



# History of Chemically and Radiatively Important Atmospheric Gases from the Advanced Global Atmospheric Gases Experiment (AGAGE)

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**Abstract.** We present the organization, instrumentation, datasets, data interpretation, modeling, and accomplishments of the multinational, global atmospheric measurement program AGAGE (Advanced Global Atmospheric Gases Experiment). AGAGE is distinguished by its capability to measure globally, at high frequency and multiple sites, all the important species in the Montreal Protocol and all the important non-carbon dioxide (CO<sub>2</sub>) gases assessed by the Intergovernmental Panel on Climate Change (CO<sub>2</sub> is also measured at several sites). The scientific objectives of AGAGE are important in furthering understanding of global chemical and climatic phenomena. They are to: (1) measure accurately the temporal and spatial distributions of anthropogenic gases that contribute the majority of reactive halogen to the stratosphere and/or are strong infrared absorbers [chlorocarbons, chlorofluorocarbons (CFCs), bromocarbons, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and polyfluorinated compounds (perfluorocarbons (PFCs), nitrogen trifluoride (NF<sub>3</sub>), sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>), and sulfur hexafluoride (SF<sub>6</sub>)), and use these measurements to determine the global rates of their emission and/or destruction (i.e. lifetimes); (2) measure accurately the global distributions and temporal behaviors and determine sources and sinks of non-CO<sub>2</sub> biogenic-anthropogenic gases important to climate change and/or ozone depletion [methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), molecular hydrogen (H<sub>2</sub>), methyl chloride (CH<sub>3</sub>Cl) and methyl bromide (CH<sub>3</sub>Br); (3) identify new long-lived greenhouse and ozone-depleting gases



[e.g.  $\text{SO}_2\text{F}_2$ ,  $\text{NF}_3$ , heavy PFCs ( $\text{C}_4\text{F}_{10}$ ,  $\text{C}_5\text{F}_{12}$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{C}_7\text{F}_{16}$ , and  $\text{C}_8\text{F}_{18}$ ) and hydrofluoro-olefins (HFOs, e.g.  $\text{CH}_2=\text{CFCF}_3$ ) have been identified in AGAGE], initiate real-time monitoring of these new gases, and reconstruct their past histories from AGAGE, air-archive and firn-air measurements; (4) determine the average concentrations and trends of tropospheric hydroxyl radicals (OH) from the rates of destruction of atmospheric trichloroethane ( $\text{CH}_3\text{CCl}_3$ ), HFCs and HCFCs, and estimates of their emissions; (5) determine from atmospheric observations and estimates of their destruction rates, the magnitudes, and distributions by region of surface sources/sinks of all measured gases; (6) provide accurate data on the global accumulation of many of these trace gases, that are used to test the synoptic/regional/global-scale circulations predicted by three-dimensional models; and (7) provide global and regional measurements of methane, carbon monoxide and molecular hydrogen, and estimates of hydroxyl levels, to test primary atmospheric oxidation pathways at mid-latitudes and the tropics. Network Information and Data Repository: <http://agage.mit.edu/data> or <http://cdiac.esd.ornl.gov/ndps/alegage.html>

## 1. Introduction

The Advanced Global Atmospheric Gases Experiment (AGAGE: 1993-present), and its predecessors (Atmospheric Lifetime Experiment, ALE: 1978-1981; Global Atmospheric Gases Experiment, GAGE: 1982-1992) have measured the composition of the global atmosphere continuously since 1978. The ALE program was instigated to measure the then 5 major ozone depleting gases (CFC-11 ( $\text{CFCl}_3$ ), CFC-12 ( $\text{CCl}_2\text{F}_2$ ),  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{N}_2\text{O}$ ) in the atmosphere 4 times per day using automated gas chromatographs with electron capture detectors (GC-ECDs) at 4 stations around the globe, and to determine the atmospheric lifetimes of the purely anthropogenic of these gases from their measurements and industry data on their emissions (Prinn et al, 1983a). The GAGE project broadened the global coverage to 5 stations, the number of gases being measured to 8 (adding CFC-113 ( $\text{CCl}_2\text{FCClF}_2$ ),  $\text{CHCl}_3$ , and  $\text{CH}_4$  to the ALE list), and the frequency to 12 per day by improving the GC-ECDs, and adding gas chromatographs with flame ionization detectors (GC-FIDs; Prinn et al, 2000). The AGAGE program then improved significantly upon the GAGE instruments increasing their measurement precision and frequency (to 36 per day), and adding gas chromatographs with mercuric oxide reduction detectors, to overall measure 10 biogenic and/or anthropogenic gases (adding  $\text{H}_2$  and  $\text{CO}$  to the GAGE list). AGAGE also introduced powerful new gas chromatographs with mass spectrometric detection and cryogenic preconcentration measuring over 50 trace gases 20 times per day. In this overview paper, while we address the entire 1978-present database and its public availability, we focus more on the evolution of the network after 2000; details of the period before that are addressed in the previous comprehensive overviews provided by Prinn et al. (2000) and Prinn et al (1983a). The case for real-time high frequency measurement networks like AGAGE is strong, and the observations and their interpretation are important inputs to the scientific understanding of ozone depletion and climate change. AGAGE is characterized by its capability to measure globally, at high frequency, the trends and emissions of all of the important species in the Montreal Protocol on Substances that Deplete the Ozone Layer, and all of the important non-carbon dioxide (non- $\text{CO}_2$ ) trace gases assessed by the Intergovernmental Panel on Climate Change. More recently, AGAGE is also measuring  $\text{CO}_2$  using high frequency optical spectroscopy (focusing on sites where such measurements are not made by other groups; Sections 2.3 and 2.4)). The scientific objectives of AGAGE (summarized in the Abstract) are of considerable significance in furthering our understanding of important global chemical and climatic phenomena. The remainder of this Introduction is devoted to describing the network of stations (Subsection 1.1), the measurements (Subsection 1.2) and the place of AGAGE in the global observing system (Subsection 1.3). Then Section 2 addresses the instrumentation, calibration and station infrastructure, Section 3 the data analysis and modeling, Section 4 the scientific accomplishments and Section 5 the AGAGE data availability.

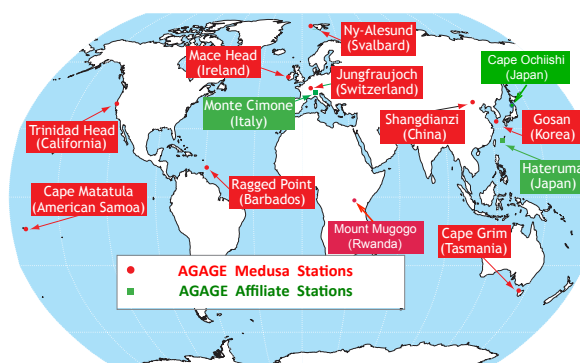
### 1.1 A Global Network of Stations

The ALE/GAGE/AGAGE stations are coastal or mountain sites around the world, chosen primarily to provide accurate measurements of trace gases whose lifetimes are long compared to global atmospheric circulation times (**Figure 1**). The 10 “primary” AGAGE stations that all share common calibrations and gas chromatographic-mass spectrometric instrumentation (see Section 1.2), are: (a) on Ireland’s west



1 coast, first at Adrigole (52°N, 10°W, 50 m (inlet height a.s.l. here and for all other stations), 1978-1983),  
 2 then at Mace Head (53°N, 10°W, 25 m 1987 to present); (b) on the U.S. west coast, first at Cape Meares,  
 3 Oregon (45°N, 124°W, 30 m, 1979-1989), then at Trinidad Head, California (41°N, 124°W, 140 m, 1995  
 4 to present); (c) at Ragged Point, Barbados (13°N, 59°W, 42 m, 1978 to present); (d) at Cape Matatula,  
 5 American Samoa (14°S, 171°W, 77 m, 1978 to present); (e) at Cape Grim, Tasmania, Australia (41°S,  
 6 145°E, 164 m, 169 m, 1978 to present); (f) on the Jungfrauoch, Switzerland (47°N, 8°E; 3580 m, 2000 to  
 7 present); (g) on Zeppelin Mountain, Ny-Ålesund, Svalbard, Norway (79°N, 12°E; 489 m, 2001 to  
 8 present); (h) at Gosan, Jeju Island, Korea (33°N, 126°E, 89 m, 2007 to present); (i) at Shangdianzi, China  
 9 (41°N, 117°E, 383 m, 2010 to present with gap) and (j) Mt. Mugogo, Rwanda (1.6°S, 29.6°E, 2640 m,  
 10 2015 to present). The AGAGE network also includes 3 AGAGE-compatible (but not identical)  
 11 instruments on: (k) Hateruma Island, Japan (24°N, 123.8°E, 47 m, 2004 to present); (l) Cape Ochiishi,  
 12 Japan (43°N, 145.5°E, 100 m, 2006 to present), and (m) Monte Cimone, Italy (44°N, 10°E, 2165 m, 2004  
 13 to present). These are called AGAGE “affiliate” stations in **Figure 1**. There are also “secondary”, usually  
 14 continental and some urban, stations that are linked to and complement the “primary” and “affiliate”  
 15 stations (discussed below).

**Figure 1.** Locations of the 10 current AGAGE primary stations (**red highlighted stations**) that have Medusa gas chromatograph-mass spectrometer (GC-MS) instruments, and the 3 current AGAGE affiliate stations (**green highlighted stations**) that have alternative pre-concentration GC-MS instruments. AGAGE and the other major global air-sampling network, NOAA-ESRL-GMD, are independent, but closely cooperating, including frequent data inter-comparisons, especially at the American Samoa shared site.



## 16 1.2 Measurements

17 At its primary stations, AGAGE uses *in situ* gas chromatography with mass spectrometry (GC-MS) in  
 18 the “Medusa” system (Miller et al., 2008; Arnold et al., 2012) to measure over 50 largely synthetic gases  
 19 including hydrochlorofluorocarbons (*e.g.* HCFC-22;  $\text{CHClF}_2$ ) and hydrofluorocarbons (*e.g.* HFC-134a;  
 20  $\text{CH}_2\text{FCF}_3$ ), which are interim or long-term alternatives to chlorofluorocarbons (CFCs) now restricted by  
 21 the Montreal Protocol, other hydrohalocarbons (*e.g.* methyl chloride;  $\text{CH}_3\text{Cl}$ ), halons (*e.g.* Halon-1211;  
 22  $\text{CBrClF}_2$ ), perfluorocarbons (*e.g.* PFC-14;  $\text{CF}_4$ ), and trace chlorofluorocarbons, all of which, except  
 23  $\text{CH}_3\text{Cl}$ , are involved in the Montreal or Kyoto Protocols. Affiliate stations use similar but not identical  
 24 cryogenic pre-concentration GC-MS systems (Maione et al., 2013; Yokouchi et al., 2006).

25 At its Mace Head, Trinidad Head, Ragged Point, Cape Matatula and Cape Grim primary stations,  
 26 AGAGE also uses *in situ* gas chromatographs (GC) with electron-capture detection (ECD), flame-  
 27 ionization detection (FID), mercuric oxide reduction detection (MRD, at Mace Head and Cape Grim only)  
 28 and pulsed discharge detection (PDD, at Cape Grim only) to measure five biogenic-anthropogenic gases  
 29 (methane -  $\text{CH}_4$ , nitrous oxide -  $\text{N}_2\text{O}$ , and chloroform -  $\text{CHCl}_3$  at all sites; carbon monoxide -  $\text{CO}$  and  
 30 hydrogen -  $\text{H}_2$  at Mace Head and Cape Grim only), and five anthropogenic gases at all 5 sites: CFC-11  
 31 ( $\text{CCl}_3\text{F}$ ), -12 ( $\text{CCl}_2\text{F}_2$ ), and -113 ( $\text{CCl}_2\text{FCClF}_2$ ), methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), and carbon tetrachloride  
 32 ( $\text{CCl}_4$ ), 36 times per day (Prinn et al., 2000). The list of gases measured with these gas chromatography  
 33 “multidetector” (GC-MD) systems includes the 3 major chlorofluorocarbons (CFCs) restricted by the  
 34 Montreal Protocol and the 4 major long-lived non- $\text{CO}_2$  greenhouse gases (GHGs). **Table 1** lists all the  
 35 major gases being measured in AGAGE using the Medusa-GC-MS and GC-MD instruments, their 2016  
 36 global average mole fractions, and their typical measurement precisions.

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**Table 1.** Primary AGAGE measured species using Medusa-GC-MS and GC-MD systems. “Medusa” and “GC-MD only” in black regular font; *both systems in italic font*. Calibrations are on AGAGE SIO gravimetric scales (Section 2.6) unless otherwise noted.

Compound	Global mean 2016 conc. (ppt) <sup>***</sup>	Typical Precision (%)	Compound	Global mean 2016 conc. (ppt) <sup>***</sup>	Typical <sup>4</sup> Precision (%)
PFC-14	82.7	0.15	<sup>a</sup> CFC-114	16.3	0.3
PFC-116	4.56	1	CFC-115	8.48	0.7
PFC-218	0.63	3	Halon-1211	3.59	0.4
PFC-c318	1.56	1.5	Halon-1301	3.37	1.7
PFC-5-1-14	0.31	3	Halon-2402	0.41	2
SF <sub>6</sub>	8.88	0.6	CH <sub>3</sub> Cl	552	0.2
SF <sub>5</sub> CF <sub>3</sub>	0.17	7	CH <sub>3</sub> Br	6.96	0.6
SO <sub>2</sub> F <sub>2</sub>	2.26	2	<sup>b</sup> CH <sub>3</sub> I	0.58	2
NF <sub>3</sub>	1.44	1	CH <sub>2</sub> Cl <sub>2</sub>	31.1	0.5
HFC-23	28.9	0.7	<sup>b</sup> CH <sub>2</sub> Br <sub>2</sub>	1.08	1.5
HFC-32	12.6	3	<i>CHCl<sub>3</sub></i>	8.78	0.4
HFC-134a	89.3	0.5	<sup>b</sup> CHBr <sub>3</sub>	1.84	0.6
HFC-152a	6.71	1.4	<i>CCl<sub>4</sub></i>	79.9	1
HFC-125	20.8	0.7	<i>CH<sub>3</sub>CCl<sub>3</sub></i>	2.61	0.7
HFC-143a	19.3	1	CHCl=CCl <sub>2</sub>	~ 0.11	3
HFC-227ea	1.24	2.2	<sup>b</sup> CCl <sub>2</sub> =CCl <sub>2</sub>	1.07	0.5
HFC-236fa	0.15	10	<sup>b</sup> COS	543	0.5
HFC-245fa	2.42	3	<sup>a</sup> C <sub>2</sub> H <sub>6</sub>	586	0.3
HFC-365mfc	1.00	5	<sup>c</sup> C <sub>3</sub> H <sub>8</sub>	9.04	0.6
HFC-43-10mee	0.27	3	<sup>a</sup> C <sub>6</sub> H <sub>6</sub>	17.9	0.3
HCFC-22	237	0.3	<sup>a</sup> C <sub>7</sub> H <sub>8</sub>	4.19	0.6
HCFC-141b	24.5	0.5			
HCFC-142b	22.6	0.4			
<sup>a</sup> HCFC-124	1.11	2	GC-MD Only (ppb) <sup>***</sup>		
<i>CFC-11</i>	<i>230</i>	<i>0.2</i>	CH <sub>4</sub>	1842	0.2
<i>CFC-12</i>	<i>516</i>	<i>0.1</i>	N <sub>2</sub> O	329.3	0.05
<sup>d</sup> CFC-13	3.28	2	*CO	54 to 115	0.2
<i>CFC-113</i>	<i>71.4</i>	<i>0.2</i>	*H <sub>2</sub>	515 to 550	0.6 (0.08)**

<sup>a</sup>CO and H<sub>2</sub> measured at Mace Head and Cape Grim only (range for annual means of these 2 stations given).

\*\*GC-PDD system at Cape Grim.

\*\*\* ppt = parts per trillion and ppb = parts per billion

<sup>a</sup>Preliminary (AGAGE) Scale (Section 2.6)

<sup>b</sup>Preliminary (transfer of NOAA) Scale (Section 2.6)

<sup>c</sup>Preliminary (Empa) Scale (Section 2.6)

<sup>d</sup>METAS-2017 (Empa) Scale (Section 2.6)

<sup>e</sup>Quasi-linear sum of CFC-114 and CFC-114a

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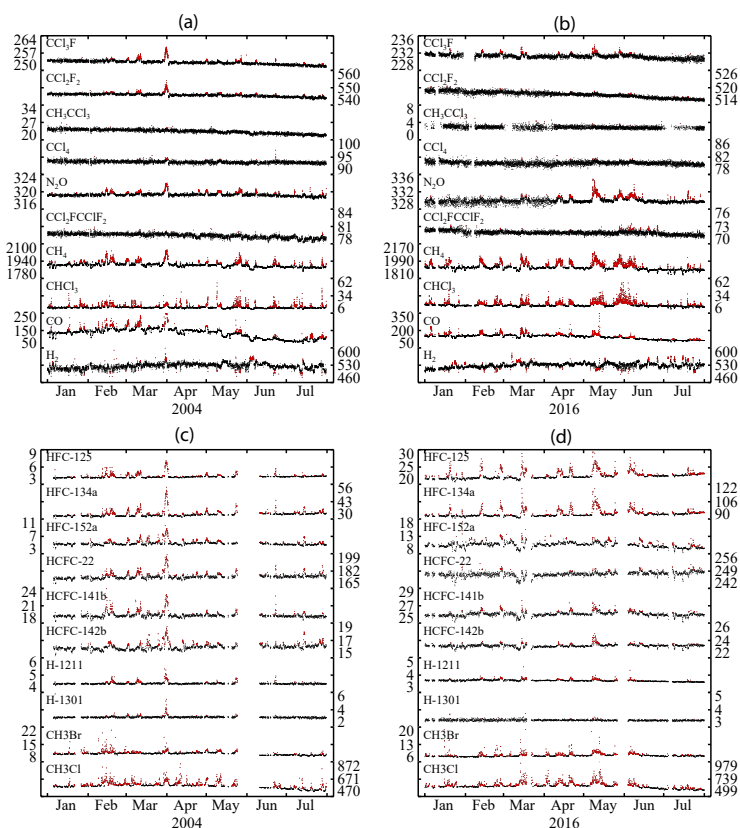
Recent developments have enabled precise analyses of CH<sub>4</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub>O by spectroscopic detection to begin in AGAGE. These optical instruments are now expanding the measurement capabilities within AGAGE, and there are advantages in switching from the GC-MD approach for measuring CH<sub>4</sub>, N<sub>2</sub>O, and CO to these less operationally-demanding optical spectroscopy methods resulting in near-continuous measurements of comparable or better precision. As discussed in Section 2.3 and 2.4, this transition is happening already at several AGAGE stations.

Each instrument system is automated and under computer control. All chromatograms, instrumental data, and operators' logs are transmitted via the internet to the data processing sites. AGAGE includes timely public archiving and publication of all data, regular inter-comparisons of AGAGE measurements and absolute calibrations with other networks (e.g. NOAA's Global Monitoring Division, GMD), and contributions to national and international assessments of ozone depletion and climate change. The data are calibrated against on-site air standards, which are calibrated relative to off-site parent standards before and after use at each station. AGAGE depends upon well-defined absolute gravimetric calibration procedures that are repeated periodically to assure the accuracy of the long-term measured trends (Prinn et al., 2000).

To emphasize the need for very frequent real-time measurements we show data for several trace gases (Figures 2a-2d) for the years 2004 and 2016. These GC-MD and GC-MS data demonstrate the existence of regional pollution-induced or local sink-induced (e.g. for H<sub>2</sub>) (shown in red) and large-scale transport-induced (shown in black) variability, which are not captured with weekly flask measurements typically designed to avoid local pollution. Note also the evolution of the sizes of these pollution events between 2004 and 2016 associated with the decreases of emissions of regulated gases and the growth of emissions of unregulated ones. This high frequency sampling enables the pollution events in particular to be used to estimate emissions from nearby source regions (e.g. Cape Grim station for SE Australian emissions (e.g., Dunse et al., 2005; Stohl et al., 2009; O'Doherty et al., 2009; Fraser et al., 2014; Lunt et al., 2015), Trinidad Head for the west coast U.S. emissions (e.g., Li et al., 2005; O'Doherty et al., 2009; Lunt et al., 2015; Fortems-Cheiney et al., 2015), Mace Head and the other European stations for European and, in some cases, eastern USA emissions (e.g., O'Doherty et al., 2009; Stohl et al., 2009; Keller et al., 2012; Simmonds et al., 2015; Lunt et al., 2015; Fortems-Cheiney et al., 2015; Graziosi et al., 2017), Hateruma, Shangdianzi and Gosan for East Asian emissions (e.g., Stohl et al., 2009, 2010; Kim et al., 2010; Li et al., 2011; Yao et al., 2012a,b; Saito et al., 2015; Fang et al., 2015; Lunt et al., 2015; Fortems-Cheiney et al., 2015). The sources of many anthropogenic and natural trace gases measured in AGAGE are often co-located so that measurement of a wide range of gases enhances the ability to accurately estimate their sources and sinks. The AGAGE data in graphical and digital forms are available for most stations at the AGAGE website: <http://agage.mit.edu> (Section 3.2).

### 1.3 Integral Element of the Global Observing System

AGAGE is part of a powerful complementary observing system that is measuring various aspects of the evolving composition of Earth's atmosphere, and providing the fundamental understanding needed to preserve this vital sphere of life on our planet. Sharing the AGAGE surface-based perspective are, for example, the remote-sensing Network for Detection of Atmospheric Composition Change (NDACC, see De Mazière et al., 2017) supported by NASA and other agencies and nations, and the NOAA-ESRL Global Monitoring Division *in situ* and flask networks. Also measuring atmospheric composition (as column profiles or abundances) are instruments on board the NASA TERRA and AURA satellites and the ESA ENVISAT satellite. Aircraft- and balloon-borne instruments provide vital *in situ* measurements in the middle troposphere and lower stratosphere. The combination of all of these complementary data with state-of-the-art global chemistry and circulation models is providing major advances in our understanding of the global sources, chemistry, transport, and sinks of the trace substances, and allows determination of atmospheric composition and air quality, the radiative forcing of climate change, and impacts on stratospheric ozone



**Figure 2.** Seven months of data for gases measured at Mace Head, Ireland: (1) with the GC-MD in (a) 2004 and (b) 2016 (units: mole fractions; ppb for  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$ ; ppt for all others), and (2) with the Medusa GC-MS for selected gases in (c) 2004 and (d) 2016 (units: mole fractions in ppt for all gases). In all 4 panels, measurements in polluted air originating from Europe (also in air affected by local sinks – see text) are shown in red, while those in clean air off the Atlantic Ocean are shown in black.

## 2. Instruments, Calibration and Infrastructure

The AGAGE program has placed a strong emphasis on instrumental innovation and gravimetric preparation of primary standards to obtain high frequency and high precision automated trace gas measurements at all the AGAGE measurement sites. In the early 1990s the GC-MD instruments were developed and deployed at the Mace Head, Trinidad Head, Ragged Point, Cape Matatula and Cape Grim stations, and at the Scripps Institution of Oceanography (SIO) calibration laboratory (Prinn et al., 2000). In the late 1990s, AGAGE pioneered the deployment of automated GC-MS instruments at our stations in Mace Head and Cape Grim, and at the University of Bristol. These instruments featured an adsorption-desorption system (ADS) with cryogenic ( $-50^\circ\text{C}$ ) pre-concentration of analytes from 2-liter air samples (Simmonds et al., 1995). The technological developments incorporated into these instruments, the methods of data collection, transmission and processing, the primary and secondary calibration standards produced at the SIO calibration laboratory, and the on-site tertiary (from SIO) and quaternary (calibrated on-site from the tertiary) standards, necessary to sustain the AGAGE network are partly described in the first AGAGE overview (Prinn et al., 2000), but updated here in Sections 2.6 and 2.7.

Beginning in the early 2000s, the AGAGE team recognized that modern refrigeration technology made it possible to make major improvements to the ADS concept and to greatly extend the range of compounds that could be measured by enhanced cryogenic pre-concentration at  $-165^\circ\text{C}$ . As a result, the



AGAGE GC-MS effort was redirected to the development of the new “Medusa” instrument (Miller et al., 2008; Arnold et al., 2012).

## 2.1 GC-Multidetector Instruments

The current AGAGE GC-MD instruments replaced the earlier GAGE GC-MD instruments in 1993-96 (Table 2). These Agilent© GC instruments employ two electron capture detector (ECD) channels and one flame ionization detection (FID) channel to measure the principal chlorine-bearing anthropogenic ozone depleting compounds now banned by the Montreal Protocol (CFC-11, CFC-12, CFC-113, CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub>), as well as the both natural and anthropogenic compounds N<sub>2</sub>O, CH<sub>4</sub> and CHCl<sub>3</sub> (see Table 1). The GC-MDs at Mace Head and Cape Grim include an extra channel for the measurement of CO and H<sub>2</sub> by a mercuric oxide reduction detector (MRD, Prinn et al., 2000). In early 2015, the GC-MD system at Cape Grim also added a further extra channel for the measurement of H<sub>2</sub> by pulsed discharge detector (PDD), bringing a more than 10-fold improvement in precision. The GC-MD measurements are made on dried whole-air samples, automatically injected by a computer-controlled sampling module. Each analysis cycle takes 20 minutes.

Compared to its ALE and GAGE predecessors, the AGAGE GC-MD provides greatly enhanced precision and measurement frequency, custom software (GCWerks©, <http://www.gcwerks.com>) for instrument control and digital acquisition of all chromatograms and measurement parameters, and use of the internet for data transmission and remote diagnosis and control (Prinn et al., 2000, Section 2.5). These instruments also can carry out pressure-programmed injections to assess their own nonlinearities, and use flexible custom algorithms for post-analysis quantitative interpretation of chromatograms. The performance and reliability of these instruments have been, and continue to be, exceptional, leading to important advances in scientific interpretation, as are discussed below. For some of the species that the GC-MDs measure, AGAGE is now also beginning to deploy new technologies including GC-MS, cavity ring-down spectroscopy (CRDS) and quantum cascade laser (QCL) (optical) methods, that offer improved sensitivity as are discussed in the following sections. The GC-MD instruments will continue to be operated until such time as they can be phased out after careful overlap in the field using these newer technologies.

**Table 2.** GC-Multidetector Instruments at current AGAGE primary and secondary stations. Detectors: ECD for CFC-11, CFC-12, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, N<sub>2</sub>O, and CHCl<sub>3</sub>; FID for CH<sub>4</sub>; MRD for CO and H<sub>2</sub>; and PDD for H<sub>2</sub>.

GC-ECD-FID	GC-ECD-FID-MRD	GC-ECD-FID-MRD-PDD
Trinidad Head, CA, USA	Mace Head, Ireland	Cape Grim, Tasmania
Ragged Point, Barbados	Tacolneston*, UK	
Cape Matatula, Samoa	Aspendale**, Australia	
La Jolla, CA, USA		
Ridge Hill*, UK		
Bilsdale*, UK		
Heathfield*, UK		

\* Modified version of the GC-MD without FID channel.

\*\* Uses 3 individual GC systems with ECD, FID, and MRD detectors

## 2.2 Medusa GC-MS Instruments

The AGAGE Medusa GC-MS instruments have become the major instruments of the AGAGE network and collaborating measurement laboratories. Instrument development work nevertheless continues, with enhancements in operational parameters and increases in the numbers of measured species being added to the basic instrument and its operation as described by Miller et al. (2008). Subsequently, important new changes were made in the Medusa flow scheme and column configuration that add the new and widely used high-GWP electronics industry chemical NF<sub>3</sub> to its measurement capability without sacrificing any of its other capabilities (Arnold et al., 2012). The reader is directed to these two papers for a full description of the current Medusa configuration – only a brief overview is given here.



1 A complement of 19 AGAGE Medusas has now been deployed (**Table 3**), with one at each of the 10  
2 “primary” stations (red labels in Figure 1), 2 at the SIO calibration and instrument development  
3 laboratory, and 7 more at other “secondary” stations or laboratories in the UK (Tacolneston & Bristol),  
4 Switzerland (Dübendorf), Australia (2 at Aspendale), Norway (Kjeller) and China (Beijing).

5 At the heart of the Medusa is a Polycold © “Cryotiger” cold end that maintains a temperature of about  
6  $-175^{\circ}\text{C}$  within the Medusa’s vacuum chamber, even with a substantial heat load, using a simple single-  
7 stage compressor with a proprietary mixed-gas refrigerant. This cold end conductively cools dual micro-  
8 traps to about  $-165^{\circ}\text{C}$ . By using standoffs of limited thermal conductivity to connect the traps to the cold  
9 head, each trap can independently be heated resistively to any temperature from  $-165^{\circ}\text{C}$  to  $+100^{\circ}\text{C}$  or  
10 more, while the cold end remains cold. The use of two traps with extraordinarily wide programmable  
11 temperature ranges, coupled with the development of appropriate trap adsorbents and the use of  
12 separating columns between traps, permits the desired analytes from 2-liter air samples to be effectively  
13 separated from more-abundant gases that would otherwise interfere with chromatographic separation or  
14 mass spectrometric detection, such as nitrogen- $\text{N}_2$ , oxygen- $\text{O}_2$ , argon- $\text{Ar}$ , water vapor- $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  
15 krypton- $\text{Kr}$  and xenon- $\text{Xe}$ . Importantly, the dual micro-trap and revised column configuration also permit  
16 the analytes to be purified of interfering compounds from the larger first-stage trap (T1) by fractional  
17 distillation, chromatographic separation, and re-focusing onto a smaller trap (T2) at very low  
18 temperatures, so that the resulting injections to the main chromatographic column in the Agilent© 5975C  
19 quadropole GC-MS are sharp and reproducible. By trapping and eluting analytes at very low  
20 temperatures, the range of compounds that can be measured is greatly extended to include a number of  
21 important volatile compounds, and problems with reaction of analytes on the traps at higher temperatures  
22 are avoided. The Medusa system uses high-precision integrating mass flow controllers for measurement  
23 of sample volumes. In addition, significant advances have been made in the software (GCWerks) to  
24 control and acquire data from the Medusa and the GC-MS itself, so that the entire system has  
25 programmability, versatility and ease of operation comparable to that of the AGAGE GC-MD  
26 instruments. The original Agilent 5973 mass-selective detectors (MSDs) used in the 6 early Medusas have  
27 been replaced with newer and more sensitive Agilent 5975C MSDs. As a result, sensitivities on the  
28 Medusas with the new MSDs increased 1.5- to 2-fold over those with the old MSDs, which has especially  
29 benefitted measurements of the lowest abundance species.

30 As noted above, instrument development work on the Medusas continues. The species routinely  
31 measured at Medusa field stations are listed in **Table 1**. Compounds added only recently to routine  
32 Medusa measurements (and therefore not yet in **Table 1**) are HCFC-133a and  $\text{CF}_3\text{CFOCF}_2$ , while the  
33 light hydrocarbons  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ , although still measured, are also not included in **Table 1** because co-  
34 elution compromises their measurement as the GC column ages. The AGAGE Medusas were the first  
35 instruments monitoring *in situ* the global distributions and trends of the high-GWP industrial gases  $\text{CF}_4$ ,  
36  $\text{NF}_3$  and  $\text{SO}_2\text{F}_2$  (Muhle et al, 2009, 2010; Weiss et al, 2008; Arnold et al, 2013). In addition to the  
37 compounds listed in **Table 1**, additional species (e.g. CFC-112) are in various stages of being added to  
38 the station measurements. Recently, the “fourth generation” halocarbons HFC-1234yf, HFC-1234ze(E),  
39 and HCFC-1233zd(E), as well as HCFC-31 and four inhalation anesthetics have been measured in the  
40 atmosphere using the Medusa system (Vollmer et al., 2015a; 2015b, Schoenenberger et al., 2015). The  
41 development work on the Medusa utilizes the two instruments in this central laboratory. These  
42 instruments allow a wide range of development work to be undertaken while maintaining the important  
43 functions of primary and secondary calibration of the global AGAGE network and also continuing  
44 “urban” AGAGE ambient measurements of air pumped from the SIO pier at La Jolla. At CSIRO  
45 Aspendale, one Medusa instrument is deployed in an urban air monitoring mode and the other is generally  
46 deployed for flask sample measurements, in particular analyses of the Cape Grim air archive. The single  
47 Medusas at the other 5 secondary stations listed in **Table 3** are deployed either for monitoring or  
48 laboratory functions.

49 The Medusa technology continues to evolve in response to the needs of AGAGE researchers to  
50 measure new compounds, improvements in software, including data processing, diagnostics and alarms,  
51 and improvements in available technology. Most notably, the Polycold “Cryotiger” cold-end technology  
52 that was so revolutionary at the outset of the Medusa program is nearing the end of its useful life, but very



fortunately Stirling cooling technology has advanced considerably, in improved performance and reliability, and reduced cost, during the same time period. One Medusa at the SIO laboratory has been retrofitted to Stirling cooling (Sunpower CryoTel-GT) and is performing extremely well, as well as offering increased flexibility in trapping parameters. At the Empa and SIO laboratories, efforts are also underway to upgrade current Medusa technology to time-of-flight mass spectrometry (TOF-MS) in place of quadrupole mass spectrometric detection. This offers the advantage of very high mass resolution (~4000) that is capable of separating gases with the same integer masses but different actual masses that interfere with each other in the chromatograms using quadrupole technology (e.g. Obersteiner et al., 2016).

There are also 3 AGAGE-affiliated stations that use similar but not identical automated GC-MS measurements with cryogenic preconcentration (stations denoted “Affiliate” in **Table 3**), but are tied to AGAGE standards, at Hateruma Island and Cape Ochi-ishi, Japan (NIES) and at Monte Cimone, Italy (University of Urbino). Monte Cimone uses a GC (Agilent 6850)–MS (Agilent 5975) with an auto-sampling/pre-concentration device (Markes International©, UNITY2-Air Server2©) to enrich the

**Table 3.** GC-MS Instruments (Medusa or Affiliate) at AGAGE primary & secondary stations (for “monitoring”, except where denoted “laboratory”).

Primary Station (by latitude)	Instrument	Secondary Station (by country)	Instrument
Ny-Ålesund	Medusa	La Jolla, USA (laboratory & monitoring)	Medusa
Mace Head	Medusa	Tacolneston, UK	Medusa
Jungfrauoch	Medusa	Bristol, UK (laboratory)	Medusa
Monte Cimone	Affiliate	Dübendorf, Switzerland (laboratory)	Medusa
Cape Ochiishi	Affiliate	Aspendale, Australia (laboratory & monitoring)	Medusa
Shangdianzi	Medusa	Kjeller, Norway (laboratory)	Medusa
Trinidad Head	Medusa	Beijing, China (laboratory)	Medusa
Gosan	Medusa		
Hateruma	Affiliate		
Ragged Point	Medusa		
Mount Mugogo	Medusa		
Cape Matatula	Medusa		
Cape Grim	Medusa		

halocarbons on a focussing adsorbent trap (Maione et al., 2013) and AGAGE-derived calibrations. Hateruma and Ochiishi use GC (Agilent 6890)–MS (Agilent 5973)’s with a unique cryogenic pre-concentration module (Yokouchi et al., 2006, 2012) and independently produced gravimetric standards that are inter-compared with AGAGE standards to provide intercalibration factors.

### 2.3 Optical Spectroscopic instruments

Recent advances in wavelength-scanned cavity ring-down spectroscopy (CRDS) have enabled precise analyses of CH<sub>4</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>O and H<sub>2</sub>O without chromatographic separation to begin in AGAGE. The analysed air sample needs to be dried or, if not dried, corrections applied using the ancillary H<sub>2</sub>O





measurement. The Nafion sample drying and gas sampling approach used in AGAGE has been adapted to a sampling module with an MKS Instruments© inlet pressure controller for CRDS instruments that has been designed by SIO and built by Earth Networks© (Welp et al., 2013). These optical instruments are now expanding the measurement capabilities within AGAGE. There are several advantages in switching from the GC-FID approach for measuring CH<sub>4</sub>, the GC-ECD approach for N<sub>2</sub>O, and the GC-MRD approach for CO in AGAGE to these optical spectroscopy methods: no chromatography, essentially continuous, reduced costs including ongoing instrument maintenance, improved linearity of response (for N<sub>2</sub>O, CO). This transition is happening already at several AGAGE stations (see **Table 4**).

The CSIRO Picarro© G2301 for CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O at Cape Grim (which is being operated at present without drying the sample gas) has been compared with the AGAGE GC-MD CH<sub>4</sub> data at Cape Grim and the agreement is very good, with a mean offset of only ~0.26 ppb (~0.02%) when reported on the same calibration scale. The AGAGE group at SIO, in collaboration with the laboratory of R. F. Keeling, the company Earth Networks, and the California Air Resources Board (CARB), has been evaluating the performance of various CRDS instruments, including calibration optimization, using Allan variance analyses. This has included the Picarro G2301, the Picarro G2401 for CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>O, the Picarro G5205 (prototype) and G5310 mid-IR for N<sub>2</sub>O and H<sub>2</sub>O, as well as the Los Gatos Research (LGR)© High-Precision mid-IR instrument for N<sub>2</sub>O, CO and H<sub>2</sub>O. For CO, the LGR mid-IR instrument is an order of magnitude more precise than the Picarro G2401, but to take full advantage of the LGR's precision requires frequent calibration (hourly or less) that is impractical for long-term atmospheric

**Table 4.** CRDS Spectroscopic Instruments at AGAGE primary stations and secondary stations (including the UK Deriving Emissions related to Climate Change (DECC) network and UK National Physical Laboratory (NPL) stations).

Instrument	Gases	Stations				
Picarro G1301	CH <sub>4</sub> , CO <sub>2</sub> , H <sub>2</sub> O	Jungfraujoch (G2401 after 2011)	Mace Head			
Picarro G2301	CH <sub>4</sub> , CO <sub>2</sub> , H <sub>2</sub> O	La Jolla (+EN drier), Trinidad Head (+EN drier)	Cape Grim	Mace Head	Bristol, Tacolneston (+EN drier), Ridge Hill (UK DECC)	Aspendale
Picarro G2401	CH <sub>4</sub> , CO <sub>2</sub> , CO, H <sub>2</sub> O	Ragged Point (+EN drier)	Cape Matatula (+EN drier)	Mt. Mugogo (+EN drier)	Heathfield (UK NPL), Bilsdale (UK DECC)	Ny-Ålesund
Picarro G5205 or G5310*	N <sub>2</sub> O, H <sub>2</sub> O	Mt. Mugogo (+EN drier)	Ny- Ålesund*			
LGR High Performance	N <sub>2</sub> O, CO, H <sub>2</sub> O	La Jolla (+EN drier)			Tacolneston	
High Precision Aerodyne QCL	CO, N <sub>2</sub> O	Aspendale, Australia				

monitoring. With only daily calibration this difference is reduced to about a factor of two. The precisions of the G5310 (and G5205) and to a lesser extent of the G2401 are improved by drying the air sample to minimize the H<sub>2</sub>O correction using the aforementioned sampling modules built by Earth Networks and these modules have been adopted at the Ragged Point, Mt. Mugogo and Cape Matatula stations. Finally, CSIRO is operating high precision Aerodyne Research© quantum cascade laser (QCL) spectroscopy systems for CO and N<sub>2</sub>O at Aspendale, Australia.



## 2.4 Isotopomer/Isotopologue Instruments

For GHGs that have natural, anthropogenic, industrial and biogenic sources, such as CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, measurements of atmospheric abundances alone are often inadequate to differentiate precisely among these different sources. High frequency *in situ* measurements of not just the total mole fractions of these gases, but also their stable isotopic compositions (<sup>12</sup>C, <sup>13</sup>C, <sup>14</sup>N, <sup>15</sup>N, <sup>16</sup>O, <sup>18</sup>O, H, D) are a new frontier in global monitoring and hold the promise of revolutionizing understanding of the global cycles of these gases (e.g. Rigby et al., 2012). High-frequency *in situ* isotopic measurements are now feasible using optical (laser) detection.

MIT and Aerodyne Research have co-developed and deployed (2015-2017) at the Mace Head station an automated high frequency instrument for analysis of the isotopic composition of N<sub>2</sub>O using tunable infrared laser differential absorption spectroscopy (TILDAS) with mid-infrared quantum cascade lasers (Harris et al., 2013). This instrument is fully automated and can be accessed and controlled via the Internet. The new instrument monitors the four major isotopologues/isotopomers of nitrous oxide (<sup>15</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O) with a precision of at least 0.3 per mil (‰). The needed pre-concentration was achieved through development of a new high efficiency cryo-focusing trap and sample transfer module (called Stheno) using concepts from the AGAGE Medusa module (Potter et al., 2013).

Similar automated N<sub>2</sub>O isotope instrumentation has been developed at Empa (Wächter et al. 2008, Heil et al., 2014) and has been used for analyzing flask samples from Jungfraujoch. Also, a similar pre-concentration system has been developed by Mohn et al. (2010) and their pre-concentration-TILDAS system has shown excellent compatibility with isotope ratio-MS in an inter-laboratory comparison campaign (Mohn et al., 2014). The pre-concentration technique has been further developed at Empa, implementing a more powerful Stirling cooler and a moveable trap design for quantitative CH<sub>4</sub> adsorption (Eyer et al., 2016). Also, CSIRO operates an Aerodyne Research quantum cascade laser system for the three stable isotopologues of CO<sub>2</sub> (<sup>12</sup>CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub> and <sup>18</sup>O <sup>12</sup>C<sup>16</sup>O) at Cape Grim.

Further developments in these instruments will facilitate their future deployment at AGAGE stations for continuous high frequency *in situ* isotopic composition measurements of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O.

## 2.5 Data Acquisition and Processing

The custom data acquisition and processing software (GCWerks) used in AGAGE for both the GC-MD and Medusa GC-MS instruments, and run under the Linux operating system is described in moderate detail by Miller et al. (2008) and Prinn et al. (2000). There are many benefits to using this custom software approach, including complete source-code control over all instrument operation software, integration and data processing algorithms, and the ability to improve the software interactively. All AGAGE stations (except Hateruma and Ochiishi) and laboratories are linked via the Internet so that such functions as instrument control and software updating can be done remotely. The strength of this approach is illustrated by the fact that, in addition to being used for all Medusa instruments in the AGAGE network, portions of the GCWerks software have been adopted by other leading laboratories engaged in non-AGAGE atmospheric and oceanic trace gas measurements, including NOAA/ESRL, CSIRO, University of Bristol and Empa.

Chromatograms are acquired and displayed in real time, and are stored in highly compressed format. Electronic stripcharts record critical instrument parameters and a multitude of log files are generated as well, which contain parameters critical for data quality control. The GCWerks software allows operators and data processors to quickly review and batch-integrate chromatograms, and produce time series and diagnostic plots of integration results to assess instrumental performance. The AGAGE data processing system relies on having identical software and databases at the field stations and at the data processing sites. This allows the station operators and investigators to review identical chromatograms and instrumental data in a timely manner, and fosters constructive exchanges among the AGAGE investigators. The SIO server maintains a complete database for all stations, and produces final results for all sites once the periodic data reviews have been completed. Data are routinely reviewed at regular intervals, and a final review is done approximately every 6 months, prior to and at each AGAGE team meeting, with all the data processing sites involved concurrently.



New software (GCompare, <http://www.gcwerks.com>) has continued to be developed for data processing, quality control and visualization. This software has greatly streamlined the review and editing of AGAGE data that takes place over the Internet and at AGAGE meetings twice a year. This software is highly interactive, and has features such as being able to click on individual measurements and display back trajectories from the UK Met Office's NAME model (Jones et al., 2007) to help diagnose observed departures from background values. Recent station software developments continue, including enhancements of automated alarms to improve oversight of day-to-day field operations and, importantly, to protect the instrumentation from damage when key components fail. Software for correction of occasional drifts in more reactive gases in the on-site tertiary and quaternary calibration standards has continued to be improved and implemented. Working in collaboration with NOAA/GMD, the software has also been modified to remove the need to divide the acquisition of peak data into time "windows". This had caused problems in optimizing dwell times on certain masses and in following small drifts in retention times of peaks located near transitions between windows. This change also allows a reduction, to some degree, in the numbers of ions acquired at a given time, improving precisions and detection limits especially for the less abundant emerging compounds.

Finally, this GCWerks software is becoming an increasingly important "spinoff" from the AGAGE project. In particular, considerable progress has been made in adapting AGAGE data acquisition, visualization and quality control software for discrete sample GC and GC-MS instruments to applications involving continuous optical instruments such as the cavity ring-down spectrometer (CRDS) instruments of Picarro and Los Gatos Research (LGR) and the quantum cascade laser (QCL) instruments of Aerodyne Research.

## 2.6 Calibration

One of the strengths of AGAGE is its dependence upon well-defined internal absolute gravimetric calibration procedures that can be repeated periodically to assure the accuracy of the long-term measured trends. During the period of AGAGE there have been seven absolute primary calibration efforts, SIO-93, SIO-98, SIO-05, SIO-07, SIO-12, SIO-14 and SIO-16, named after the SIO laboratory and the year in which the scale was completed. The "bootstrap" methods used to prepare primary gravimetric standards at ppt levels and the way in which these standards are integrated to define a calibration scale are described in the AGAGE "history paper" (Prinn et al., 2000). The methods used to propagate these scales to the species measured by the Medusa GC-MS are discussed by Miller et al. (2008). At present, ambient level SIO primary calibration scales have been prepared for 42 AGAGE species ( $\text{N}_2\text{O}$ , PFC-14 ( $\text{CF}_4$ ), PFC-116 ( $\text{C}_2\text{F}_6$ ), PFC-218 ( $\text{C}_3\text{F}_8$ ), PFC-318 ( $\text{c-C}_4\text{F}_8$ ), PFC-3-1-10 ( $\text{C}_4\text{F}_{10}$ ), PFC-4-1-12 ( $\text{C}_5\text{F}_{12}$ ), PFC-5-1-14 ( $\text{C}_6\text{F}_{14}$ ), PFC-6-1-16 ( $\text{C}_7\text{F}_{16}$ ), PFC-7-1-18 ( $\text{C}_8\text{F}_{18}$ ),  $\text{SF}_6$ ,  $\text{SF}_5\text{CF}_3$ ,  $\text{SO}_2\text{F}_2$ ,  $\text{NF}_3$ , HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-227ea, HFC-236fa, HFC-245fa, HFC-356mfc, HFC-43-10mee, HCFC-22, HCFC-141b, HCFC-142b, CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, Halon-1211, Halon-1301, Halon-2402,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$ ). Among them,  $\text{NF}_3$ ,  $\text{C}_4\text{F}_{10}$ ,  $\text{C}_5\text{F}_{12}$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{C}_7\text{F}_{16}$  and  $\text{C}_8\text{F}_{18}$  were calibrated by the method of internal additions, that is by spiking real air with gravimetrically determined amounts of the analyte (Arnold et al., 2012), while the remaining gases were calibrated by the conventional AGAGE method of adding gravimetrically determined amounts of the analytes to analyte-free artificial "zero air". For  $\text{CF}_4$ , the primary calibrations have been made both ways with excellent agreement. The precisions of these calibration scales, based on the internal consistency among the individual primary standards, range from about 2% for the least abundant compounds to <0.1% for the more abundant compounds. The absolute accuracies of these scales, based on estimates of maximum systematic uncertainties, including the purities of the reagents used in their preparation and possible systematic analytical interferences, are between 0.3% and 2% greater than the statistical uncertainties, depending on the compound and its atmospheric abundance.

The evolution of GC-MS techniques in AGAGE has greatly increased the number of species that are measured in the program, and has thus exceeded, at least temporarily, our capacity to prepare and maintain gravimetric primary calibration scales. To bridge this gap and, very importantly, to decouple the long-term measurement program for the evolving and independent primary calibration process, AGAGE has adopted a relative calibration scale for all Medusa and GC-MD measurements. This scale, designated



R1, is defined by regular intercomparisons of trace gas concentrations in a suite of whole-air secondary (“gold”) tanks maintained at the SIO laboratory. These tanks are compared against each other to assess possible drift, and against primary standards for those species for which we have primary standard calibrations. Every year, this suite of secondary (“gold”) tanks is extended with at least one new tank filled under clean air conditions in winter or spring and the intercomparison is repeated. Other tanks filled at the same time are calibrated against this suite of tanks and sent to each station as calibration “tertiary” standards, where they are either directly measured (GC-MD) or used to calibrate working “quaternary” standards (Medusa) at each measurement site. As primary calibration scales evolve at SIO, NOAA/ESRL, Bristol, Empa, NCAR, NIES, or any other laboratory, the relationships of their scales to the R1 scale can be measured to obtain a set of factors by which our R1 values can be multiplied to report Medusa data on any of these calibration scales. The R1 scale is flexible to designate other tanks than “R1” as reference tank for individual compounds, which were not present at sufficient concentrations or were not measured in the original “R1” tank. Looking to the future, this enables us to keep pace with changing atmospheric concentrations of many species, and to incorporate corrections for possible nonlinearities in the calibration process, as well as for possible drifts in standard mixtures. This technique has been used to provide calibrations for species not on an SIO scale such as CFC-13 (METAS-2017), CHBr<sub>3</sub> (NOAA-2009P), PCE (NOAA-2003B) and HCFC-133a (Empa-2013; Vollmer et al., 2015c).

AGAGE gravimetric calibration activities are independent from those in other laboratories (except for the CO<sub>2</sub> calibrations used in the “bootstrap” method that come from the Keeling laboratory at SIO), but there are also strong synergies, especially with NOAA/ESRL. For example, the SIO-14 calibrations showed excellent agreement with NOAA for Halon-2402 (Vollmer et al., 2016), while AGAGE atmospheric CH<sub>2</sub>Cl<sub>2</sub> mole fractions based on the SIO-14 scale are significantly higher than those reported by NOAA (Carpenter et al., 2014).

Whole air and synthetic mixture calibration standards used in AGAGE are stored in 34-liter high-pressure (60 bar) electropolished stainless steel canisters designed at SIO and manufactured by Essex Industries©, that are legal for international shipment.

## 2.7 Primary and Affiliate Station Facilities and Infrastructure

While the individual station size and infrastructure varies depending on their location and presence of other complementary gas and aerosol measurement programs, all stations consist of permanent buildings (wood, concrete, steel, fiberglass) with air samples drawn using non-contaminating pumps through lines with inlets located on adjacent high towers. All stations (except Hateruma and Cape Ochiishi) periodically exchange stainless steel on site Essex calibration tanks (tertiary standards) calibrated at SIO linking the measurements to the AGAGE SIO primary and secondary standards. Some stations also use modified RIX© oil-free air compressors and the tertiary standards to prepare quaternary standards either on site, in their home laboratories or supplied by SIO, to extend the lifetime of the tertiary standards. At Cape Grim and Ny-Ålesund, the quaternary standards are prepared by a cryogenic collection of whole air with subsequent ejection of condensed water.

## 2.8 Secondary Stations

In addition to the primary and affiliate stations in AGAGE, there are complementary “secondary” stations, usually in either more polluted urban locations or in more remote sites that share some or all of the AGAGE technology and calibrations.

SIO carries out continuous measurements of all AGAGE gases in La Jolla in conjunction with its extensive calibration and instrument development operations.

The University of Bristol runs the UK DECC (Deriving Emissions related to Climate Change) network of Tall Towers at Ridge Hill, Angus (now decommissioned), Tacolneston (in collaboration with the University of East Anglia), Heathfield (UK National Physical Laboratory) and Bilsdale in the UK measuring CO<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>O and SF<sub>6</sub> and linked to the AGAGE Mace Head station and to AGAGE calibrations and some technologies. Tacolneston also includes measurements of H<sub>2</sub> and CO via MRD, as well as a Medusa-GCMS.



CSIRO is operating two Medusa-GCMSs at Aspendale, and Picarro CRDS CH<sub>4</sub> and CO<sub>2</sub> (and CO at one station) instruments at Burncluith (26°S, G2401), Ironbark (27°S, G2301), Aspendale (38°S, G2301), Macquarie Island (55°S, G2301), Casey Station, Antarctica (66°S, originally a G1301 now replaced by a G2301) and on board the new CSIRO research vessel the RV Investigator (G2301). Picarro CRDS CH<sub>4</sub> and CO<sub>2</sub> instruments were also previously operated at Gunn Point, northern tropical Australia (11°S, G1301, 2010-2017, currently suspended), Arcturus (22°S, G1301 replaced by G2301, 2010-2014) and Otway (38°S, ESP1000, 2009-2012). CSIRO is also operating high precision Aerodyne Research QCL systems for CO and N<sub>2</sub>O and another for the stable isotopes of CO<sub>2</sub> at Aspendale. All of these instruments are configured to run with AGAGE/GCWerks software (see Section 3.3).

## 2.9 Air Archives

CSIRO has been collecting and archiving pressurized 34-liter electropolished canisters of cryotrapped air collected during clean air conditions at Cape Grim since the mid-1970s to date and plans to continue into the future (Fraser et al., 2017). This “southern hemisphere air archive” has proven to be an invaluable resource to the international atmospheric chemistry community, including AGAGE, because a wide range of species that could not be measured at the time of collection can be measured retrospectively in the archive as long as those species are conserved in these canisters. Until 2013 a target of 4 Cape Grim air archive samples were collected each year, while from 2014 onwards 6 air archive tanks are collected each year. Measurements from this “southern hemisphere archive” have made significant contributions to several recent AGAGE papers, addressing HFC-23 (Miller et al., 2010), PFCs (Mühle et al., 2010, Trudinger et al., 2016), SF<sub>6</sub> (Rigby et al., 2010), CFCs -13, -114 and -115 (Vollmer et al., 2017), Halons-1211, -1301 and -2402 (Vollmer et al., 2016), and HFC-365mfc, -245fa, -227ea and -236fa (Vollmer et al., 2011). There was a parallel “northern hemisphere archive” collected by R. Rasmussen at Cape Meares, Oregon, during the ALE and GAGE programs, but these samples are no longer accessible to this program and are mostly used up. The SIO AGAGE group has been storing a “northern hemisphere archive” of air compressed at Trinidad Head and La Jolla since the mid-1990s, and has collected a series of northern hemisphere air samples from various sources (e.g., SIO (laboratories of C. D. Keeling and R. F. Weiss), NOAA-GMD and NILU) and of varying integrity for trace gas measurements that extends this record back to the early 1970s. Measurements from this “northern hemisphere archive” have made significant contributions to several recent AGAGE papers, especially for more inert species such as the PFCs, NF<sub>3</sub> and SF<sub>6</sub> (e.g., Mühle et al., 2009; 2010; Rigby et al., 2010; Weiss et al., 2008; Arnold et al., 2013).

Additional air archive samples used in AGAGE studies were derived from firn air collections in Greenland and Antarctica obtained by international consortia. The AGAGE analyses of firn air used Medusa-GC-MS instruments and substantially extended mole fraction data back in time along with emission estimates derived from the data, specifically for Halons (Vollmer et al., 2016), PFCs (Trudinger et al., 2016), and minor CFCs (Vollmer et al., 2017).

## 3. Data Analysis and Modeling

### 3.1 Meteorological Interpretation

As part of processing the AGAGE data, we place an identification flag on each measured value in an attempt to separate regional and/or local pollution events from background measurements. The current, objective (statistically based) algorithm, has been successfully implemented and uniformly applied to the entire ALE/GAGE/AGAGE time series including data from all AGAGE primary and affiliate stations (except Hateruma and Cape Ochiishi) and all instruments (GC-MS, GC-MD, Picarro). Moreover, the algorithm has been designed to be easily re-applied to the entire data set in the event of (minor) modifications to the algorithm. The concept of the algorithm is to examine the statistical distributions of 4-month bins of measurements (approximately 4320 GC-MD or 1440 Medusa GC-MS values) of any species at a specified site and centered on one day at a time after removing the trend over the period (O'Doherty et al., 2001; Cunnold et al., 2002). The algorithm can be applied to the results from 3D models to separate the background and polluted values (Ryall et al., 2001; Simmonds et al., 2005). We also use a 3D Lagrangian back trajectory model driven by analysed meteorology, specifically the UK Met





Office's Numerical Atmospheric dispersion Modelling Environment (NAME, Ryall et al., 1998, Jones et al., 2007) to further evaluate the pollution algorithm and include it as part of the pollution/background identification flag associated with each measurement. NAME back trajectories are automatically computed for every AGAGE measurement and used extensively in the semi-annual AGAGE data reviews.

### 3.2 Data Intercomparisons

AGAGE cooperates with other groups carrying out flask sampling and/or *in situ* real-time tropospheric measurements in order to produce harmonized global data sets for use by theoreticians. Toward this end, AGAGE routinely collaborates with NOAA/ESRL/GMD to develop best estimates of the differences in absolute calibrations and field site calibrations between them and the AGAGE-SIO scales (see Elkins et al., 2015 and the NOAA/ESRL/GMD website for the NOAA/ESRL/GMD database). This is undertaken in several ways: comparisons involving exchanges of tanks (checking absolute calibration); comparisons of hemispheric and global mean trends estimated by the two networks; examination of differences between the AGAGE and GMD *in situ* instruments at our common *in situ* site, Cape Matatula (checking propagation of standards to remote sites); and ongoing extensive comparisons between AGAGE *in situ* GC-MD and GC-MS data, and GMD flask data at the six AGAGE sites where GMD flasks are filled (Zeppelin, Mace Head, Trinidad Head, Ragged Point, Cape Matatula and Cape Grim), with the results reported at the semi-annual AGAGE meetings. To help ensure progress on this and other cooperative endeavors, leaders and members of the relevant NOAA/GMD group regularly attend the semi-annual AGAGE meetings; other joint meetings with GMD personnel are held from time to time. Also, comparisons between AGAGE *in situ* GC-MD and GC-MS data at Cape Grim and flask data from other groups (CSIRO, NIES, U. East Anglia, SIO, U. Heidelberg, Max Planck Inst. Mainz) have been, and continue to be made. Exchanges of tanks between the collaborating NIES group and AGAGE-SIO are also performed to compare absolute calibrations. Also, there are routine data inter-comparisons carried out within AGAGE for those gases measured on both the AGAGE Medusa GC-MS and AGAGE GC-MD instruments. Finally, three AGAGE sites (SIO, Mace Head and Cape Grim) participated in the WMO-organized IHALACE (International HALocarbon in Air Comparison Experiment), round robin intercomparisons (Hall et al., 2014).

### 3.3 Flux Estimation using Measurements and Models

A major goal of AGAGE is to estimate surface fluxes and/or atmospheric sinks (lifetimes) of trace gases by merging measurements and models using advanced statistical methods (Prinn et al., 2000; Weiss and Prinn, 2011). Specifically, we use a range of Bayesian methods, in which *a priori* estimates of atmospheric sinks, and surface fluxes (or uncertain parameters in flux models) are adjusted to improve agreement with the trace-gas observations, within estimated uncertainties, and it is important to ensure that the problems are well-posed, that ill-conditioning inherent in our emission estimations is minimized, and that model and measurement imperfections are accounted for properly (e.g. Prinn, 2000, Tarantola, 2005). A basic requirement for all our inverse schemes is an accurate and realistic atmospheric chemical transport model (CTM). Even small transport errors can lead to significant errors in estimated sources or sinks (Hartley and Prinn, 1993; Mahowald et al., 1997; Mulquiney et al., 1998). We use a range of CTMs to estimate trace gas budgets at different spatial scales: two dimensional "box" models provide global source and sink estimates using baseline observations, global three dimensional Eulerian models are used for estimating fluxes at national to continental scales, and high-resolution regional Lagrangian models provide fine-scale source estimation close to AGAGE monitoring sites.

We relate the vector of measured atmospheric mole fractions ( $\mathbf{y}$ ) to emissions or initial conditions in a "parameters vector" ( $\mathbf{x}$ ) using the "measurement" equation  $\mathbf{y}_{\text{obs}} = \mathbf{H}\mathbf{x} + \mathbf{e}$ . Here  $\mathbf{H}$  is a matrix of sensitivities, or partial derivatives, of simulated measurements in  $\mathbf{y}$  ( $= \mathbf{H}\mathbf{x}$ ) to each element in  $\mathbf{x}$ , and is derived using the CTMs, and  $\mathbf{e}$  describes the random component of the error due to errors in the measurements and in the CTM. These errors form the error covariance matrix  $\mathbf{R}$ . A prior estimate of  $\mathbf{x}$  ( $\mathbf{x}_{\text{prior}}$ ) is generally needed, with uncertainties contained in the error covariance matrix  $\mathbf{P}_{\text{prior}}$ . There are a number of statistical approaches that have been developed and implemented to make these estimations,



which are described briefly below (e.g. Kasibhatla et al., 2000; Prinn, 2000; Rigby et al., 2011; Ganesan et al., 2014).

A common Bayesian statistical approach is “optimal estimation” (e.g. Kasibhatla et al., 2000) in which one minimizes a “cost” function ( $J$ ) that is the sum of two quadratic forms:  $(\mathbf{y}_{\text{obs}} - \mathbf{y})^T \mathbf{R}^{-1} (\mathbf{y}_{\text{obs}} - \mathbf{y})$  that minimizes the weighted difference between measured and modeled mole fractions, and  $(\mathbf{x} - \mathbf{x}_{\text{prior}})^T \mathbf{P}^{-1} (\mathbf{x} - \mathbf{x}_{\text{prior}})$  that minimizes the weighted difference between the estimated parameters and their prior. This minimization yields analytical solutions to  $\mathbf{x} = \mathbf{x}_{\text{prior}} + \mathbf{G} (\mathbf{y}_{\text{obs}} - \mathbf{y})$ ,  $\mathbf{P} = (\mathbf{I} - \mathbf{G}\mathbf{H}) \mathbf{P}_{\text{prior}}$ , and the “gain” matrix  $\mathbf{G} = \mathbf{P}_{\text{prior}} \mathbf{H}^T (\mathbf{H} \mathbf{P}_{\text{prior}} \mathbf{H}^T + \mathbf{R})^{-1}$ . Examples of this approach using global 3D Eulerian models are provided by Chen and Prinn (2005, 2006) for  $\text{CH}_4$ , Xiao et al. (2010a) for  $\text{CH}_3\text{Cl}$ , Xiao et al. (2010b) for  $\text{CCl}_4$ , Rigby et al. (2010, 2011) for  $\text{SF}_6$ , Saikawa et al. (2012, 2014b) for HCFC-22, and Huang et al. (2008) and Saikawa et al. (2014a) for  $\text{N}_2\text{O}$ . Weak nonlinearities may occur when lifetimes vary with emissions (e.g. OH depends on CO and  $\text{CH}_4$  emissions). This problem can be addressed by recalculating the time dependent partial derivative (sensitivity)  $\mathbf{H}$  matrix after inversion of all the data, and then repeating the inversion with the new  $\mathbf{H}$  matrix to ensure convergence (Prinn, 2000).

Random measurement imperfections are associated with *in situ* instrument precision, satellite retrieval errors, and inadequate sampling in space and time. If known, random model errors can also be incorporated into the model-measurement error covariance matrix ( $\mathbf{R}$ ). It is also important to recognize that correlated model-measurement errors, which comprise  $\mathbf{R}$ , as well as errors in the prior contained in  $\mathbf{P}_{\text{prior}}$  are often poorly known quantities. Ganesan et al. (2014) explicitly allow such uncertainties to be derived in the inversion to minimize the effect of subjective assumptions on derived fluxes. This hierarchical Bayesian method (Ganesan et al., 2014) incorporates “hyper parameters” that describe the model-measurement and/or prior uncertainty covariance matrices ( $\mathbf{R}$  and  $\mathbf{P}$ ) in the inversion. This approach leads to solutions that are less sensitive to the (often subjective) assumptions that are required about uncertainties in traditional Bayesian approaches. The hierarchical inversion scheme cannot, in general, be solved analytically, and therefore Markov Chain Monte Carlo (MCMC) methods must be applied that sample from the posterior distribution using a large number ( $\sim 10^4 - 10^5$ ) of realisations of the parameter space (e.g. Rigby et al., 2011). Recently, this MCMC approach has been extended to include problems in which the dimension of the parameter space is itself considered unknown using a so-called “reversible-jump” MCMC algorithm (Lunt et al., 2016). This method has been applied to high-resolution regional inversions using a Lagrangian model to sample from a range of possible basis function decompositions of the flux space, objectively determining the level of decomposition that is appropriate to effectively minimize “aggregation error” (i.e. an inflexibility in the space that could lead to errors in the prior distribution unduly influencing the outcome of the inversion), whilst maintaining an acceptable level of uncertainty reduction.

We also address model structural errors and random and systematic transport errors (i.e. errors in  $\mathbf{H}$ ) through utilization of multiple model versions (Locatelli et al., 2013) and Monte-Carlo methods (Prinn et al., 2001, 2005, Huang et al., 2008). The Monte Carlo methods also include systematic errors in measurement calibration.

For determination of the regional sources of trace gases, beginning with Chen and Prinn (2006) we now frequently merge measurements from the AGAGE and NOAA/ESRL/GMD stations, and also aircraft, and satellites whenever appropriate (e.g. Ganesan et al., 2017). Because source and sink estimation is very sensitive to errors in time and space gradients, we ensure inter-calibration among instruments of the same type, and inter-comparison between different instruments measuring the same quantity. We also objectively determine the accuracy and precision of each measurement when combining data, since data are weighted inversely to their variances (contained in  $\mathbf{R}$ ).

### 3.4 Flux Estimation using 3D Eulerian Models

For our inverse studies we initially used the 3D MATCH Model of the National Center for Atmospheric Research, NCAR (Mahowald et al., 1997; Rasch et al., 1997; Lawrence et al., 1999).



MATCH was driven by data from the NCEP, ECMWF, and GSFC/NASA/DAO re-analyses (Rasch et al., 1997; Mahowald et al., 1997). Subgrid mixing processes, which include dry convective mixing, moist convective mixing and large-scale precipitation processes, were computed in the model. MATCH was used at a horizontal resolution as fine as T62 ( $1.8^\circ \times 1.8^\circ$ ), with either 42 or 28 levels in the vertical. Utilizing MATCH with AGAGE, ESRL and other data, we estimated monthly regional and global emissions for many AGAGE species (e.g., Chen and Prinn, 2005, 2006; Huang et al., 2008; Xiao et al., 2010a, 2010b). The ability of MATCH to accurately simulate the effects of transport on long-lived trace gases is well illustrated by  $\text{CH}_4$  simulations (Chen and Prinn, 2005).

More recently we use the newer NCAR Model for Ozone and Related Tracers (MOZART) that also simulates global three-dimensional mole fractions of atmospheric trace species (Emmons et al., 2010). Like MATCH, the MOZART model can be run off-line, driven by a variety of state of the art reanalysis meteorological fields, including the National Center for Environmental Prediction/NCAR reanalysis (Kalnay et al., 1996) and the NASA Modern Era Retrospective-Analysis for Research and Applications, NASA-MERRA (Bosilovich et al., 2008). We have specifically used MOZART inversions to estimate regional emissions for  $\text{SF}_6$  (Rigby et al., 2010), heavy PFCs (Ivy et al., 2012a,b), HCFC-22 (Saikawa et al., 2012, 2014b), and  $\text{N}_2\text{O}$  (Saikawa et al., 2014a).

### 3.5 Flux Estimation using 3D Lagrangian Models

Another modeling approach that we have used utilizes air histories or “footprints” computed from Lagrangian models driven by analysed observed winds. These air histories, computed over a pre-defined region, quantify the time and locations that air masses have interacted with the surface (and therefore fluxes from the surface) prior to measurement at a station. Using this information and the measurements, we can solve for fluxes from these predefined regions. The method requires accurate simulation of both advective back trajectories as well as diffusion. We had earlier examined the use of the HYSPLIT model (Draxler and Hess, 1997) for this purpose (Kleiman and Prinn, 2000) but now utilize Lagrangian particle dispersion models (LPDMs). In particular, the LPDM, NAME of the UK (Ryall et al., 1998) has been used to determine source strengths for observed species on regional scales (e.g., Cox et al., 2003; O’Doherty et al., 2004, 2009; Reimann et al., 2005; Derwent et al., 2007; Ganesan et al., 2015; Manning et al., 2011; Rigby et al., 2011; Lunt et al., 2015). The LPDM FLEXPART model has also been applied to inversion of AGAGE data for several species (Stohl et al., 2009, 2010; Maione et al., 2014; Graziosi et al., 2015, 2016, 2017; Fang et al., 2014).

### 3.6 Flux Estimation using merged Eulerian and Lagrangian models

Given the high-frequency nature of the AGAGE measurements, we can extract a great deal of information on sources close to the monitoring sites. LPDM models like NAME have the useful property that they directly calculate the sensitivity of the measurements to emissions from every grid cell in the domain. However, one limitation of these models is that boundary conditions must be specified or estimated (e.g., Stohl et al., 2009). In contrast, inversions using global Eulerian CTMs, such as MOZART, do not usually require boundary conditions but can only estimate emissions from a limited number of regions (unless an adjoint model of the CTM is available). In addition, these models are sensitive to uncertainties in species lifetimes.

To combine the Eulerian and Lagrangian approaches, we can decompose the sensitivity matrix  $\mathbf{H}$  into components that represent the sensitivities of the observations to initial conditions ( $\mathbf{H}_{\text{IC}}$ ), emission from model grid cells close to AGAGE stations ( $\mathbf{H}_{\text{LE}}$ ), and emissions from aggregated regions that are farther from the AGAGE sites ( $\mathbf{H}_{\text{NLE}}$ ): that is  $\mathbf{H} = (\mathbf{H}_{\text{IC}}, \mathbf{H}_{\text{NLE}}, \mathbf{H}_{\text{LE}})$  (Rigby et al., 2011).  $\mathbf{H}_{\text{IC}}$  and  $\mathbf{H}_{\text{NLE}}$  can be estimated using the Eulerian model at reasonable computational cost, whilst the term  $\mathbf{H}_{\text{LE}}$  can be determined using the Lagrangian model. Consideration must be made of the fate of emissions close to AGAGE sites that leave the LPDM region and gradually become mixed into the global atmosphere.  $\mathbf{H}_{\text{LE}}$  must therefore be decomposed into a short-timescale term  $\mathbf{H}_{\text{LE,LAM}}$ , for which the Lagrangian model is used, and a long-timescale term  $\mathbf{H}_{\text{LE,EUM}}$ , which can be approximated using the Eulerian model. Once  $\mathbf{H}$  is constructed, the inversion can be solved using any Bayesian inverse method incorporating measurement, model and state error covariance matrices (Section 3.4). This approach has the advantage



over previous global emissions estimates that only used a LPDM in that constant background mole fractions do not have to be assumed (*e.g.*, Stohl et al., 2009). Further, by solving for regional and global emissions and covariance in a single step, we can avoid many of the problems encountered in two-step “nested” inverse methods (*e.g.*, covariance between emissions in the “Lagrangian region” and those outside, as in the method of Roedenbeck et al., 2009).

Inverse estimates of global sulfur hexafluoride (SF<sub>6</sub>) emissions have been carried out using this method (Rigby et al., 2011). The derived global total emission rate agrees well with previous CTM-based estimates by Rigby et al. (2010), and the regional emissions qualitatively agree with their findings.

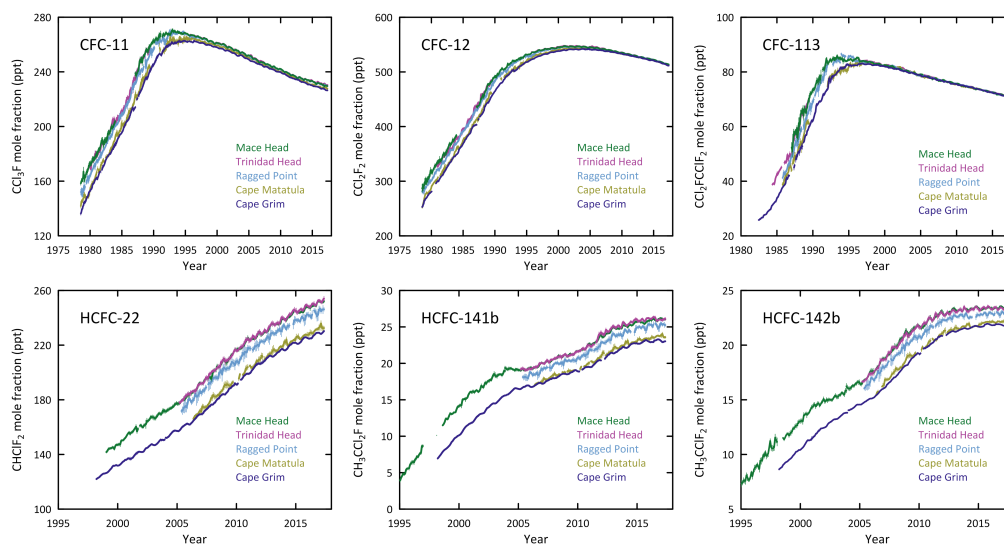
### 3.7 Application of Simplified Models

The 3D models being computationally expensive, do not always lend themselves well to doing very long-time integrations, and multiple runs to address uncertainty (*e.g.*, thousands of runs for Monte Carlo treatments of model, rate constant, and absolute calibration errors). A 2D (12-box) model (Cunnold et al., 1994; Prinn et al., 2001, 2005; Rigby et al., 2013, 2014) is well suited to full uncertainty analysis of the AGAGE data, because its transport is ‘tunable’ to simulate observed latitudinal gradients, and it possesses a horizontal resolution similar to that effectively described by the AGAGE monthly mean observations with pollution events removed (Prinn et al., 2005). This 2D model has been used to estimate emissions of 3 light PFCs (PFC-14, PFC-116, and PFC-218; Mühle et al., 2010), NF<sub>3</sub> (Arnold et al., 2013), and combined with the 3D MATCH model has provided estimates of the influence of model errors on overall emission uncertainties for N<sub>2</sub>O (Huang et al., 2008).

## 4. Sample Scientific Accomplishments

### 4.1 Trends in Montreal Protocol Gases and their Replacements

The Montreal Protocol on Substances that Deplete the Ozone Layer, enacted to protect the ozone layer, regulates many ozone-depleting gases for the primary purpose of lowering stratosphere chlorine and bromine concentrations. From AGAGE measurements (**Figure 3**), two of the major CFCs (CFC-11, CFC-113) have both been decreasing in the atmosphere since the mid-1990s. While their emissions have decreased very substantially in response to the Montreal Protocol, their long lifetimes of around 50 and 90 years respectively mean that their sinks can reduce their levels only at about 2% and 1% per year respectively. The other major CFC (CFC-12) has a somewhat longer lifetime (about 100 years) and slower phase-out of emissions, and consequently its atmospheric levels have reached a plateau more recently and are now decreasing. The three major HCFCs (HCFC-22, -141b, and -142b) are replacements for the CFCs and continue to rise in recent years. Rates of rise decreased somewhat in the late 1990s for HCFC-141b (9-year lifetime) and HCFC-142b (18-year lifetime) consistent with decreases in their emissions from developed countries, then increased again consistent with increases in developing country emissions. In contrast, rates of rise have slowly declined post-2008 for HCFC-22 (12-year lifetime). AGAGE mole fraction data and derived emissions of a wide range of ozone-depleting species have been published in multiple recent papers (Fraser et al., 2014; Graziosi et al., 2015, 2016; Keller et al., 2011; Kim et al., 2010, 2012; Li et al., 2011, 2014; Lunt et al., 2015; Maione et al., 2013, 2014; Miller et al., 1998; Rigby et al., 2013; Saikawa et al., 2012, 2014b; Stohl et al., 2010; Vollmer et al., 2016, 2017; Xiang et al., 2014; Xiao et al., 2010b).



**Figure 3.** Monthly mean mole fractions (ppt) and their standard deviations (vertical bars) for selected AGAGE Montreal Protocol gases through 2017.

#### 4.2 Is the Montreal Protocol Working?

The global abundance of tropospheric chlorine and emissions, via inverse methods, of ozone-depleting gases are estimated from AGAGE measurements (**Figure 4**). Some specific conclusions are as follows:

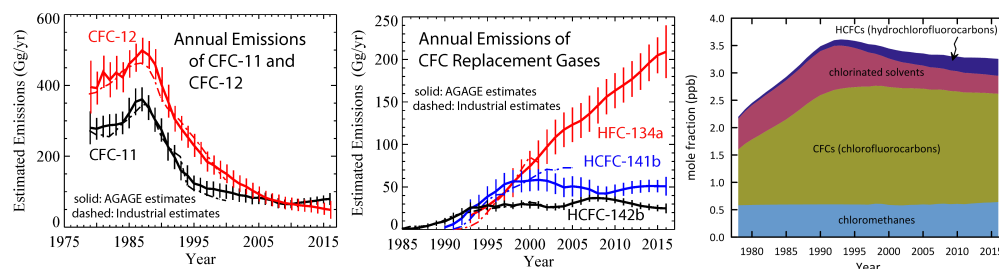
- (1) International compliance with the Montreal Protocol is so far resulting in CFC and chlorocarbon abundances comparable to the target levels — the Protocol is working (although CFC-11 emissions post-2010 are rising, **Figure 4**);
- (2) The abundance of total chlorine in long-lived CFCs and other chlorocarbons (CFCs-11, -12, -13, -113, -114, -115, HCFCs-22, -141b, -142b,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_2\text{CCl}_2$ ) in the lower troposphere reached a maximum of about 3.6 ppb in 1993 and is beginning slowly to decrease in the global lower atmosphere driven initially by  $\text{CH}_3\text{CCl}_3$  and later by CFC decreases (note  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CCl}_2\text{CCl}_2$  are not regulated in the Montreal Protocol, yet  $\text{CH}_2\text{Cl}_2$  is increasing);
- (3) The CFCs have atmospheric lifetimes consistent with destruction in the stratosphere being their principal removal mechanism;
- (4) Multi-annual variations in measured CFC, HCFC, HFC and other chlorocarbon emissions deduced from ALE/GAGE/AGAGE data are approximately consistent with variations estimated independently from industrial production and sales data where available. HCFC-141b shows the greatest discrepancies. The processes producing the deduced  $\text{CCl}_4$  emissions are not well understood;
- (5) The mole fractions of the HCFCs, which are interim replacements for CFCs, rose very rapidly in the atmosphere until the early 2000s, but are now only rising relatively slowly; the exception is HCFC-22, which has been in use almost as long as the CFCs. HCFC-22 continues to increase rapidly in the atmosphere and contributes significantly to atmospheric chlorine loading.
- (6) The mole fractions of HFCs, which are long term replacements for CFCs and HCFCs, continue to rise rapidly in the atmosphere and are the major Kyoto synthetic greenhouse gases contributing to increased radiative forcing. They were added to the Montreal Protocol in the 2016 Kigali Amendment.

AGAGE scientists, AGAGE data and AGAGE modeling results played a prominent role in all the WMO-UNEP Ozone Assessments, most recently the WMO-UNEP 2010 (Montzka et al, 2011a) and





1 WMO-UNEP 2014 (Carpenter et al., 2014) Ozone Assessments, also providing many coordinating and  
 2 lead authors, co-authors, contributing authors and reviewers. The AGAGE-led paper on the re-evaluation  
 3 of the lifetimes of the major CFCs and  $\text{CH}_3\text{CCl}_3$  using atmospheric trends (Rigby et al., 2013), was an  
 4 important input into the 2014 Ozone Assessment (Carpenter et al., 2014).



**Figure 4.** Inversely estimated emissions of: Selected AGAGE regulated gases (**left panel**), and selected AGAGE replacement gases (**center panel**), compared to estimates from industrial/national/UNEP reports; Estimates of total tropospheric chlorine from all AGAGE data (chlorinated solvents are  $\text{CCl}_4$  and  $\text{CH}_3\text{CCl}_3$ ; chloromethanes are  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ ; see **Table 1** for full list of AGAGE chlorine-containing compounds)(**right panel**).

#### 4.3 Trends in Kyoto Protocol Gases

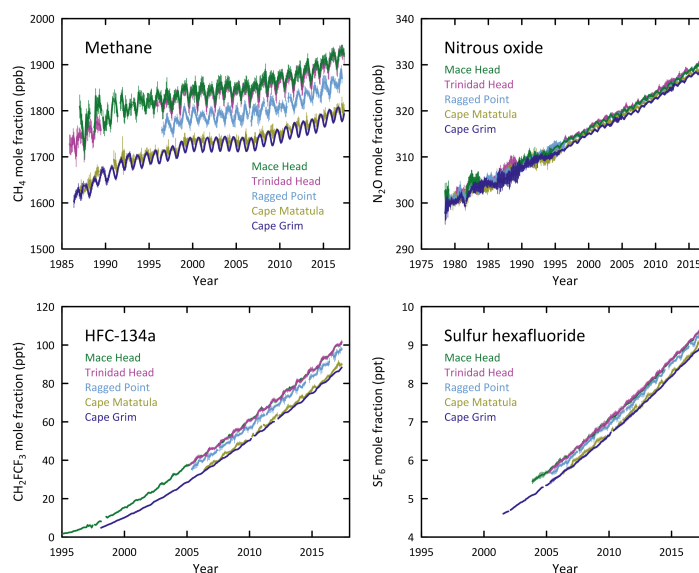
The Kyoto Protocol, followed now by the Paris Accord, regulates several powerful GHGs in addition to  $\text{CO}_2$ . Methane is the second most important long-lived GHG. AGAGE measurements (**Figure 5**) show that its concentration has been rising in recent decades with large year-to-year variations. Its multi-year average rate of increase had been decelerating, with no significant increase over a 9-year period, perhaps as a result of an approach to a state where its multiple sources are balanced by a roughly constant sink rate (reaction with OH). Methane then began to rise again around 2006. AGAGE data and emission estimates for methane have appeared in multiple recent papers (Rigby et al., 2008; Kirschke et al., 2013; Loh et al., 2015; Manning et al., 2011; Patra et al., 2011; Saito et al., 2013; Thompson et al., 2015; Saunio et al., 2016, 2017). Nitrous oxide is the third most important long-lived greenhouse gas (after  $\text{CO}_2$  and  $\text{CH}_4$ ) and the major source of ozone-depleting nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) in the stratosphere (Ravishankara et al., 2009). The atmospheric  $\text{N}_2\text{O}$  concentrations have been increasing almost linearly over recent decades. Estimated pre-industrial  $\text{N}_2\text{O}$  levels are around 270 parts per billion (ppb) (see MacFarling-Meure et al., 2006) compared to the 22% higher levels of 329.3 ppb in 2016. The primary cause of its recent increase, and the reasons for its atmospheric cycles, are addressed by Huang et al. (2008), Nevison et al. (2011), Thompson et al. (2013, 2014a, 2014b, 2014c) and Saikawa et al. (2014a) using AGAGE and NOAA-ESRL data.

AGAGE measurements and estimated emissions of the purely synthetic Kyoto Protocol-type gases (HFCs, PFCs,  $\text{SF}_6$ ,  $\text{NF}_3$ ) have been published in many recent AGAGE papers (Arnold et al., 2013, 2014; Graziosi et al., 2017; Ivy et al., 2012a, 2012b; Keller et al., 2011; Kim et al., 2010, 2012, 2014; Li et al., 2011, 2014; Miller et al., 2010; Mühle et al., 2010; O'Doherty et al., 2014; Rigby et al., 2010, 2011, 2014; Saikawa et al., 2014b; Simmonds et al., 2015, 2016; Stohl et al., 2009, 2010; Vollmer et al., 2011; Xiang et al., 2014). Two examples of these, HFC-134a the most abundant HFC, and sulfur hexafluoride are given here. The atmospheric abundance of the air-conditioning refrigerant HFC-134a is increasing at a rapid rate, in response to its growing emissions arising from its role as the major replacement for the



refrigerant CFC-12. With a lifetime of about 14 years, its current atmospheric abundance is determined primarily by its emissions and secondarily by its atmospheric destruction.  $\text{SF}_6$  is produced largely for use as an insulating gas in electrical distribution equipment. Its concentrations have been increasing continuously since AGAGE measurements began in the 2000s and archive tanks began to be filled in the 1970s. Its very long lifetime ensures that its emissions accumulate essentially unabated in the atmosphere.

AGAGE data have been used to quantify the recent decline of HCFC emissions and rise in HFC emissions (Simmonds et al., 2017).



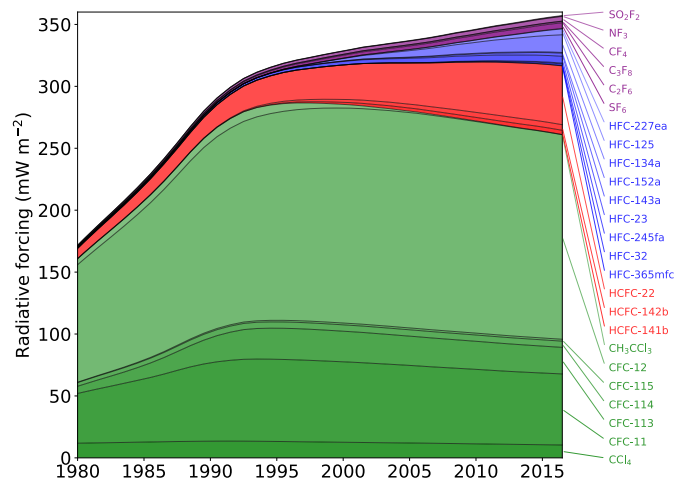
**Figure 5.** Monthly mean mole fractions and standard deviations for selected Kyoto Protocol gases through 2017.

AGAGE scientists and AGAGE data and modeling results played a significant role in multiple IPCC Climate Change Assessments, most recently the IPCC 4<sup>th</sup> Assessment: Climate Change 2007, WG1, Chapter 2 (Forster et al (2007), and the IPCC 5<sup>th</sup> Assessment: Climate Change 2013, WG1, Chapter 2 (Hartmann et al, 2013), also providing lead authors, contributing authors and reviewers. AGAGE data also contributed significantly to the recent history of greenhouse gas mole fractions to drive climate model simulations for use in the IPCC 6<sup>th</sup> Assessment (Meinshausen et al., 2017).

#### 4.4. Recent Rise of Powerful Synthetic Greenhouse Gases

While the radiative forcing of purely synthetic greenhouse gases (SGHGs) regulated by the Montreal Protocol have decreased substantially since around 1993, newer SGHGs with global warming potentials (GWPs) of many thousands have become more and more important in recent years, and unabated are expected to become even more so in the future (Rigby et al., 2014). These gases are used in many high technology applications (*e.g.*, HFCs in refrigeration and air conditioning, PFCs as solvents and emitted from aluminum, semiconductor, and rare earth metal production,  $\text{SF}_6$  in electric power distribution, and  $\text{NF}_3$  in flat screen displays and semi-conductor production). Regulations forcing their recycling or their replacement may be needed.

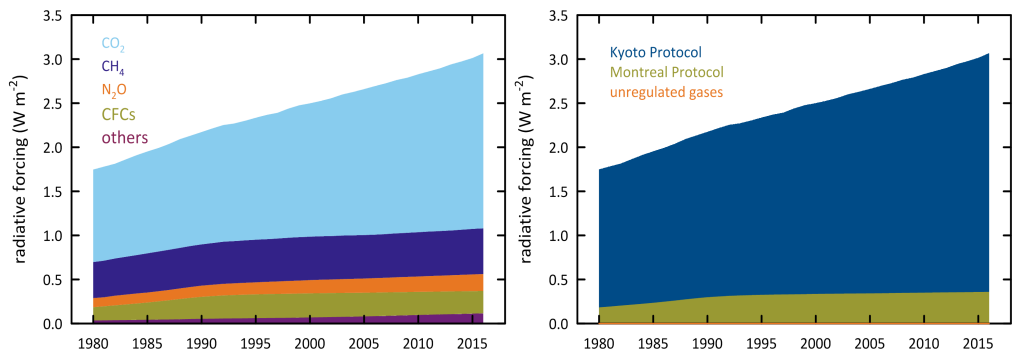
AGAGE measures all of the significant SGHGs and **Figure 6** shows global radiative forcing by each of these gases, based on observations (Rigby et al., 2014, extended to 2017).  $\text{CO}_2$ -equivalent emissions have been derived from AGAGE observations for HFCs, and PFCs plus  $\text{SF}_6$ ,  $\text{NF}_3$  and  $\text{SO}_2\text{F}_2$ , and compared to reported emissions from Annex-1 countries. Unreported emissions from non-Annex-1 countries (*i.e.* AGAGE-derived Total Emissions minus Annex-1 Reported Emissions) have been rapidly increasing since 1990 for both these classes of SGHGs, and are now 35% more than Annex-1 for the HFCs and 600% more for the PFCs plus  $\text{SF}_6$ . The mole fractions and derived emissions of AGAGE-measured heavy HFCs have all been increasing rapidly since the early 2000s for HFC-365mfc and HFC-245fa, and since 1995 for HFC-227ea and HFC-236fa (Vollmer et al., 2011).



**Figure 6.** Global radiative forcing due to long-lived SGHGs derived from AGAGE observations from 1980 to 2017 (update of Rigby et al., 2014).

#### 4.5 Trends in Total Radiative Forcing

By adding the radiative forcing ( $\text{W m}^{-2}$ ) of the Montreal Protocol, Kyoto Protocol and recent unregulated synthetic greenhouse gases, the overall radiative forcing due to all long-lived substances is obtained. **Figure 7** shows that for radiative forcing by  $\text{CO}_2$  still dominates, and the percentage of the total forcing due to the non- $\text{CO}_2$  AGAGE greenhouse gases is slowly decreasing reaching ~36% by the end of 2016. However, the emissions, mole fractions and absolute radiative forcing of non- $\text{CO}_2$  gases continue to rise.



**Figure 7.** Global total radiative forcing due to long-lived greenhouse gases derived from NOAA-GMD measurements for  $\text{CO}_2$  and AGAGE observations for all others (**left hand panel**). Also shown are the contributions from the gases in the Kyoto and Montreal Protocols and those not regulated by either Protocol (**right hand panel**).

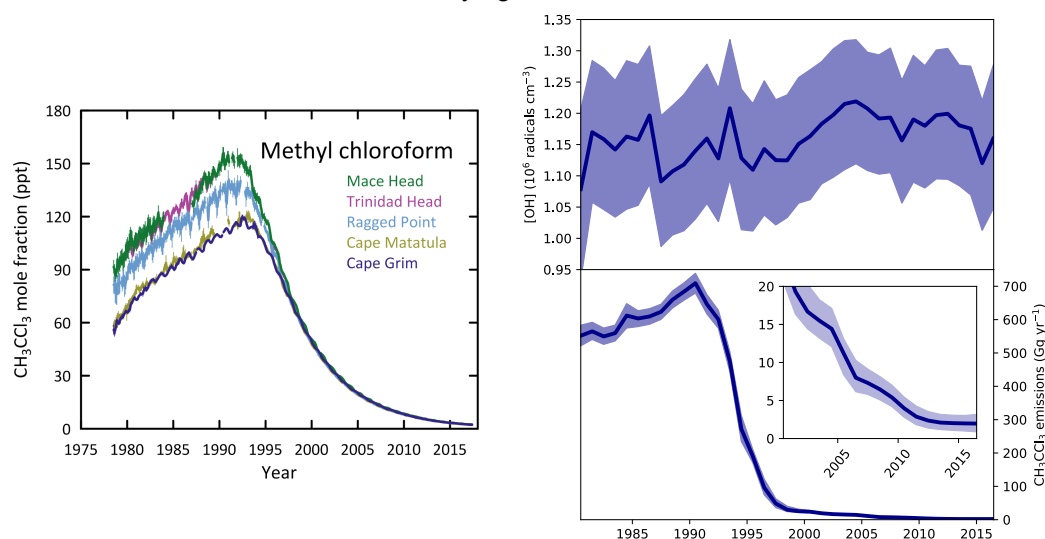
#### 4.6. Determination of OH Concentrations using Models and Multiple species

The hydroxyl free radical is the major oxidizing chemical in the atmosphere, destroying about 3.7 petagrams of trace gases each year, including many gases involved in ozone depletion, the greenhouse effect and urban air pollution. The large-scale concentrations and long-term trends in OH can in principle be measured indirectly using global measurements of trace gases whose emissions are well known and whose primary sink is OH. The best trace gas for this purpose is the industrial chemical  $\text{CH}_3\text{CCl}_3$ . First,



1 there are accurate long-term measurements of  $\text{CH}_3\text{CCl}_3$  beginning in 1978 in the ALE/GAGE/AGAGE  
2 network (Prinn et al., 1983b, 2000, 2001, 2005, Rigby et al., 2008, 2013, 2017), and beginning in 1992 in  
3 the NOAA/CMDL network (Montzka et al., 2000, 2011). Second,  $\text{CH}_3\text{CCl}_3$  has fairly simple end uses as  
4 a solvent, and voluntary chemical industry reports since 1970, along with the national reporting  
5 procedures under the Montreal Protocol in more recent years, have produced reasonably accurate  
6 emissions estimates for this chemical (McCulloch and Midgley, 2001). The use of  $\text{CH}_3\text{CCl}_3$  for OH  
7 concentration and trend estimation has been extensive (Prinn et al., 1987, 1995, 2001, 2005; Spivakovsky  
8 et al., 2000; Montzka et al., 2000, 2011b; Krol and Lelieveld, 2003; Bousquet et al., 2005). Other gases  
9 that are useful OH indicators include  $^{14}\text{CO}$ , which is produced primarily by cosmic rays (Manning et al.,  
10 2005). Another useful AGAGE gas is HCFC-22 that yields OH concentrations similar to those derived  
11 from  $\text{CH}_3\text{CCl}_3$  but with less accuracy (Miller et al., 1998). The industrial gases HFC-134a, HCFC-141b  
12 and HCFC-142b are potentially useful OH estimators but the accuracy of their emission estimates needs  
13 improvement (Huang and Prinn, 2002). At the present time, to augment  $\text{CH}_3\text{CCl}_3$ , the potential OH  
14 estimation species (major tropospheric sink is reaction with OH and industrial emissions estimations are  
15 relatively good) are: HFC-134a, HCFC-141b, HCFC-142b, and possibly some of the newly introduced  
16 HFCs (Liang et al., 2017).

17 AGAGE data (**Figure 8**) show that  $\text{CH}_3\text{CCl}_3$  levels and latitudinal gradient rose steadily from 1978 to  
18 reach a maximum in 1992 and have both since rapidly decreased as the Montreal Protocol drove  
19 emissions to near zero. In 2010 the levels were about 3% of those when AGAGE measurements began in  
20 1978. Analysis of these observations shows that global average OH levels vary, but only occasionally  
21 significantly, from year to year but exhibit no significant long-term trend (Prinn et al., 2001, 2005, Rigby  
22 et al., 2008, 2013, 2017, latter updated in **Figure 8**). This analysis includes effects of observationally  
23 derived corrections to emissions, and model as well as measurement errors. The 1997-1999 OH minimum  
24 coincides with, and is perhaps caused by, major global wildfires and an intense El Niño event at that time.  
25 Recent  $\text{CH}_3\text{CCl}_3$  inversions have proposed a role for a rise and fall in OH in the pause and renewed  
26 growth of atmospheric methane (McNorton et al., 2016; Rigby et al., 2017; Turner et al., 2017). However,  
27 these trends were not found to be statistically significant when all uncertainties were considered.



28 **Figure 8. Left:**  $\text{CH}_3\text{CCl}_3$  monthly mean mole fractions and 1-sigma standard deviations at selected  
29 AGAGE stations. **Right:** Global 12-month running mean OH concentrations and emissions from the  
30 AGAGE data and AGAGE 2D model inversion. Shaded areas give 1-sigma uncertainty (Rigby et al.,  
31 2017, updated).



#### 4.7 AGAGE Emissions Estimates for All Gases

A major objective of all the AGAGE GC-MD and GC-MS measurements is to produce estimates of global emissions, spatial distributions of emissions and their trends. These results are given in a large number of AGAGE publications (see Section 4.9, Section 5, References) and a selected few will be reviewed here. These AGAGE estimates are then be critically compared against estimates provided from manufacturing and sales information for anthropogenic chemicals, and from independently derived estimates for natural emissions, to improve emission estimates and models. The error bars on the inferred emissions of trace gases in **Figure 4** reflect the uncertainties in the estimates that are generally dominated by uncertainties in point measurement to grid box model extrapolations and the species lifetimes.

AGAGE data have helped resolve some important emission controversies. For example,  $\text{CH}_3\text{CCl}_3$  is an ozone-depleting industrial solvent whose phase-out was introduced under the Montreal Protocol. However, as the phase-out continued the reported emissions appeared too low to explain observations, and unreported European emissions were claimed to be a major cause (Krol et al., 2003). Long-term high-frequency AGAGE data from Mace Head and Jungfraujoch were used to infer European  $\text{CH}_3\text{CCl}_3$  emissions to help resolve this issue. European emission estimates declined from about 60 gigagrams per year in the mid-1990s to 0.3-3.4 gigagrams per year in 2000-2003, based on Mace Head and Jungfraujoch data, respectively. These European  $\text{CH}_3\text{CCl}_3$  emission estimates were higher than calculated from consumption data, but were considerably lower than those derived for 2000 in the earlier study (Reimann et al., 2005). AGAGE is unusual amongst global networks in that 30% of its *in situ* Medusa-GC-MS observational capacity is located in the tropics (**Figure 1**). A consistent feature that has emerged from AGAGE research over the period 2011-2015 is the importance of the tropics as the major source region for several important trace gases of biological origin: methane, nitrous oxide, methyl chloride and hydrogen. Rigby et al. (2008) showed that the recent increase in methane growth rate in the atmosphere was likely due to a combination of emissions from unusually warm boreal summers and unusually wet tropical regions. Xiao et al. (2010a) confirmed the major role (>50%) that tropical plants play as a source of methyl chloride, the largest natural source of chlorine for the stratosphere. Huang et al. (2008) showed the importance of tropical regions and the Indian sub-continent as major source regions (>80%) for nitrous oxide and Xiao et al. (2007) demonstrated the importance of tropical regions as the major (70%) source (oxidation of formaldehyde, biomass burning) and major (70%) sink (surface uptake, oxidation by OH) region for atmospheric hydrogen.

#### 4.8 Emission Estimates from Multiple Networks and Measurement Platforms

In the last decade there has been a distinct move toward trace gas emission estimations using measurements from multiple networks and platforms. The methane flux estimations by Chen and Prinn (2006) merged for the first time the high frequency AGAGE data with the low frequency NOAA/ESRL/GMD, CSIRO, Environment Canada, NIES, and Japan Meteorological Agency flask data. The intercalibration process proved to be very important to this merger, and showed that, done correctly, the merger increased the precision and accuracy of the fluxes significantly. A formal intercalibration exercise began between the AGAGE, NOAA/ESRL/GMD and other networks that used intercomparisons between instruments and flask sampling at the same station led by P. B. Krummel (CSIRO), and intercomparisons of tanks of compressed air circulated among laboratories (IHALACE, Hall et al., 2014). This has enabled a significant number of subsequent studies that involve merging of AGAGE data with data from other surface networks and platforms (towers, aircraft, satellites). AGAGE data and GMD (flask/tower/aircraft) data were used to obtain sources and/or sinks of  $\text{SF}_6$  (Rigby et al., 2010), CFCs and  $\text{CH}_3\text{CCl}_3$  (Rigby et al., 2013), HCFC-22 (Saikawa et al., 2012, 2014b), CFCs and  $\text{N}_2\text{O}$  (Simmonds et al., 2013),  $\text{N}_2\text{O}$  (Nevison et al., 2011, Thompson et al., 2013, 2014a,b,c), methane (Thompson et al., 2015),  $\text{CH}_3\text{Cl}$  (Xiao et al., 2010a) and  $\text{CCl}_4$  (Xiao et al., 2010b). HIPPO aircraft, AGAGE and ESRL data were used for seasonal emissions of HCFC-22 and HFC-134a (Xiang et al., 2014), and for OH estimation (Patra et al., 2014). Kirschke et al. (2013) used AGAGE, GMD flask, CSIRO flask, and UCI aircraft data, for estimating methane emissions. MIPAS, AGAGE and GMD data, were used by Chirkov et al. (2016) for estimating HCFC-22 emissions, AGAGE and GMD data for estimating  $\text{CCl}_4$  emissions (Chipperfield et al., 2016) and GOSAT, AGAGE and GMD data were used for regional methane emissions (Fraser et al., 2013). Finally, Rigby et al. (2017) used AGAGE and GMD data for estimation of OH concentrations





and CH<sub>4</sub> emissions, and Ganesan et al. (2017) used GOSAT satellite, CARIBIC aircraft and AGAGE-calibrated surface measurements to estimate Indian subcontinent CH<sub>4</sub> emissions.

#### 4.9 AGAGE Publications

The central accomplishments of the ALE/GAGE/AGAGE program are documented in several hundred journal publications and theses. A full list of all ALE/GAGE/AGAGE publications in the 1983-2017 time period supported by, and/or collaborating with AGAGE, is available on the official AGAGE website <http://agage.mit.edu> then RESEARCH then AGAGE PUBLICATIONS then AGAGE Accomplishments (for abstracts). For AGAGE publications with “et al.”, the full author list can be seen by clicking on the paper title given in orange text. ALE/GAGE/AGAGE measurements and derived lifetimes, OH concentrations, and emissions are of considerable policy significance and are widely used in international and national ozone layer and climate assessments. AGAGE team members have specifically contributed as authors to almost all of the major international assessments under the IPCC and WMO.

#### 5. AGAGE Data Availability

After calibration, validation and conversion to a prescribed format, AGAGE data for 9 stations (Ny-Ålesund, Mace Head, Trinidad Head, Jungfraujoch, Monte Cimone, Gosan (monthly means), Ragged Point, Cape Matatula, Cape Grim) are made available on the AGAGE public website (<http://agage.mit.edu/data>). The data from the newest station, Mt. Mugogo, will be added to this site once internally validated and the first data published in peer-reviewed journals. Data from Shangdianzi (B. Yao; [yaob@cma.gov.cn](mailto:yaob@cma.gov.cn)), Hateruma and Cape Ochiishi (T. Saito; [saito.takuya@nies.go.jp](mailto:saito.takuya@nies.go.jp)) can be obtained by contacting the indicated station scientists. Data files for individual measurements and for monthly mean summaries are updated at approximately six-month intervals, following the semi-annual meetings of the international AGAGE team. Data considered a pollution event or a local sink event are flagged. Monthly means and standard deviations of the data with and without these events are included. The data are currently available through March 2017.

The data on the AGAGE website are also made available on the public U.S. Department of Energy (DOE) Carbon Dioxide Information Analysis Center (CDIAC) website for public access (<http://cdiac.esd.ornl.gov/ndps/aleage.html>). Note that data previously stored at the CDIAC archive are being transitioned to the new, DOE ESS-DIVE archive. The above website will continue to provide access to the CDIAC data during the transition. Please contact [ess-dive-support@lbl.gov](mailto:ess-dive-support@lbl.gov) for further information on the transition. CDIAC also passes on these data to the World Data Center for Greenhouse Gases (WDCGG) in Japan (<http://ds.data.jma.go.jp/gmd/wdcgg/>). The AGAGE data in the WDCGG data center, however, are further processed by WDCGG's staff and are converted to a different format from that used by the CDIAC and AGAGE websites. Thus, we do not recommend this site as a primary source of AGAGE data.

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