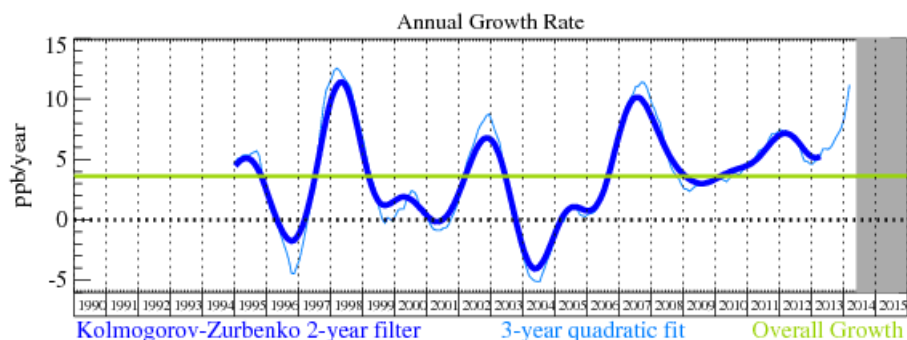
The points defined as baseline using the above methodology still have a certain level of noise e.g. from unexpected emissions (forest fires in Canada or shipping); or incorrectly modelled meteorology or transport. To capture such events the minimum observation when the baseline criteria are satisfied are used to estimate the daily baseline value. The daily values (where they exist) are fitted to a 4th order polynomial within a 180-day moving window centred on each day in turn. If there are few data points in the 180-day window the fit is linear. The uncertainty of the baseline is the root mean square error (rmse) of the fit. Each day therefore has 180 estimated baseline values. The daily baselines estimated when the current day is within 15 days of the centre of the fitted time window are averaged to estimate the baseline for the current day. The baseline uncertainty (σ_b) for the current day is the maximum of the rmse values within these 31 estimates. Days with fewer than 20 estimated daily values are defined to not have a baseline. The resulting daily time-series is then averaged up to monthly and annual values and are presented each quarter to BEIS (e.g. Figure 20a).

Monthly growth rates are estimated for each gas so that changes in the underlying trends can be identified and investigated. The daily baseline data are de-seasonalised (two methods) before a local annual growth rate is defined for each day. These daily growth rate values are then averaged per month (and per year) to estimate the annual growth rate per month (and per year) for each gas and reported to BEIS (e.g. Figure 20b).

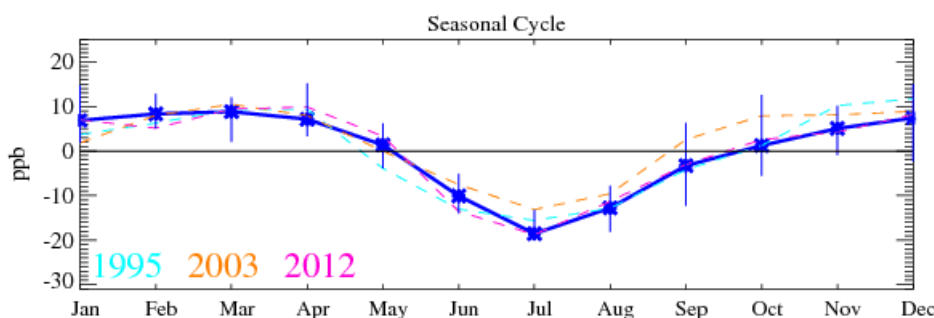
The seasonal cycle is estimated by subtracting the baseline concentration from the underlying trend value (as discussed in the previous paragraph). Estimates of the monthly seasonal cycles of each gas are also reported to BEIS (e.g. Figure 20c).



(a)



(b)



(c)

Figure 20: Example baseline analysis plot for methane (CH_4). (a) monthly (blue) and annual (red) mid-latitude Northern Hemisphere baseline mole fractions. (b) Monthly (seasonal cycle removed) baseline growth rate (blue – 2 methods) and overall growth rate (green). (c) Average seasonal cycle with year to year variability (uncertainty bars), the first (light blue), middle (orange) and last (pink) year of data are also shown. Grey shaded area indicates currently un-ratified data.

3.3.2. Solving on a Gridded Domain

In order for robust emission estimates for every area, an area being defined as a collection of the native 25 km grid-boxes, within the domain to be described, each area needs to significantly contribute to the concentrations recorded by the observation network a reasonable number of times. If the signal from an area is only rarely or poorly seen in the observation time-series then its impact on the cost function is minimal and the inversion method has little skill at determining emissions from the area. The contribution that different areas make to the observed concentration varies from area to area. Atmospheric dispersion processes mean areas that are distant from the observation sites contribute relatively little to the observations, whereas those that are in close proximity can have a large impact. In order to more equally balance the contribution from different areas, those areas that make a large contribution to the signal seen at the measurement station are split into progressively smaller areas (the smallest grid used in this work is defined as 25 km). The starting areas are defined by country boundaries or collections of countries in the case of the Benelux (Belgium, Luxembourg, the Netherlands) countries or countries further east and south of Germany. Figure 21a shows an example of the grid that results when only MHD data at three-year resolution

are used. Figure 21b shows an example grid with improved geographical resolution, particularly over the UK, when the full DECC network is used at one-year resolution. The splitting varies for each time period considered and between the different gases due to varying meteorology and the impact of missing observations respectively.

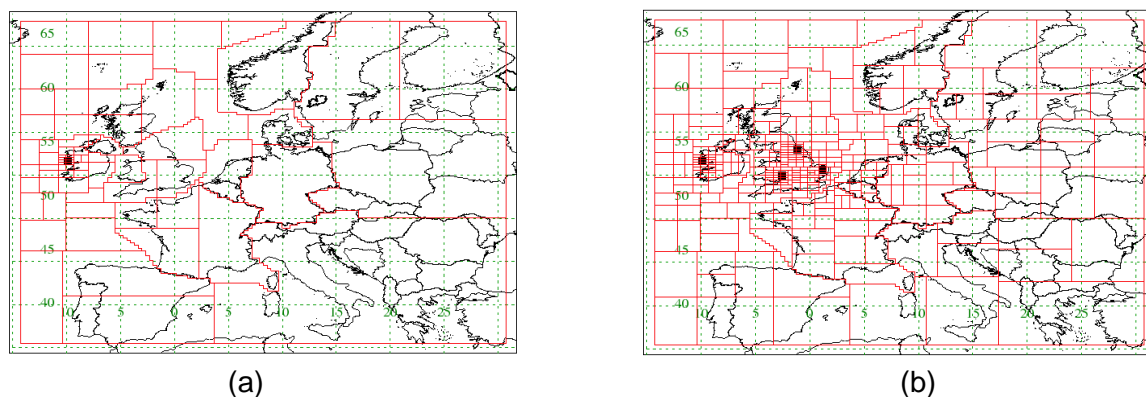


Figure 21: Example of the distribution of the different sized regions used by the inversion method to estimate regional emissions (smallest grid ~25 km): (a) MHD-only, 2-hourly resolution, 3-year inversion period (b) proposed DECC network 2-hourly resolution, 1-year inversion period.

As an integral part of InTEM, as the inversion proceeds, the grid used to estimate the emission field is refined. The best-fitting estimated emission distribution using the starting grid is calculated using the Bayesian function given above. The area in the grid that is estimated to have the most significant impact on the observation network given this emission distribution is found and this area is split in two. A new best-fit solution is then calculated and so on 8 times. This iterative re-gridding allows significant point emission sources to be better resolved and estimated.

3.3.3. Direction Specific Baseline

With the introduction of a network of stations it is necessary to define a baseline for each of the stations across the network. A baseline for each station cannot be estimated in the same way as for MHD because the other stations within the network do not receive air that is unaffected by UK (and regional) emissions. The MHD baseline cannot be used directly for each station as the different stations do not receive air from the same direction and height as MHD at the same time. For example, TAC in East Anglia may be observing air from the north at the same time as MHD is observing air from the south-west. The impact of air from the upper troposphere is also important and is variable across the network at different times. Gas concentrations usually have a vertical and latitudinal gradient due to heterogeneous global emissions, i.e. more emissions may occur in the Northern Hemisphere where the majority of the land mass (and people) can be found. It is therefore important to reflect these differing baselines within the inversion system. InTEM has a method that directly solves for adjustments to the MHD baseline

depending on the direction and height the air entered the regional modelled domain, so as these contributions differ across the network each station has a unique baseline time-series.

The direction and height the air enters the regional modelled domain is recorded for each observation time-step (e.g. 2-hour) for each station within the network. This information is interrogated and the percentage contribution from eleven different directions and heights are determined for each observation time-step for each station. The eleven directions are: WSW, WNW, NNW, NNE, ENE, ESE, SSE, SSW (all below 6 km); From the south 6-9 km; From the North 6-9 km; Above 9 km. Figure 22 shows a schematic of the different directions used within InTEM. The Bayesian cost function has an extra term which describes the time-series of baseline influence at each observation station separately using these direction specific parameters. It is comprised of the eleven terms that are solved as part of the inversion process. In addition the six outer regions shown in Figure 18 are also solved for in the inversion.

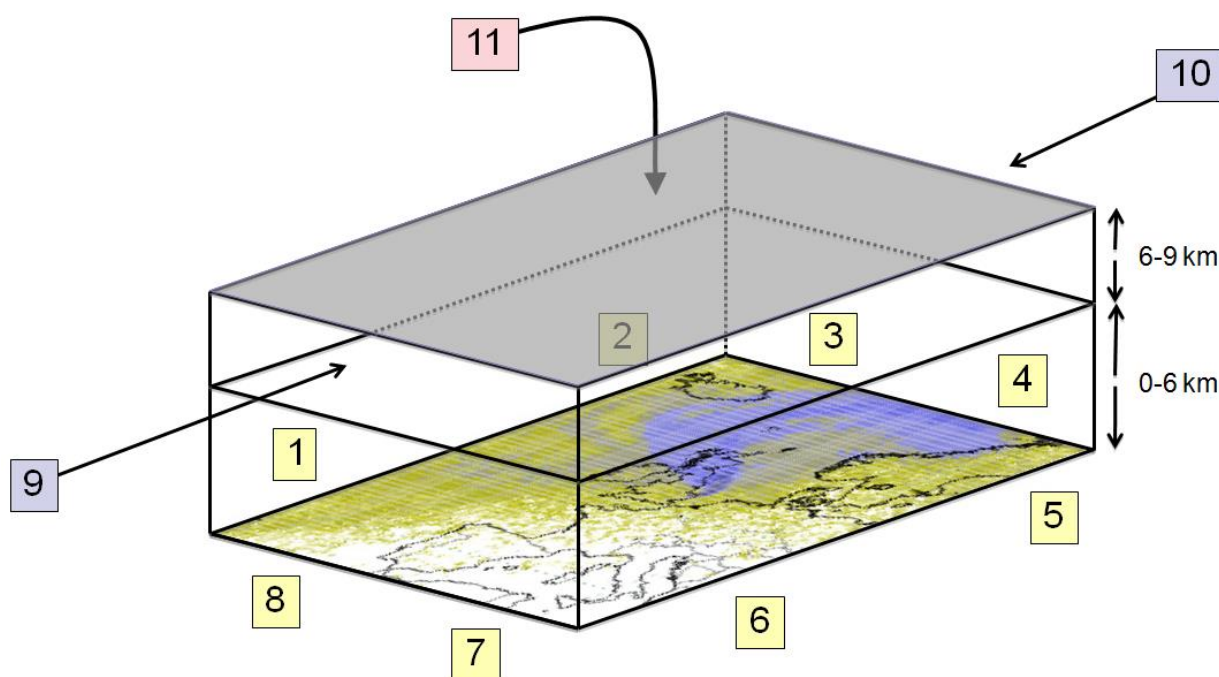


Figure 22: Schematic of the 11 different directions used within InTEM.

3.4 Uncertainty

A Bayesian framework is used to assess the uncertainties in the inversion system. This framework has a rigorous mathematical method for estimating the uncertainty reduction due to increased knowledge, in this case more observations. The errors are assumed Gaussian (i.e. there is an equal and symmetric likelihood of the error being positive or

negative), this is an assumption that is widely used. For most of the gases investigated (methane being a possible exception) the emissions are always positive, i.e. the gas is emitted rather than being absorbed by the ground, therefore we truncate the errors so that the final emission cannot be negative. A key point to note is that the uncertainties in the observations and in the model transport (and also in any prior emissions, if they are included) are assumed well characterised and known. Robustly quantifying these three areas of uncertainty is extremely challenging and is an area of on-going research. The overall model-observation uncertainties are combined together to define the uncertainty matrix R . It is assumed that each two-hour period is correlated with those around it. This simulates the fact that any error in a two-hour period is likely to be felt in the preceding and following periods. The correlation exponentially decays with a time correlation of twelve hours. Likewise, observation stations close to each other are potentially affected by similar errors and do not provide entirely independent information. Therefore, an exponentially decaying, geographical distance correlation of 200 km is also applied.

It is usually the case that the model uncertainty is much greater than observation uncertainty. The values in R vary from gas-to-gas and from one model-observation time-step (2-hour) to the next depending on different time-varying factors (described below), so there is no single number per gas. As a result, the uncertainty per annual UK estimate from InTEM varies from gas-to-gas and from year-to-year, but usually falls within 30-100% in the absence of any prior uncertainty estimates.

3.4.1. Uncertainty in the Observations

The observation uncertainty is derived from a combination of repeatability uncertainty and averaging uncertainty. The former is from the instrument and is the variability (expressed as a standard deviation, σ_r) observed when the same tank of air is repeatedly measured in the same day. The latter is from the variability (expressed as the standard deviation, σ_v) in the observations when they are averaged to the model time window (2-hours). The CH_4 observations are measured at ~ 0.3 Hz at the tower stations (although there are regular data gaps as different heights are sampled) and 40 minute intervals at MHD. For gases where there are fewer than seven observations in a two-hour window, for example, for the gases measured on the Medusa, which takes one sample approximately every two hours, the variability across three contiguous two-hour time periods (the preceding, current and next time periods) is used to estimate the averaging uncertainty.

3.4.2. Uncertainty in the Atmospheric Modelling

The model transport uncertainties are very difficult to quantify, but are assumed to be related to the modelled height of the atmospheric boundary layer (ABL). The ABL is the volume of air directly in contact with, and affected by, the ground surface, which varies from day to night and depends on the strength of the sun on the ground and the strength of the wind. If it is a hot day in summer a typical ABL in the UK would reach more than 2 km, whereas on a cold still night the ABL can fall below 50 m. The atmospheric turbulence (mixing) in the ABL ensures that ground surface emissions are readily mixed throughout the ABL. The mixing from the ABL to the free-troposphere, the volume of air directly above the ABL extending up to the tropopause, 10-12 km above the ground, can be much slower. Therefore, modelling the ABL correctly is vitally important in order to be able to understand the ability of the atmosphere to mix and dilute the surface emissions. If the ABL is high (1-2 km), an error in the modelled ABL of 50 m would not have a strong impact on the ability of the model to accurately model the atmospheric dispersion. However, if the ABL is low (50 m) an error of 10-50 m could be extremely significant. Also times when the ABL is low are associated with times when the wind is weak, during such times local atmospheric flows, for example drainage flows in valleys and land-sea breezes, can be significant and these sub-grid scale flows are not modelled well, if at all. It is also important to know the height of the ABL with respect to the height of the measurement inlet. If the ABL is close to the inlet height, small errors in the ABL can have a significant impact on the quality of the modelled concentration. The other key factor is the 'localness' factor, this is the sum of the nine grid cells in the NAME air history map centred on the observation location. When this is high it means that the air is more stagnant around the station and therefore the flow will be more complex to model and therefore more prone to uncertainty. It is akin to a low ABL condition. The mismatch between the modelled and actual topography at the station also complicates the modelling and adds to the uncertainty. The following formula was developed to describe these effects.

$$\sigma_a = (\text{Factor}_{\text{local}} \times \text{Factor}_{\text{ABL}} \times \text{Factor}_{\text{topog}}) \times (\text{median Pollution over year})$$

Where,

$\text{Factor}_{\text{local}}$ = Uncertainty increases as impact of local sources increase

$\text{Factor}_{\text{ABL}}$ = Model will be more uncertain when the boundary layer is low

$\text{Factor}_{\text{topog}}$ = Topography mismatch between actual and model

σ_a = Overall meteorological model uncertainty (mole fraction).

3.4.3. Overall Model-Observation Uncertainty

The total model uncertainty is given by:

$$\sigma = \sqrt{(\sigma_r)^2 + (\sigma_v)^2 + (\sigma_a)^2 + (\sigma_b)^2}$$

Where,

σ_b = Baseline uncertainty (mole fraction)

(the other terms are described above)

The variance (σ^2) is calculated for each time-period (2-hour) and used to populate the main diagonal in the R matrix. The off-diagonals of R are populated with the cross-correlation terms:

$$\sigma_i \sigma_j \exp\left(\frac{-\Delta t}{12 \text{ hours}}\right) \exp\left(\frac{-\Delta x}{200 \text{ km}}\right)$$

Where,

i and j are the row and column respectively relating to two different observations, Δt is the time difference between the observations and Δx is the horizontal distance between the observation stations (if the observations come from different stations).

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5. Glossary of Acronyms

ABL: Atmospheric Boundary Layer
AGAGE: Advanced Global Atmospheric Gases Experiment
ALE: Atmospheric Lifetime Experiment
BSD: Bilsdale observation station
CFC: ChloroFluoroCarbon
CH₄: Methane
CO: Carbon monoxide
CO₂: Carbon dioxide
CRDS: Cavity Ring-Down Spectrometer
CSIRO: Commonwealth Scientific and Industrial Research Organisation
DECC: Department of Energy and Climate Change
ECD: Electron Capture Detector
Empa: Swiss Federal Laboratories for Materials Science and Technology
ERA-Interim: ECMWF Re-Analysis meteorology – Interim product
EU: European Union
FID: Flame Ionisation Detector
GAGE: Global Atmospheric Gases Experiment
GAUGE: Greenhouse gAs Uk and Global Emissions
GAW: Global Atmospheric Watch
GC: Gas chromatograph
GHG: GreenHouse Gas
H₂: Hydrogen
H₂O: Water
HCFC: HydroChloroFluoroCarbon
HFC: HydroFluoroCarbon
Hg: Mercury
HgO: Mercuric oxide
ICOS: Integrated Carbon Observation System
InGOS: Integrated non-CO₂ Greenhouse gas Observing System
InTEM: Inversion Technique for Emission Modelling
LGR: Los Gatos Research
LSCE: Laboratoire des Sciences du Climat et de l'Environnement
MD: Multi-Detector
MHD: Mace Head observation station
MPI: Max Planck Institute
MS: Mass spectrometry
N₂O: Nitrous oxide
NAME: Numerical Atmospheric dispersion Modelling Environment
NERC: Natural Environment Research Council
NF₃: Nitrogen trifluoride
NOAA: National Oceanic and Atmospheric Administration
NWEU: North West Europe
OA-ICOS: Off Axis-Integrated Cavity Output Spectroscopy
ODS: Ozone Depleting Substance
PFC: PerFluoroCarbon
RGA: Reduction Gas Analyser
RGL: Ridge Hill observation station
SIO: Scripps Institution of Oceanography
SF₆: Sulphur hexafluoride
TAC: Tacolneston observation station
TTA: Tall Tower Angus observation station
UK DECC Network: United Kingdom Deriving Emissions linked to Climate Change Network
UM: UK Met Office Unified Model
UoB: University of Bristol
UNFCCC: United Nations Framework Convention on Climate Change
WMO: World Meteorological Organisation