Atmospheric measurements

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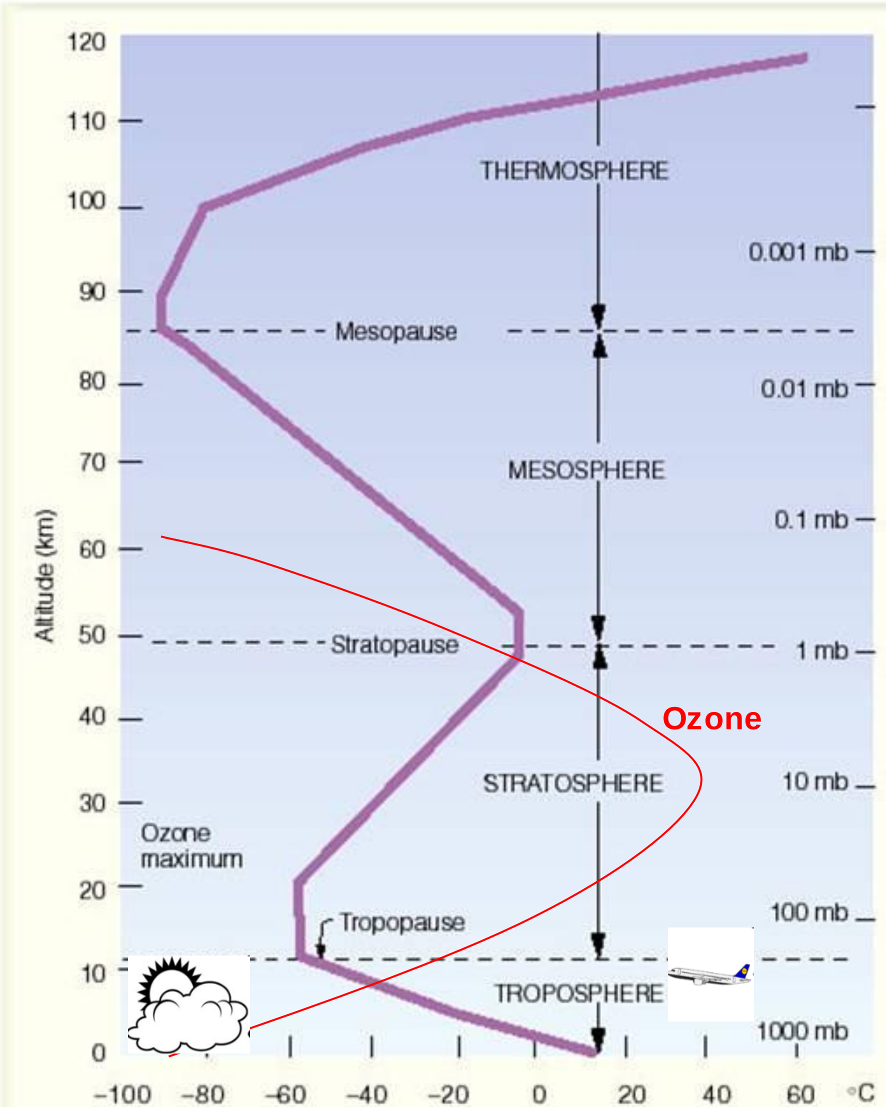
Aims

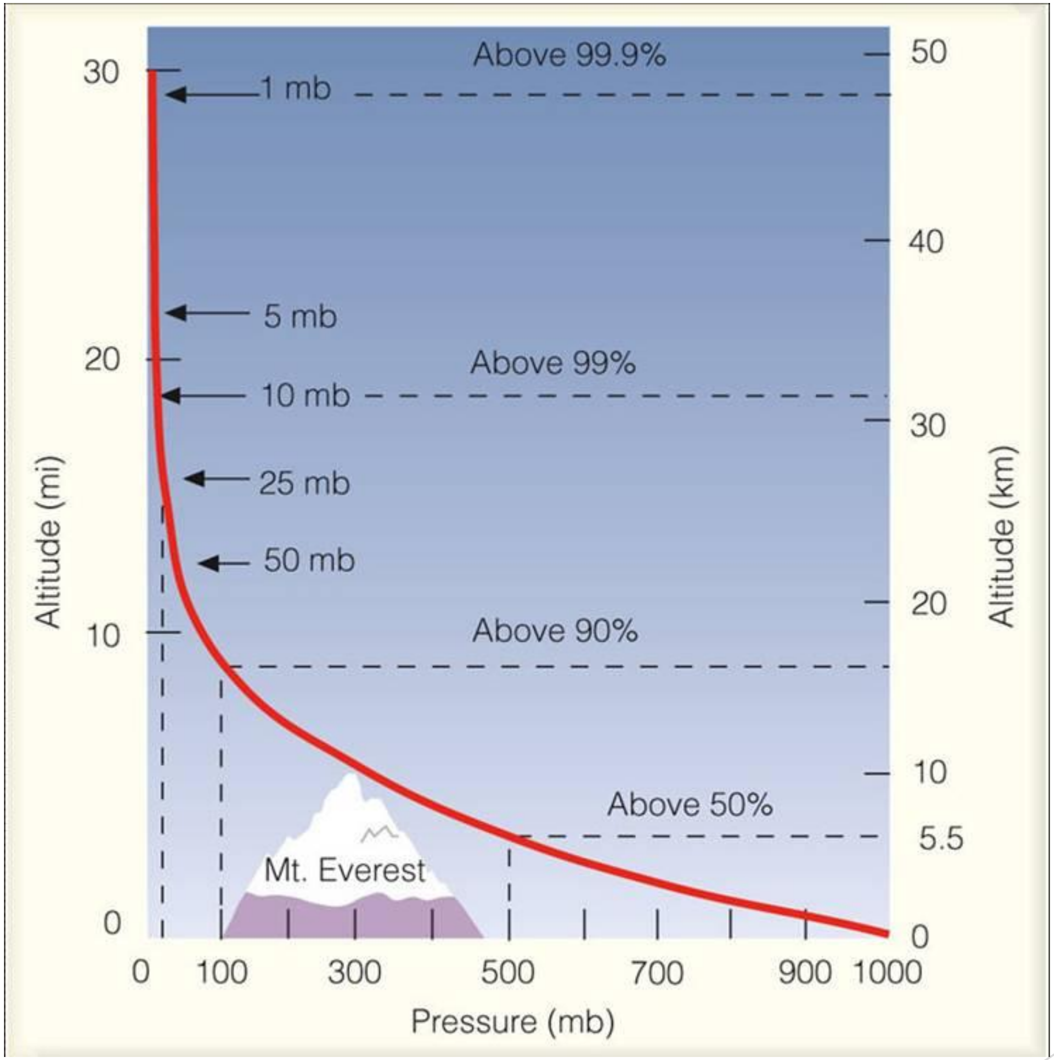
- Overview of trace compounds in the atmosphere
- Instrumentation used to measure trace compounds
- Understanding measurements
- Calibration and Non-linearity
- Interpretation of measurements (Practical)

The Atmosphere

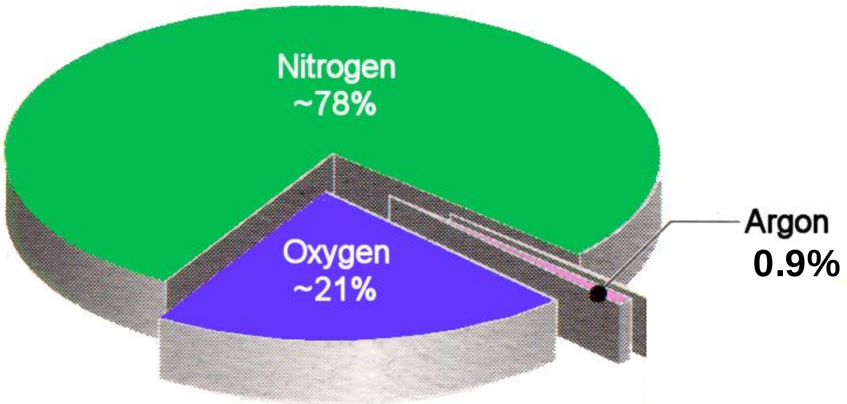
Temperature structure of the atmosphere and ozone layer



Pressure structure of the atmosphere



Trace components in the atmosphere



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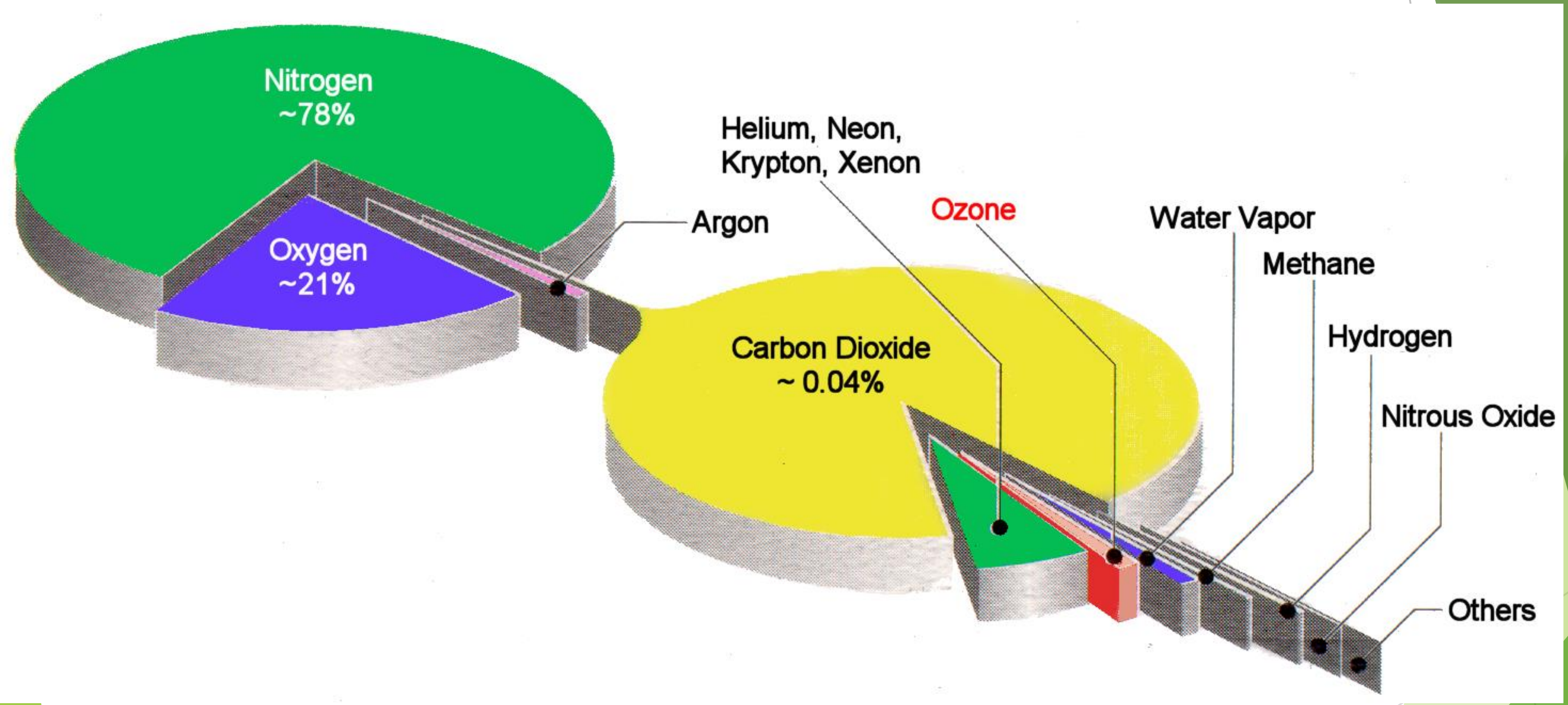
Trace components in the atmosphere



Motivation for trace gas measurements in the atmosphere

Summer smog

O_3 (VOCs/NO_x)

Winter smog

particles, CO

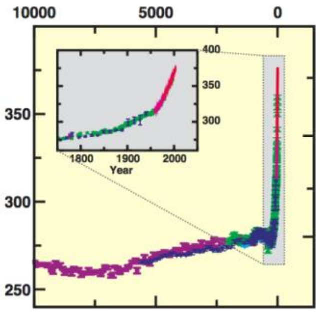
Acid rain

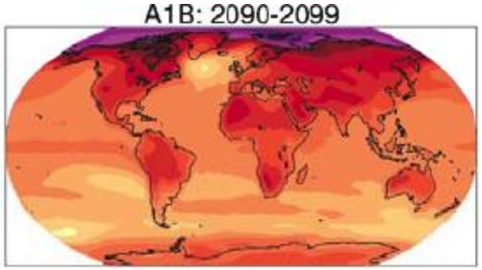
SO_2, NO_x

Motivation for trace gas measurements in the atmosphere

Global warming

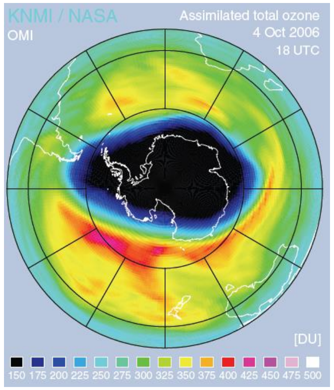
$CO_2/CH_4/N_2O/O_3$/halocarbons



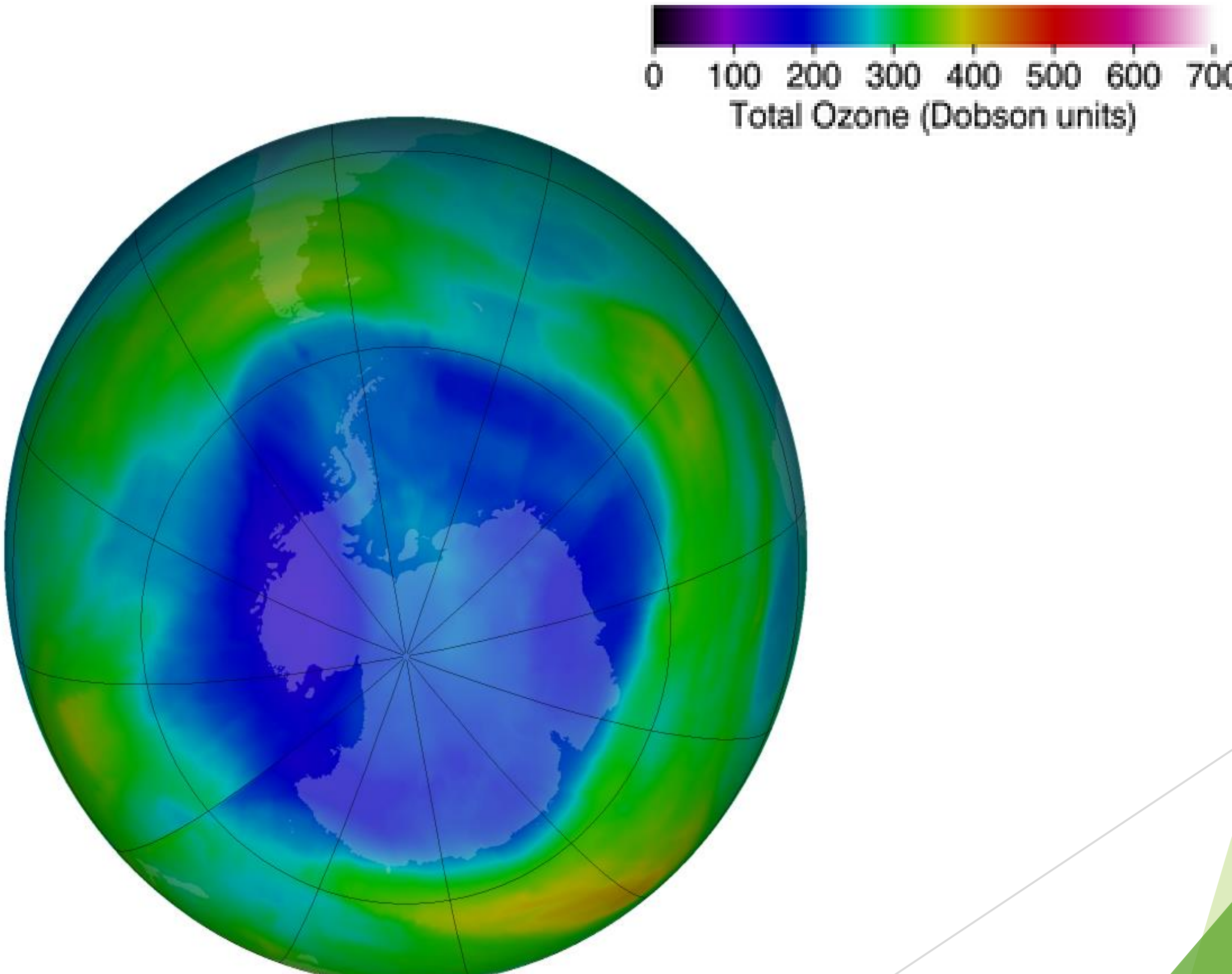


Ozone depletion

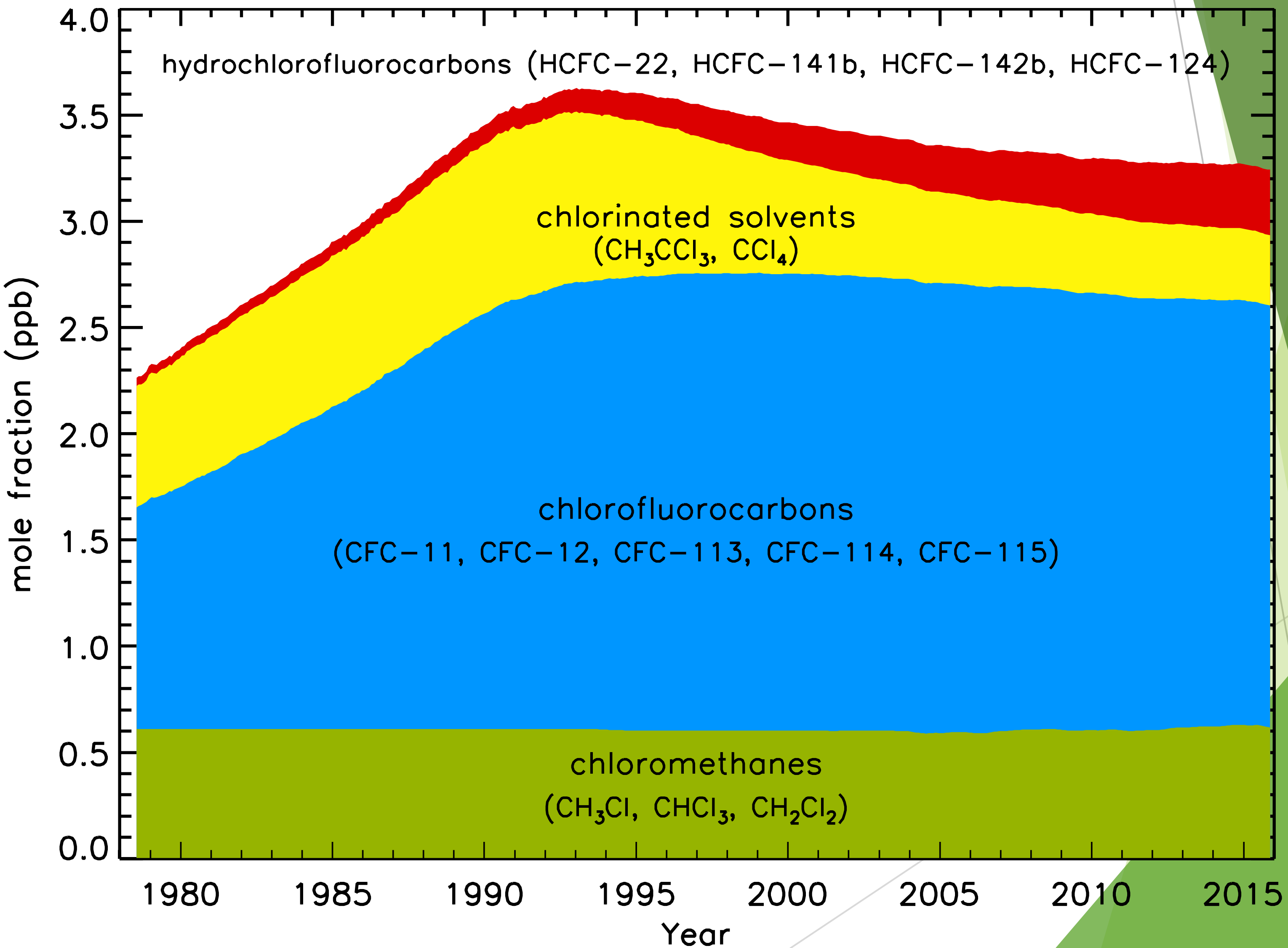
halocarbons



Motivation for atmospheric measurements
1. Ozone Depletion



Motivation for atmospheric measurements
1. Ozone Depletion



Gas	Pre-1750 tropospheric concentration[1]	Recent tropospheric concentration[2,3]	GWP[4](100-yr time horizon)	Atmospheric lifetime[5](years)	Increased radiative forcing [6] (W/m^2)
Concentrations in parts per trillion (ppt)					
CFC-11 (CCl_3F)	zero	232[3]	4,660	45	0.060
CFC-12 (CCl_2F_2)	zero	516[3]	10,200	100	0.166
CFC-113(CCl_2CClF_2)	zero	72[3]	5,820	85	0.022
HCFC-22($CHClF_2$)	zero	233[3]	1,760	11.9	0.049
HCFC-141b(CH_3CCl_2F)	zero	24[3]	782	9.2	0.0039
HCFC-142b(CH_3CClF_2)	zero	22[3]	1,980	17.2	0.0041
Halon 1211 ($CBrClF_2$)	zero	3.6[3]	1,750	16	0.0010
Halon 1301 ($CBrClF_3$)	zero	3.3[3]	6,290	65	0.0010
HFC-134a(CH_2FCF_3)	zero	84[3]	1,300	13.4	0.0134
Carbon tetrachloride (CCl_4)	zero	82[3]	1,730	26	0.0140

Source: http://cdiac.ornl.gov/pns/current_ghg.html **Accessed 28/07/2016**

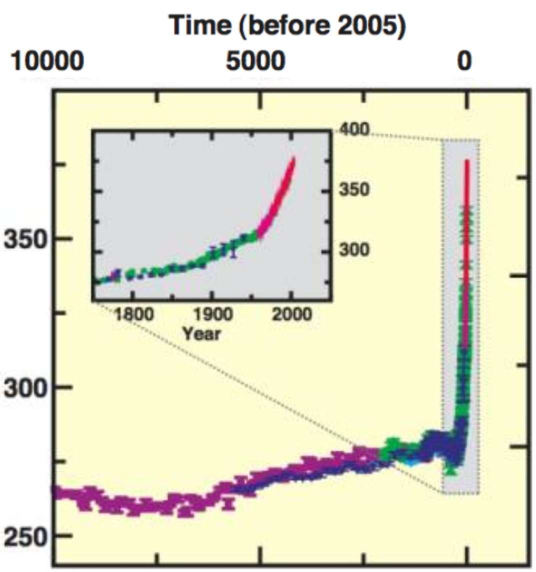
1 part per trillion = 1 ppt
1 ppt = 1 drop diluted into 20 Olympic swimming pools

1 ppt =

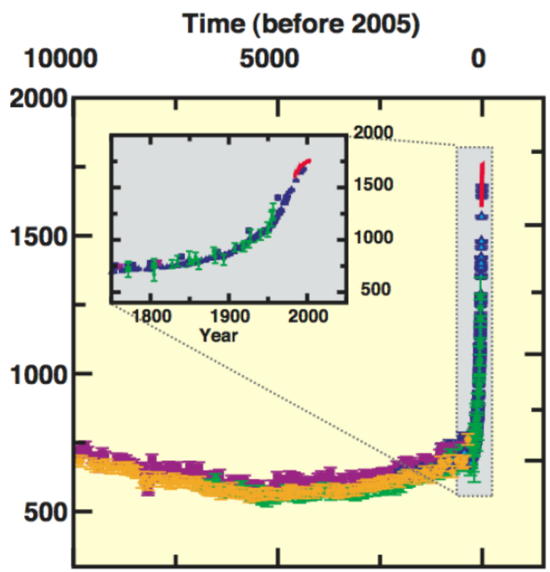
20 ×

Motivation for atmospheric measurements
2. Global warming

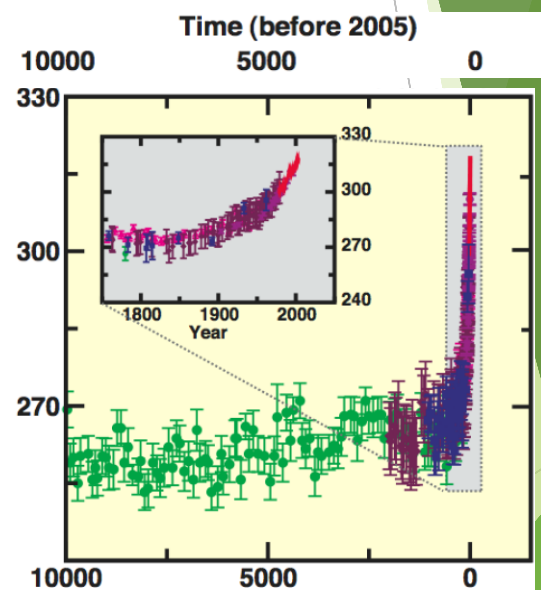
CO_2 [ppm]



CH_4 [ppb]

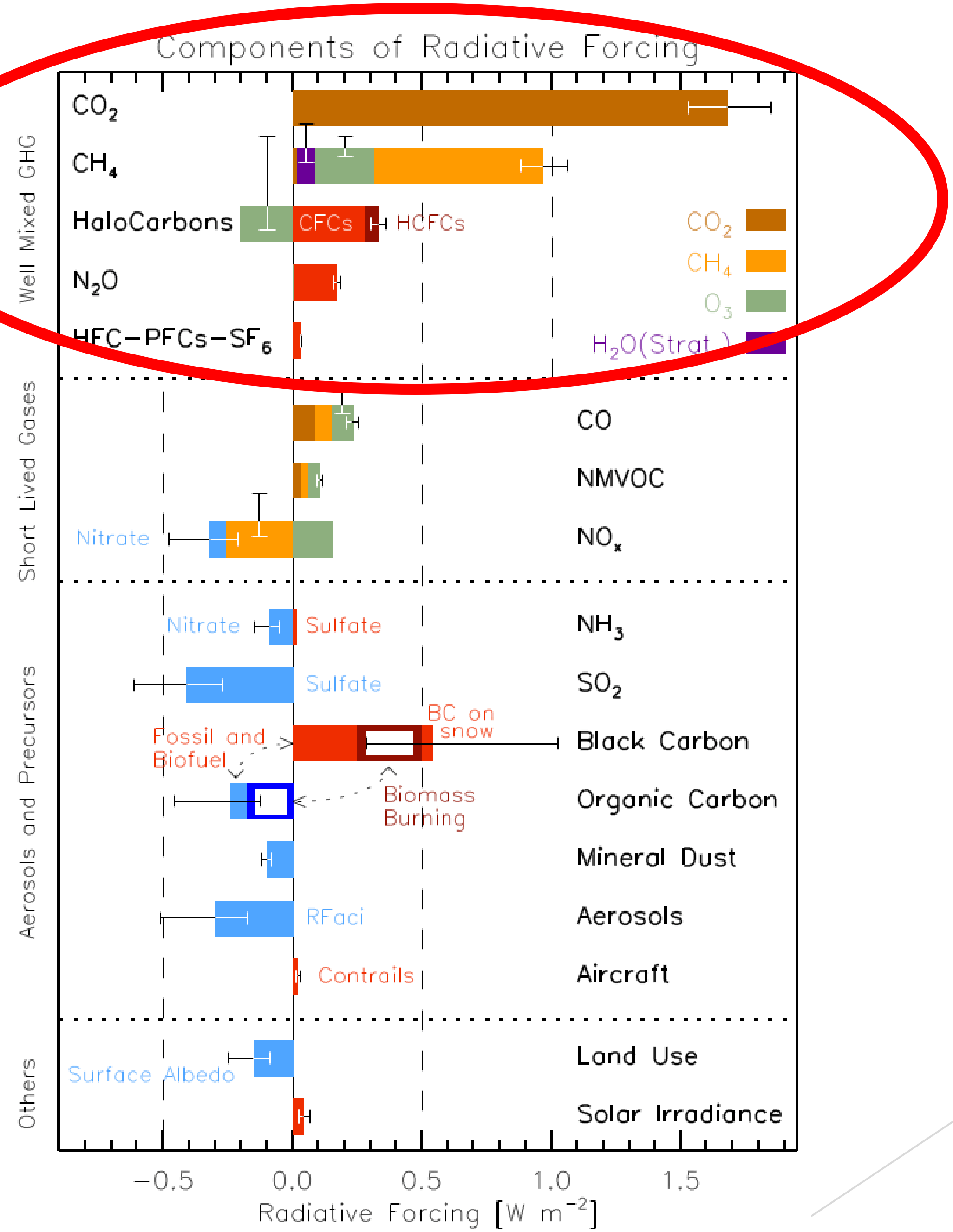


N_2O[ppb]



Source: IPCC 2007

http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html

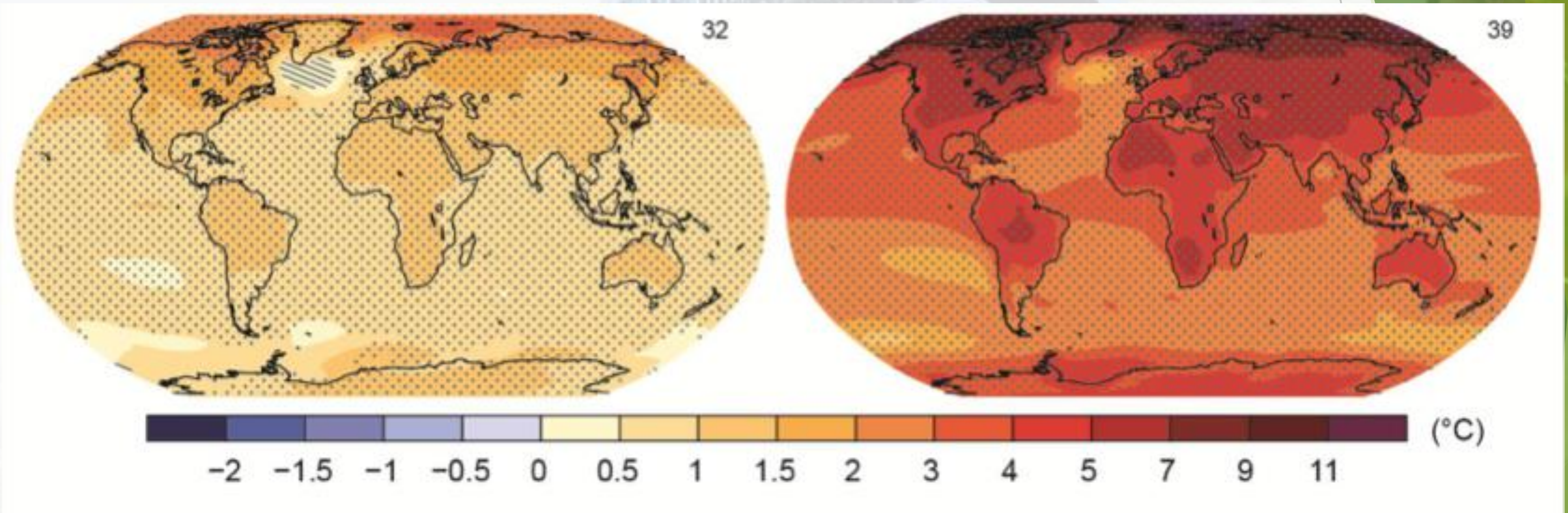


Source: IPCC 2013

The Choices We Make Will Create Different Outcomes

With substantial mitigation

Without additional mitigation



Change in average surface temperature (1986–2005 to 2081–2100)

AR5 WGI SPM

What can be done?

Measurements

Instruments

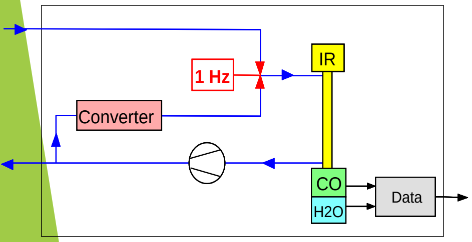
Recent GHG mole fractions

Gas	Pre-1750 tropospheric concentration[1]	Recent tropospheric concentration[2,3]	GWP[4](100-yr time horizon)	Atmospheric lifetime[5](years)	Increased radiative forcing [6] (W/m^2)
Concentrations in parts per million (ppm)					
Carbon dioxide (CO_2)	~280[7]	399.5[2,8]	1	~ 100-300[5]	1.94
Concentrations in parts per billion (ppb)					
Methane (CH_4)	722[9]	1834[2]	28	12.4[5]	0.50
Nitrous oxide (N_2O)	270[10]	328[3]	265	121[5]	0.20
Tropospheric ozone (O_3)	237[1]	337[2]	n.a.[3]	hours-days	0.40
Concentrations in parts per trillion (ppt)					
Sulfur hexafluoride (SF_6)	zero	8.6[3,11]	23,500	3200	0.0049

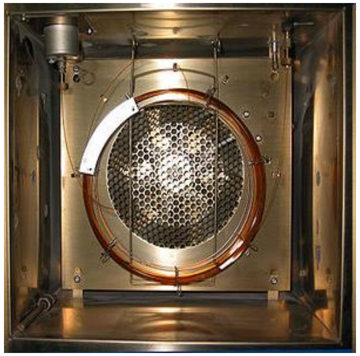
Source: http://cdiac.ornl.gov/pns/current_ghg.html **Accessed 28/07/2016**

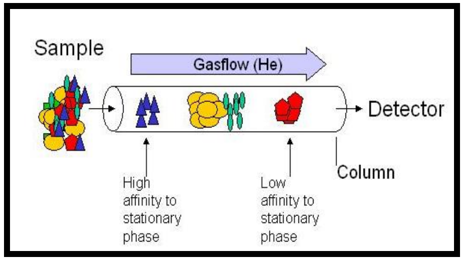
Overview of measurement techniques used for atmospheric trace gases

General

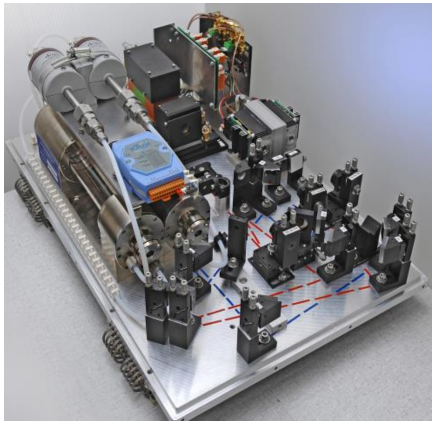


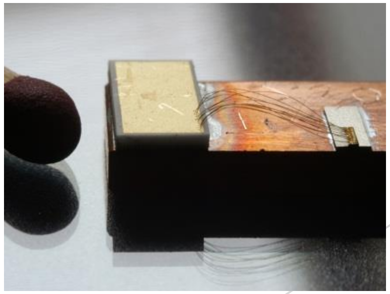
GC (and GC–MS)



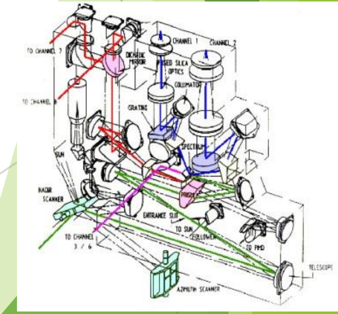


Optical



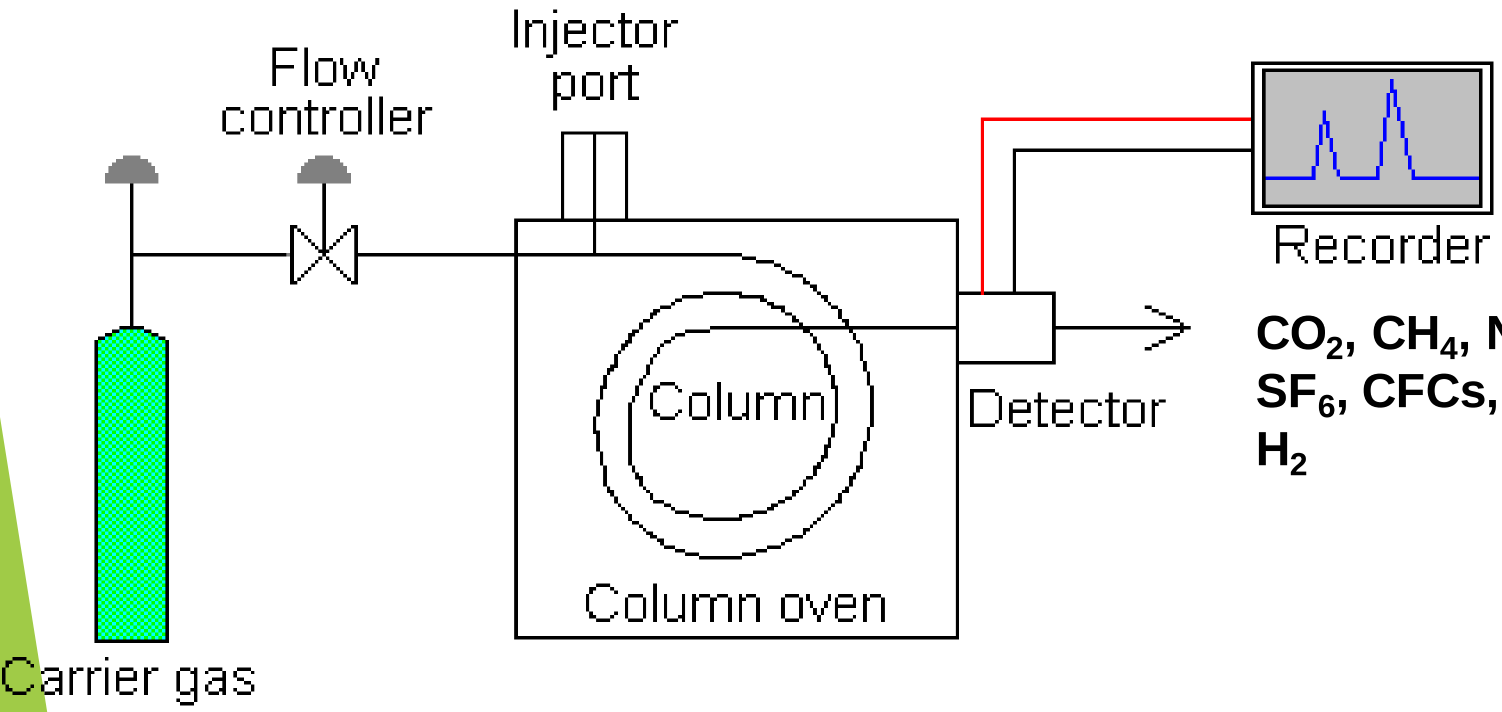


Satellite



Gas Chromatography

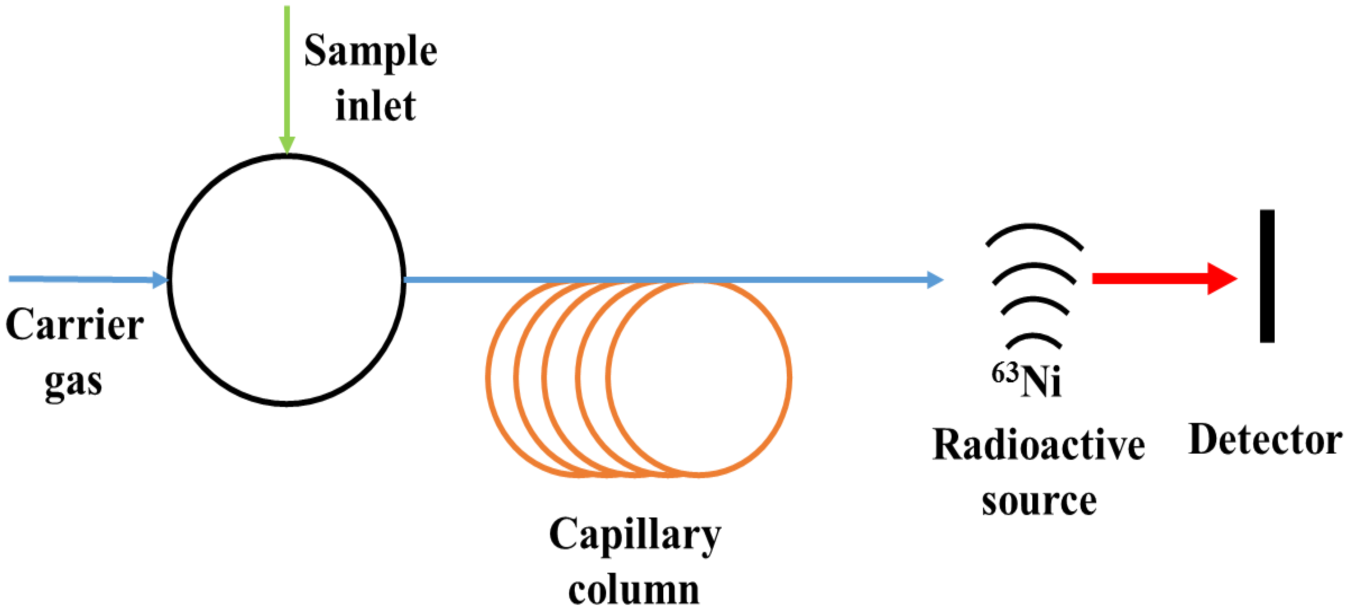
Gas Chromatography – simple schematic



CO_2, CH_4, N_2O, SF_6, CFCs, CO, H_2

Detector	Type	Support Gas	Selectivity	Detectability	Dynamic Range
Flame ionization (FID)	Mass flow	Hydrogen and air	Most organics. **(CH_4)**	100pg	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides. **(N_2O, SF_6, CFCs)**	50fg	10^5
Thermal Conductivity (TCD)	Mass Flow	Hydrogen and air	Nitrogen, phosphorous	10pg	10^6
Photo-ionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2pg	10^7

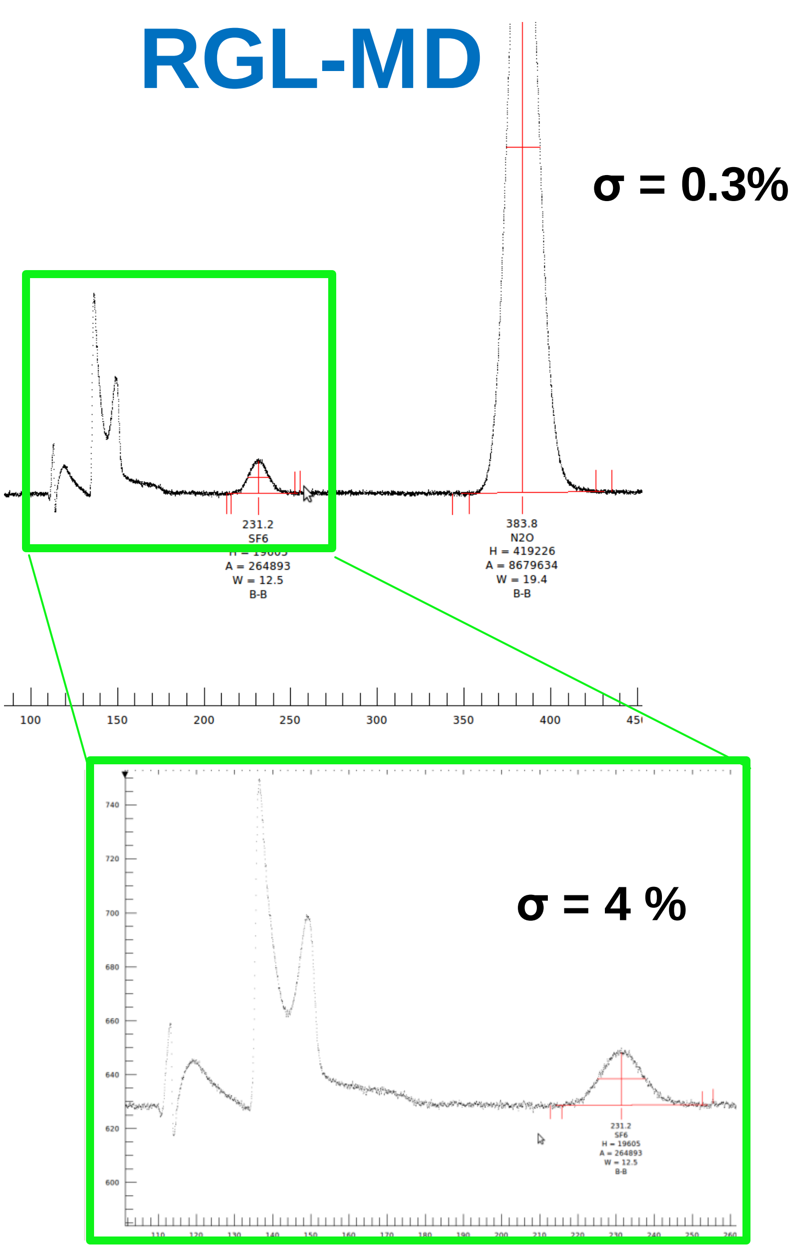
GC-ECD: N_2O and SF_6



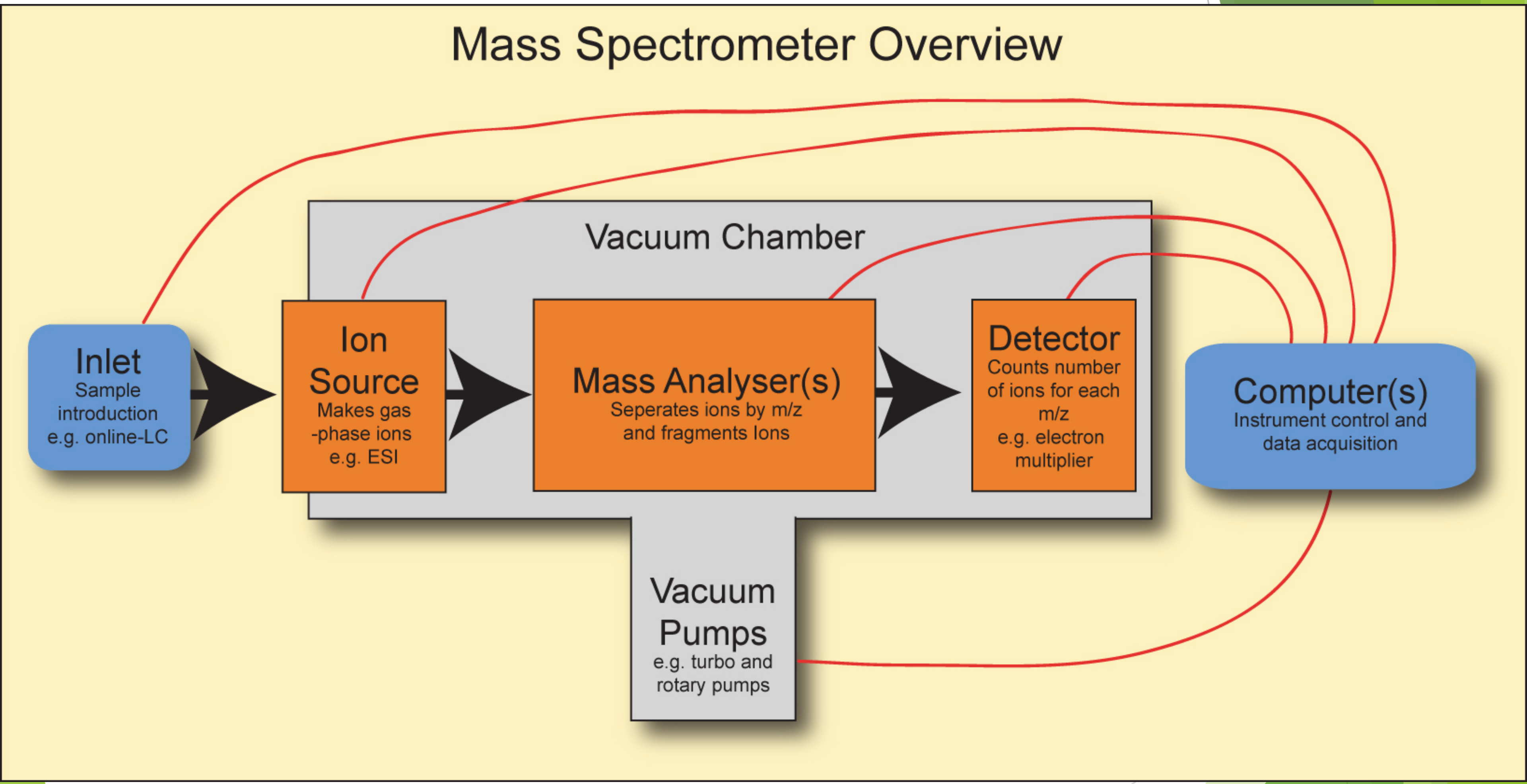
Ridge Hill µECD

- Constructed July-Sept 2011

SF_6 & N_2O Chromatography

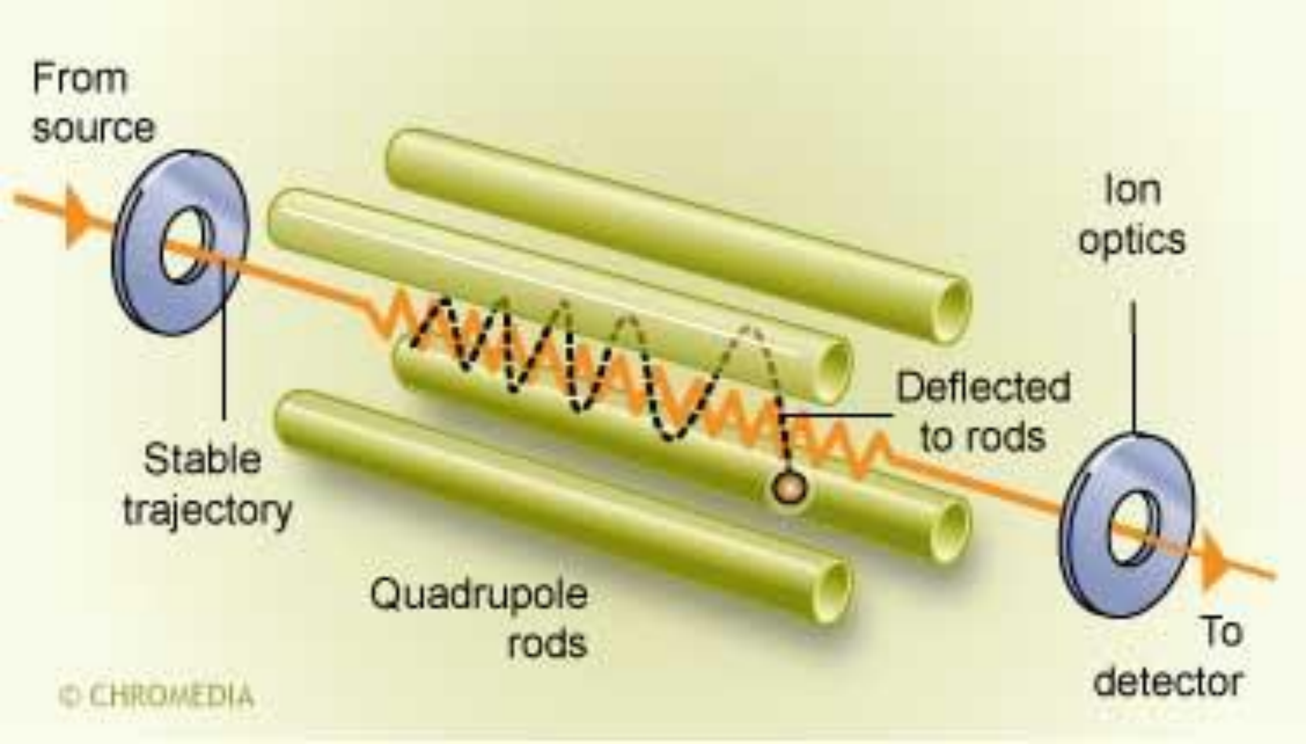


Mass Spectrometry

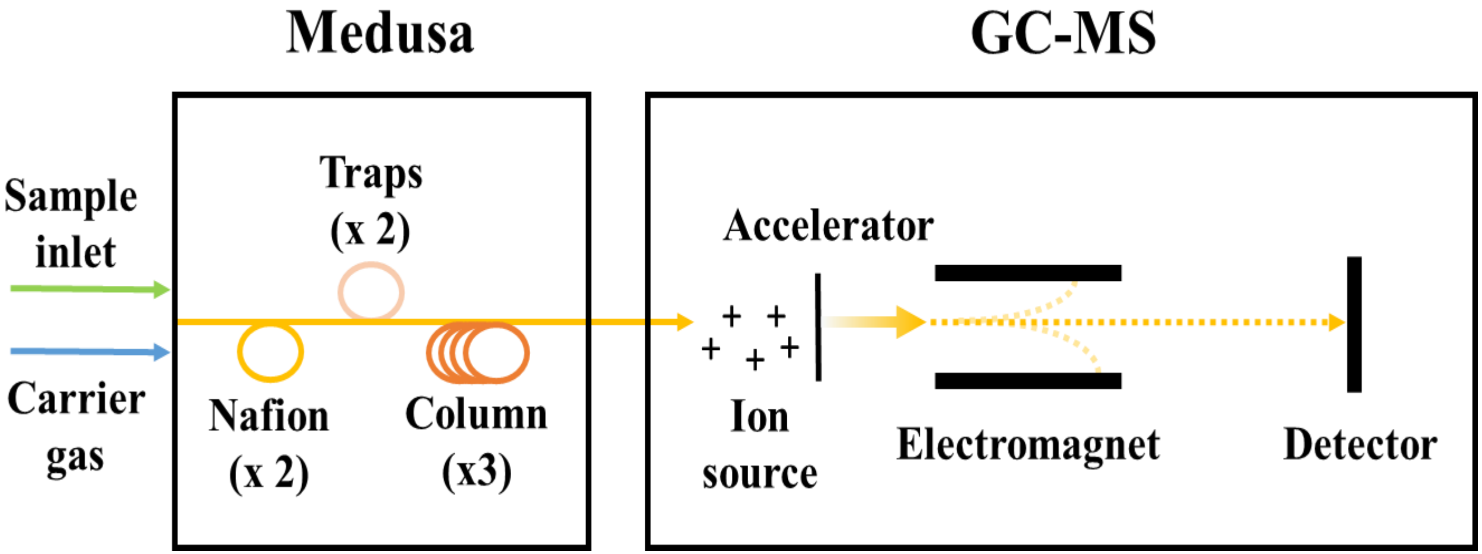

Mass Spectrometer Overview
Vacuum Chamber
Inlet
Sample introduction
e.g. online-LC
Ion Source
Makes gas -phase ions
e.g. ESI
Mass Analyser(s)
Seperates ions by m/z and fragments Ions
Detector
Counts number of ions for each m/z
e.g. electron multiplier
Computer(s)
Instrument control and data acquisition
Vacuum Pumps
e.g. turbo and rotary pumps

Quadrupole Mass Analyser

- Consists of 4 parallel metal rods with different charges
- Oscillating DC and AC electric fields are applied that effect the trajectory of the ions travelling down the flight path
- For given AC and DC voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter

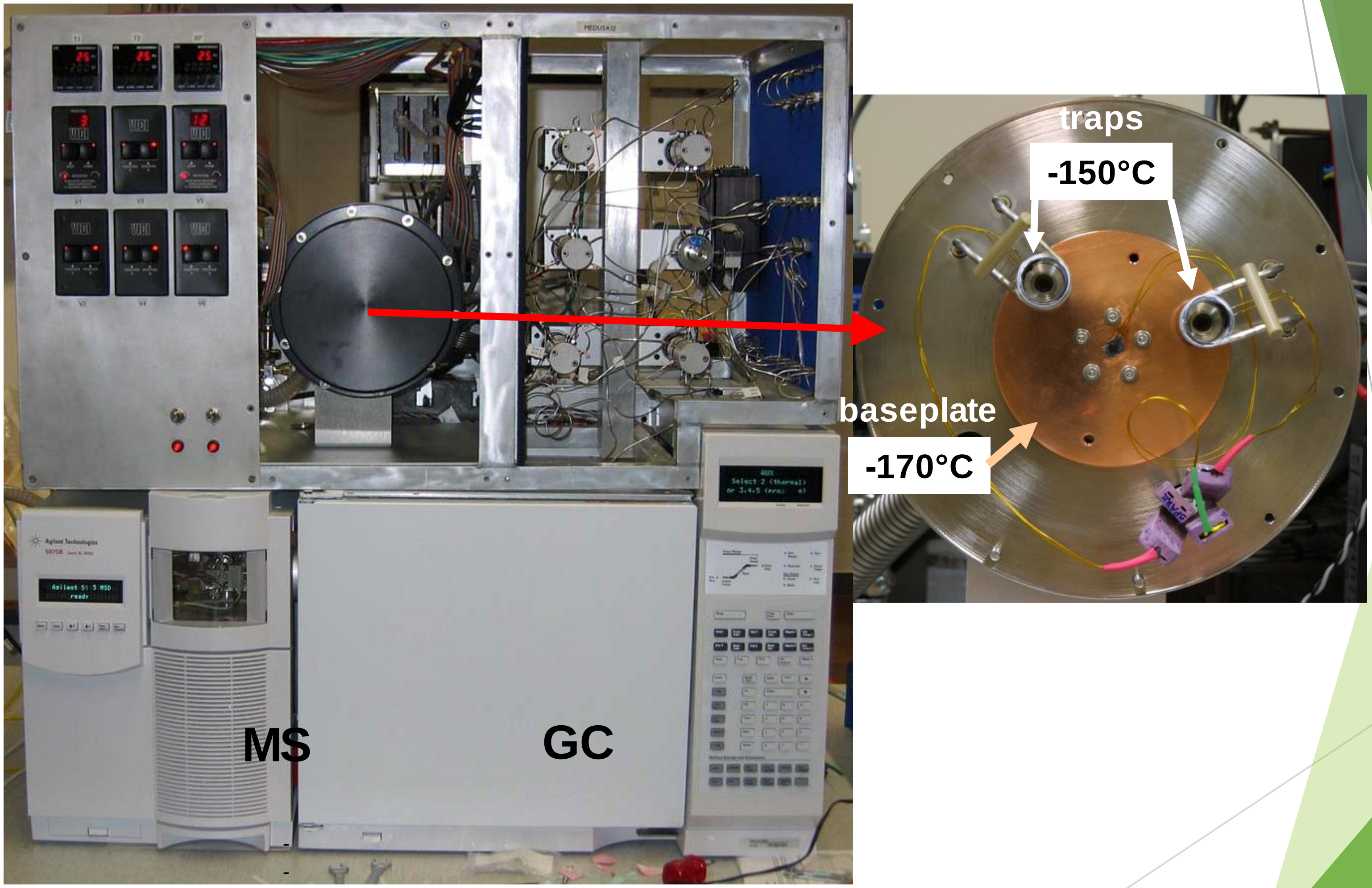


Medusa-GCMS



Medusa
GC-MS
Sample inlet
Carrier gas
Traps (x 2)
Nafion (x 2)
Column (x3)
Accelerator
Ion source
Electromagnet
Detector

The Medusa-GCMS used within AGAGE to measure lots of GHGs



http://agage.eas.gatech.edu/instruments-gcms-medusa.htm
Miller et al., Anal. Chem., 2008.

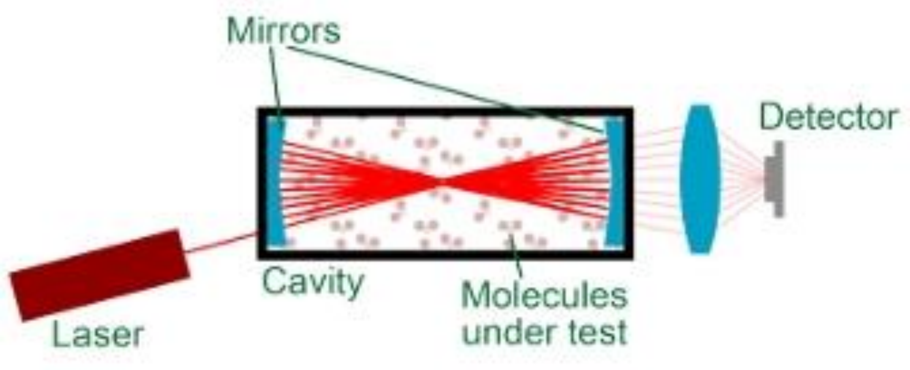
Medusa-GCMS compounds

Compound	[2014] (ppt)	Typical % precision	Compound	[2014] (ppt)	Typical % precision	Compound	[2014] (ppt)	Typical % precision
CF_4	81.8	0.11	HFC-365mfc	1.03	1.82	CH_3Br	7.61	0.26
PFC-116	4.10	0.31	HFC-4310mee	0.26	2.13	CH_3I	0.58	0.64
PFC-218	0.61	1.22	HCFC-22	241.5	0.17	CH_2Cl_2	49.1	0.31
PFC-318	1.48	0.60	HCFC-124	1.27	1.57	$CHCl_3$	11.6	0.22
C_6F_{14}	0.30	1.51	HCFC-141b	25.4	0.19	CCl_4	82.8	0.30
SF_6	8.45	0.17	HCFC-142b	23.4	0.21	CH_2Br_2	1.55	0.51
SO_2F_2	2.14	0.64	CFC-11	233.9	0.11	$CHBr_3$	4.24	0.35
HFC-23	27.8	0.39	CFC-12	523.4	0.07	CH_3CCl_3	3.73	1.24
HFC-32	11.6	0.69	CFC-13	3.01	0.82	$CHClCCl_2$	0.36	1.28
HFC-125	18.1	0.54	CFC-113	72.8	0.12	COS	446.5	0.13
HFC-134a	84.2	0.19	CFC-114	16.3	0.23			
HFC-143a	17.4	0.40	CFC-115	8.40	0.31			
HFC-152a	10.0	0.41	H-1211	3.87	0.31			
HFC-227ea	1.10	0.83	H-1301	3.41	0.72			
HFC-236fa	0.14	3.28	H-2402	0.43	0.75			
HFC-245fa	2.40	0.75	CH_3Cl	532.9	0.16			

Optical instruments

Optical instruments

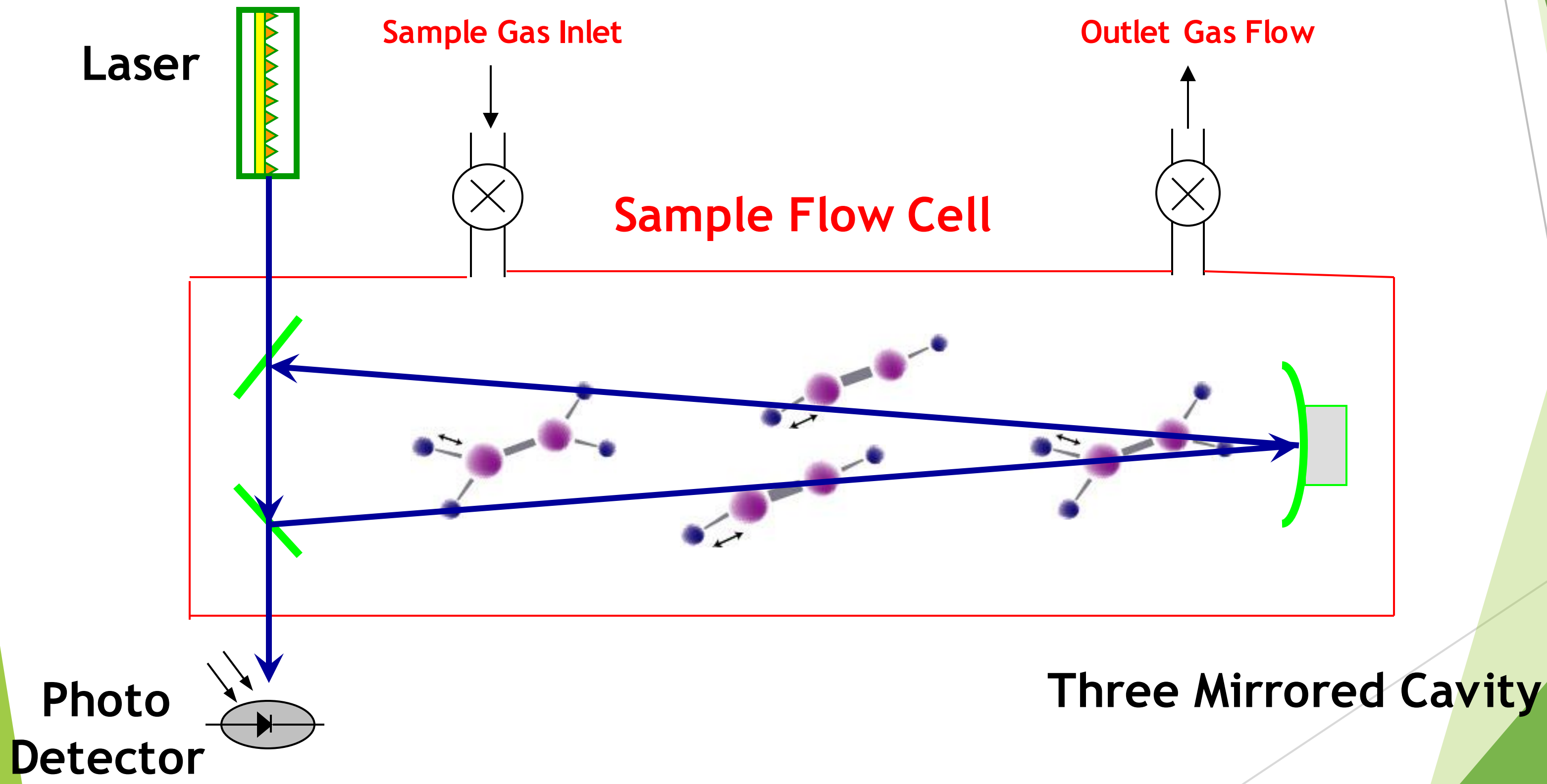
- Cavity ring-down spectroscopy
- Off-axis integrated cavity output spectroscopy
- Fourier transform infrared spectroscopy
- Nondispersive infrared spectroscopy
- Quantum cascade laser absorption spectroscopy



Cavity ring-down spectrometry

What is CRDS?

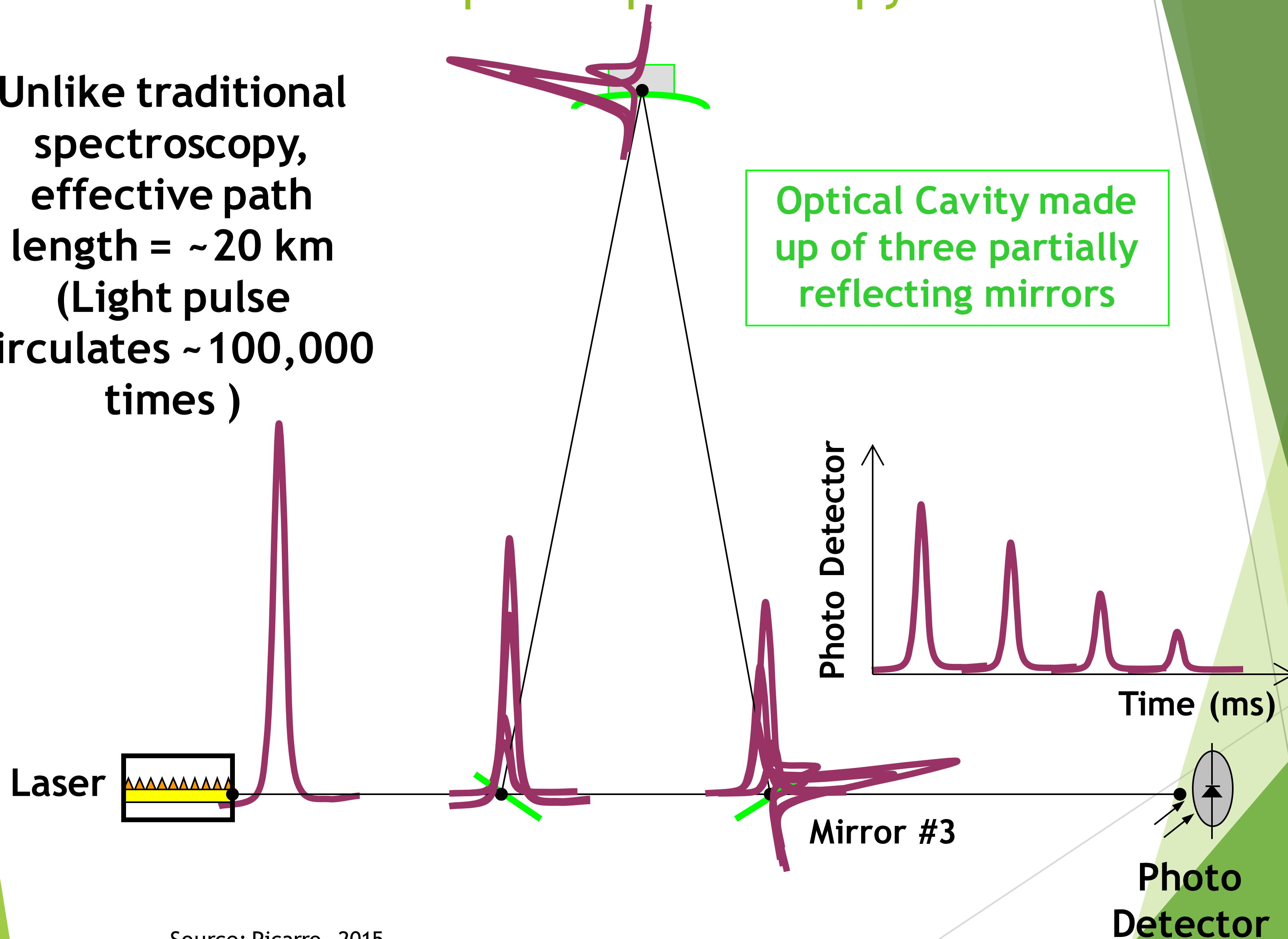
- Cavity Ring Down Spectroscopy (CRDS)
  - Laser based, TIME BASED, linear optical absorption technique for measuring gas concentration or isotopes



Source: Picarro, 2015

CRDS is a time-based measurement – different than absorption spectroscopy

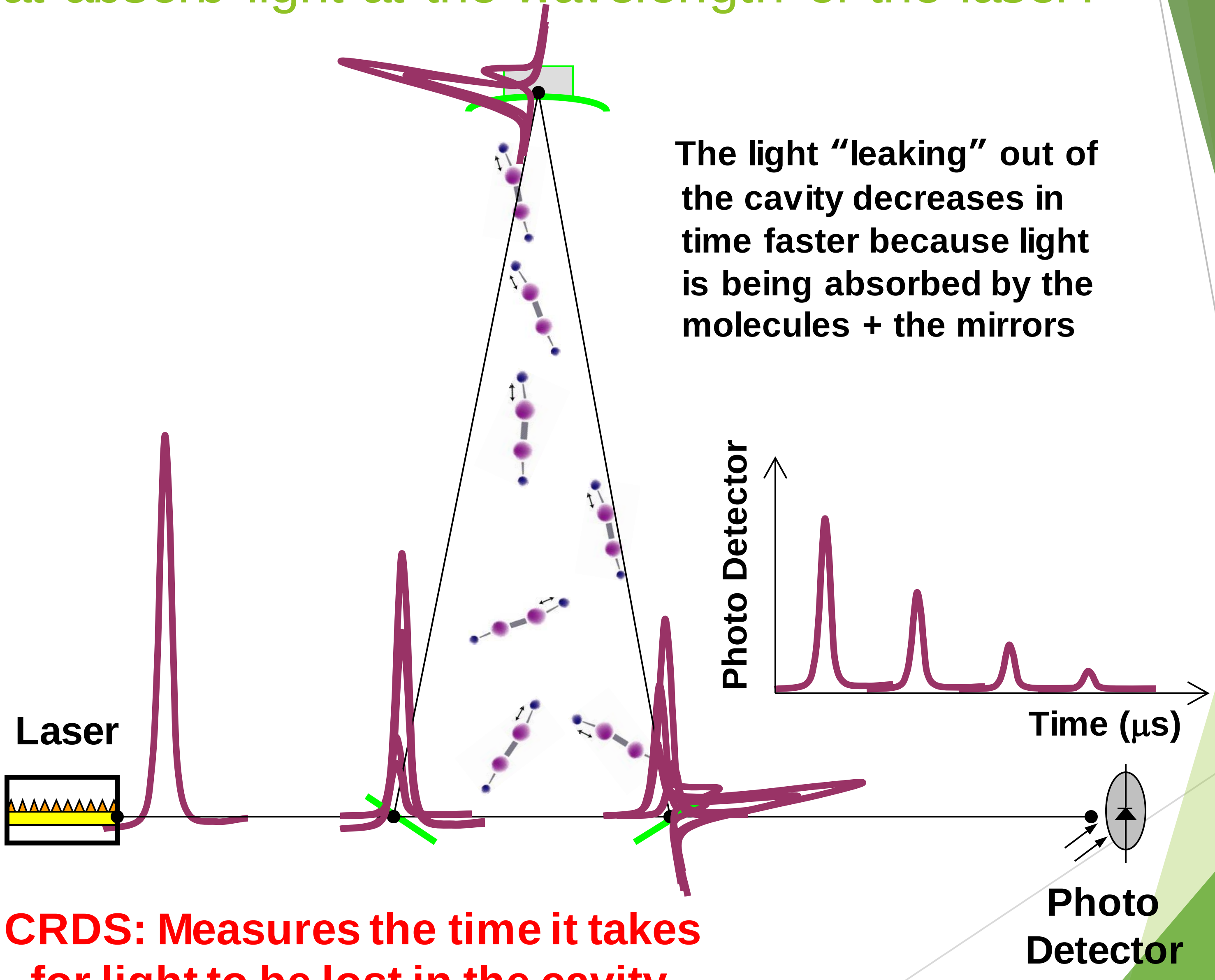
Unlike traditional spectroscopy, effective path length = ~20 km (Light pulse circulates ~100,000 times)



Source: Picarro, 2015

What happens when you introduce molecules that absorb light at the wavelength of the laser?

The light “leaking” out of the cavity decreases in time faster because light is being absorbed by the molecules + the mirrors

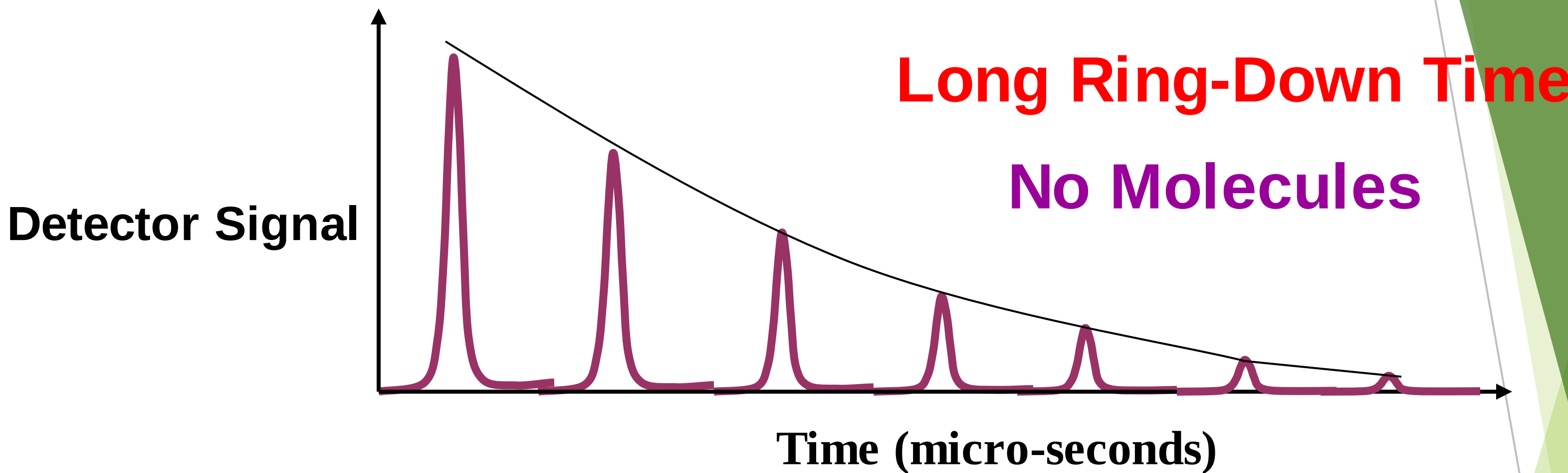


CRDS: Measures the time it takes for light to be lost in the cavity.

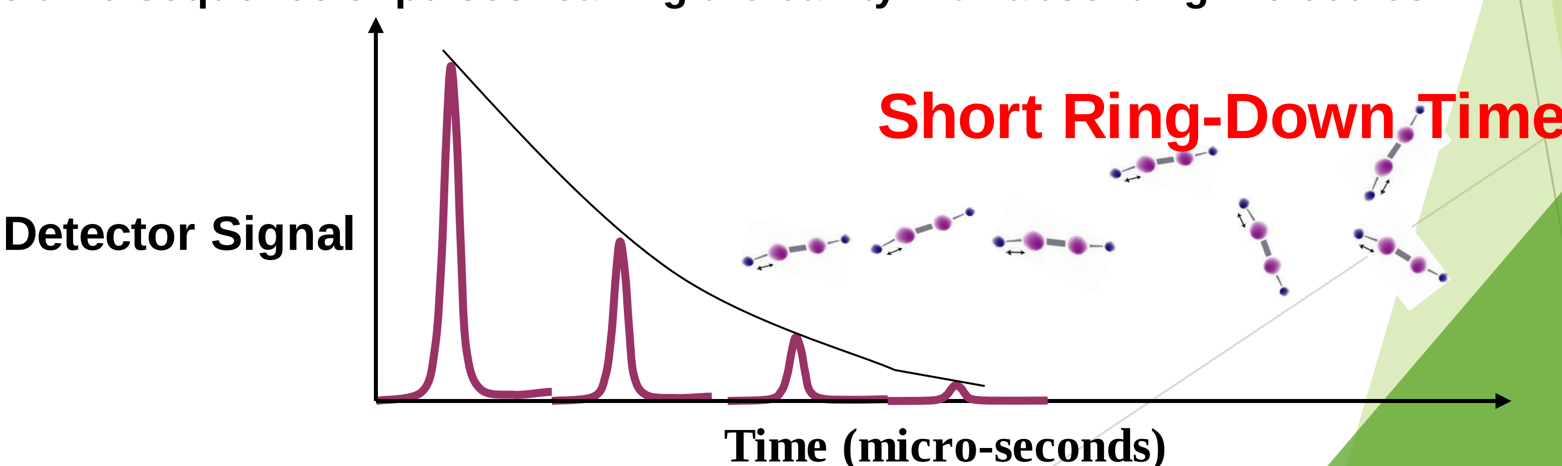
Source: Picarro, 2015

CRDS: Time Based Measurement

- The time sequence of pulses leaving the cavity with NO absorbing molecules.



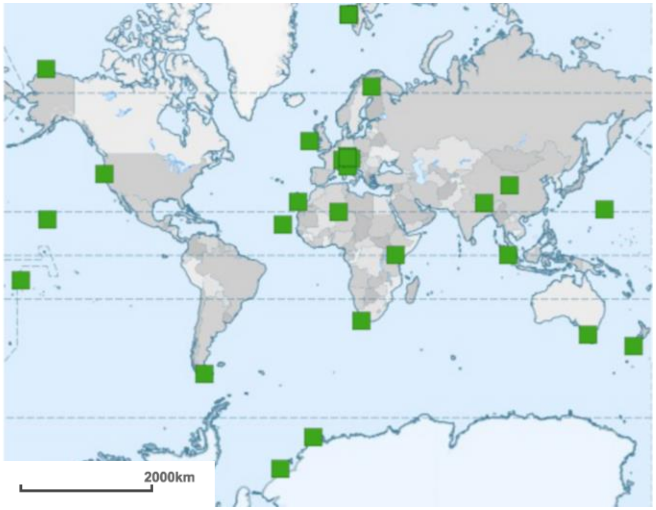
The time sequence of pulses leaving the cavity with absorbing molecules.



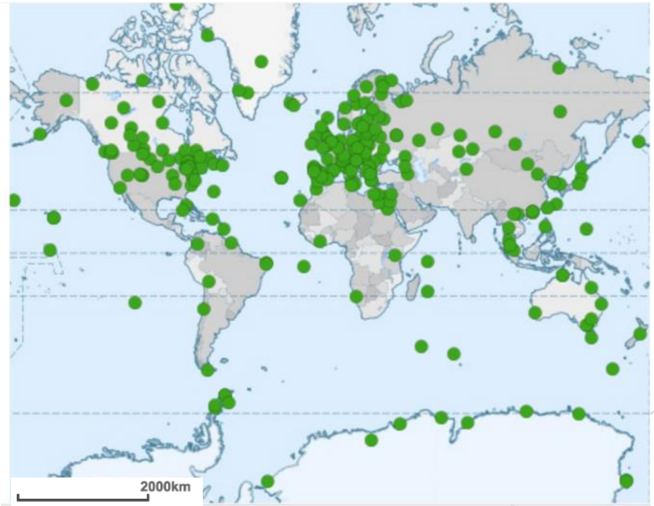
Understanding Measurements

Type of network/site

- Global or baseline



- Regional



Source: https://gawsis.meteoswiss.ch/GAWSIS//index.html#/ Accessed 28/7/16

Global/baseline sites

Cape Grim, Tasmania

- Made from stations on islands, near to the coast or at mountain stations
  - Highly dependent on the prevailing wind direction
- Produce baseline data that is free from strong pollution sources
- Representative concentrations at that latitude of the station
- Historically used as models were not able to disentangle the complex terrestrial signals.

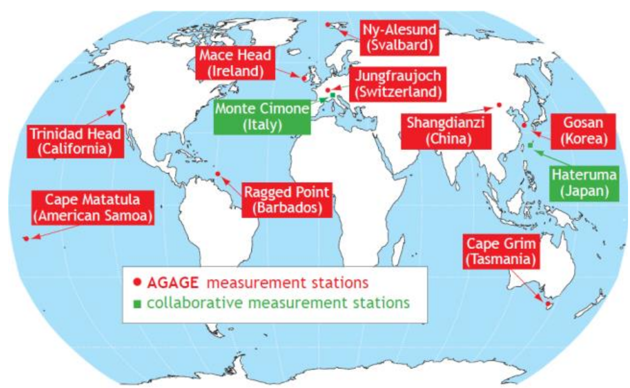
Global AGAGE GHG and ODS measurement network

Mace Head, Ireland

Trinidad Head, California

Cape Matatula, Samoa

Ragged Point, Barbados

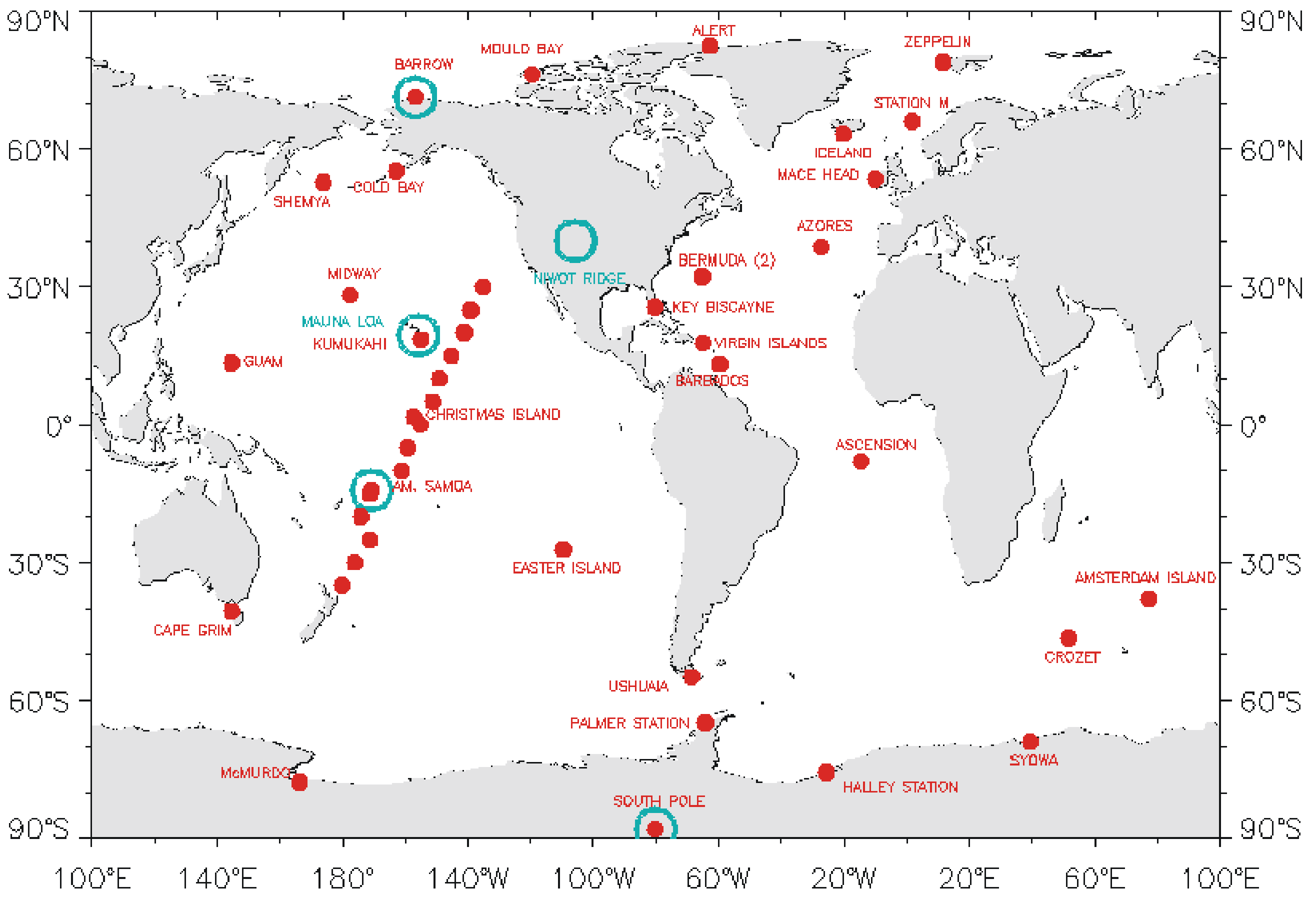


Cape Grim, Tasmania

AGAGE

- Measure over 50 compounds in situ using two instruments
  - Medusa-GCMS
    - ODS (CFC, HFC, HCFC, PFC, Halons, etc.)
  - GC-ECD-FID
    - CH_4, N_2O, $CHCl_3$, CO, H_2, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and CCl_4
- Data available via https://agage.mit.edu/data/agage-data

NOAA/GMD network for measurements of atmospheric pollutants

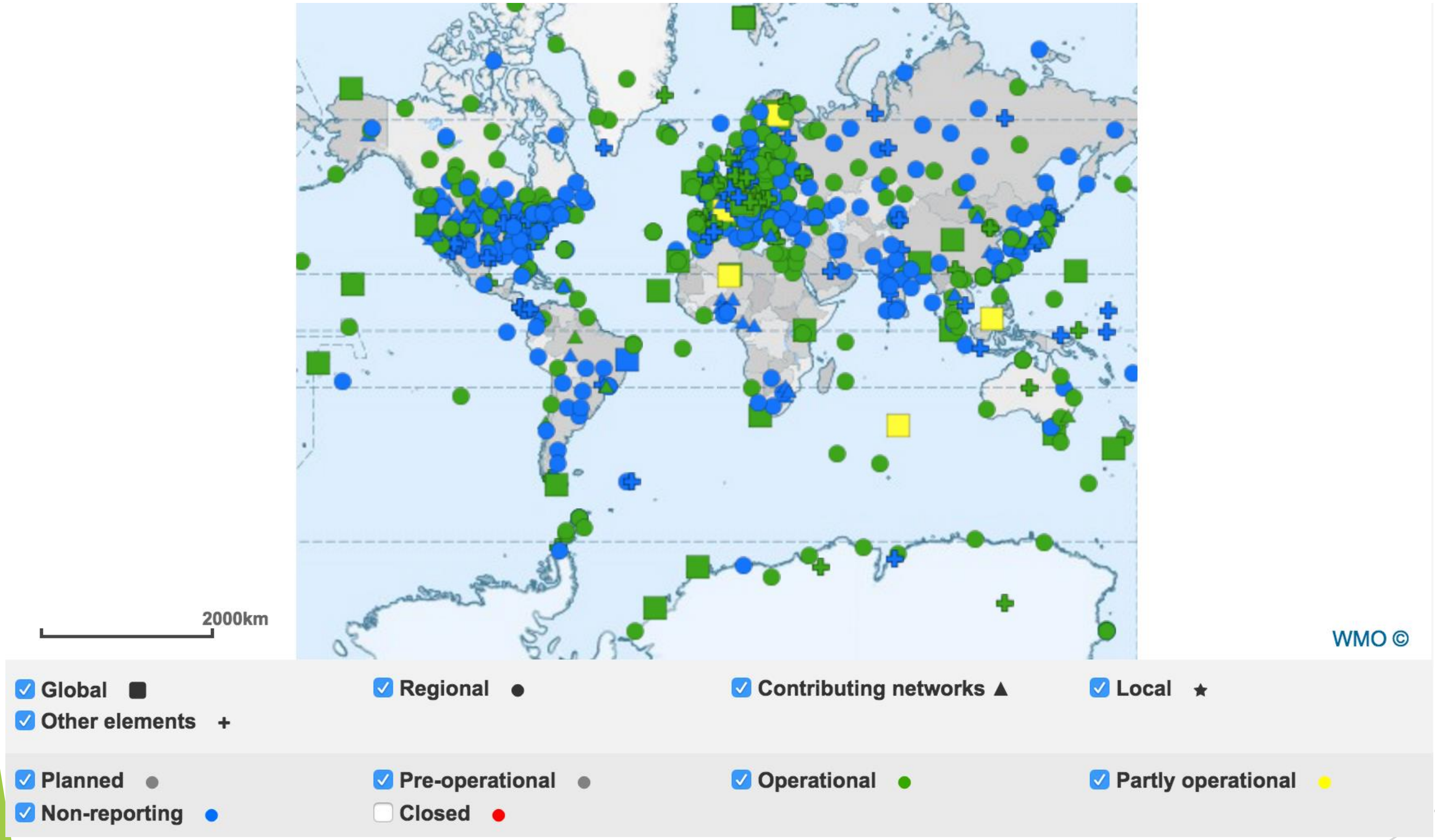


NOAA GMD

- Composed of 6 staffed in situ measurement locations and ~ 160 unmanned locations.
- Most stations fill flasks and send them back to a central lab to be analysed.
- Data available from: http://www.esrl.noaa.gov/gmd/dv/ftpdata.html

Source: http://www.esrl.noaa.gov/gmd/ccgg/ **Accessed 29/7/16**

Global Atmospheric Watch



Source: https://gawsis.meteoswiss.ch/GAWSIS//index.html#/ **Accessed 28/7/16**

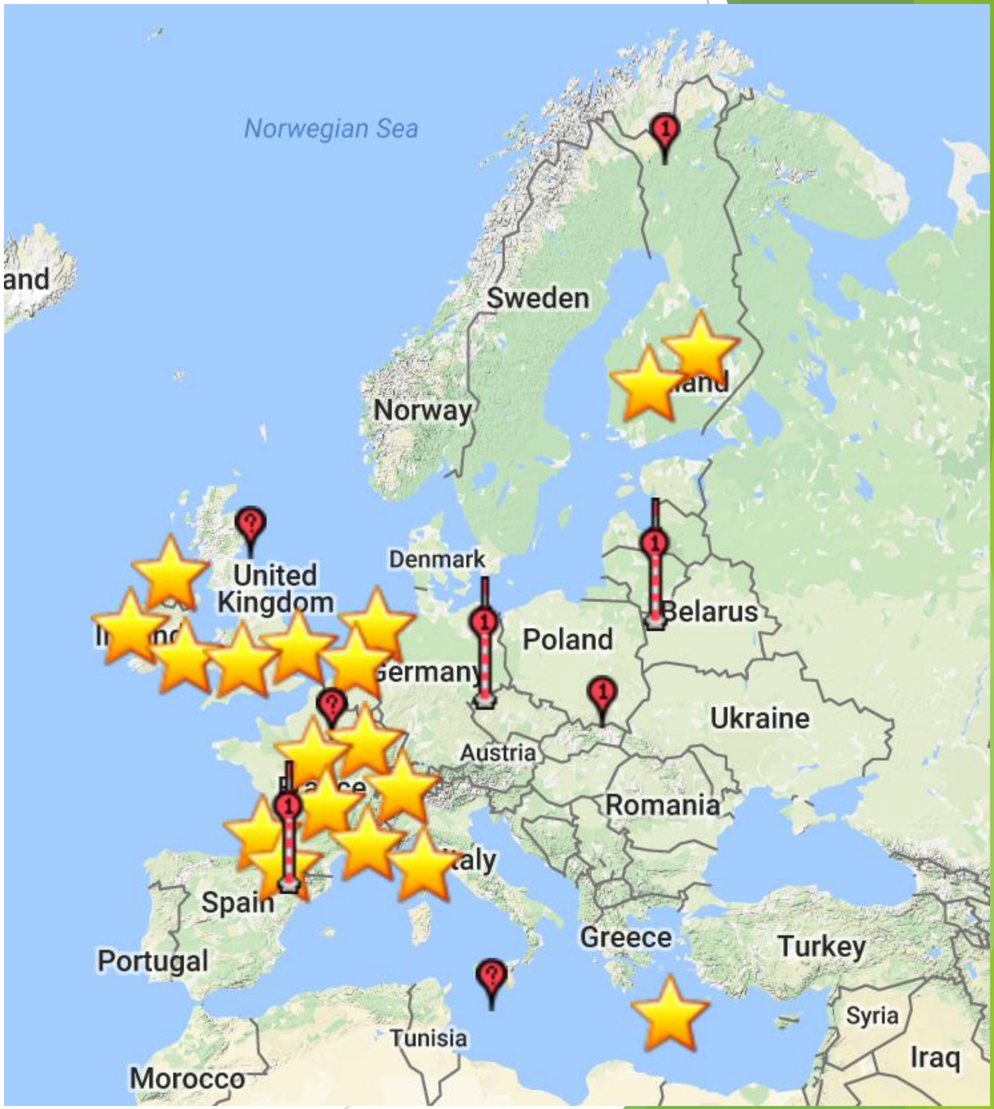
Regional sites

- Often made from tall towers.
  - Help reduce the influence of localised fluxes.
- Constrain regional fluxes of GHGs using measurements combined with transport models.
- Can give a concentration footprint of an area as large as 10^6 km^2.
- Tall platforms allow for multiple inlets
  - Can observe nocturnal planetary boundary layer movement.

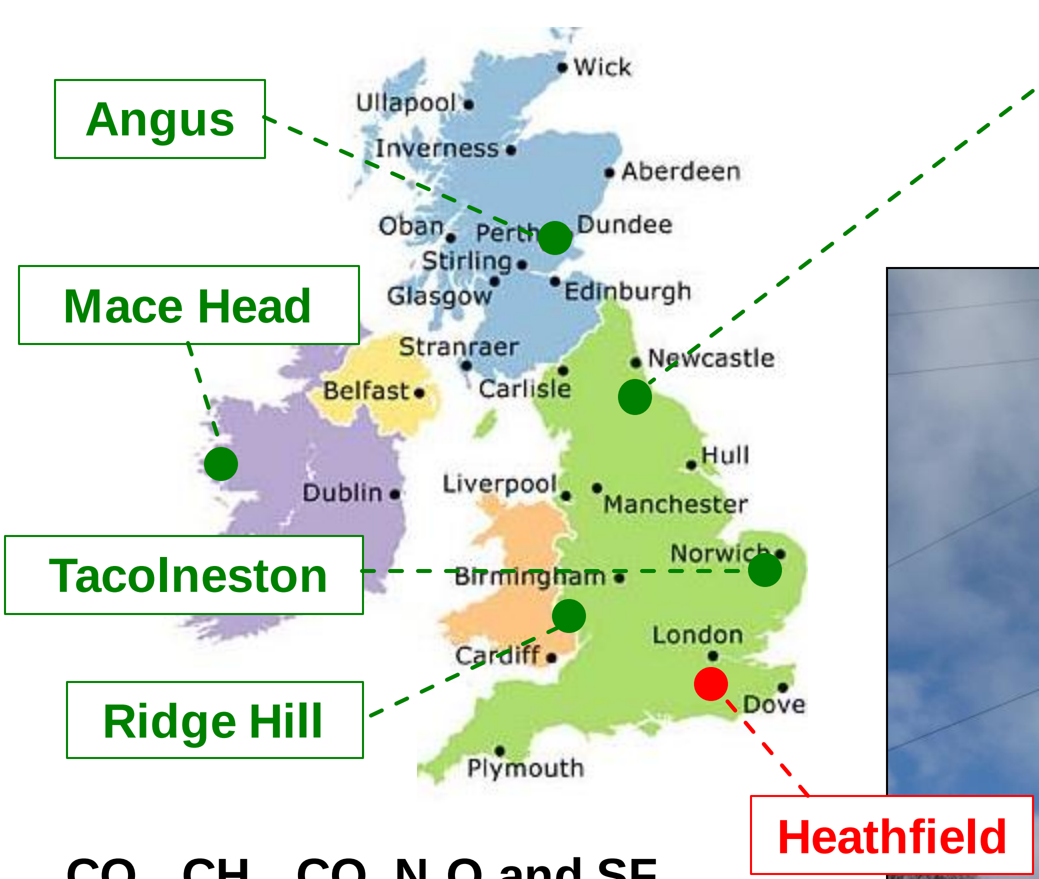
Bilsdale, UK

Integrated Carbon Observation System

- European research infrastructure dedicated to measuring, analysing and understanding GHGs in the atmosphere, over the oceans and at the ecosystem level
- Focussed on C mole fractions within Europe.
- Use near real time (NRT) data
- Composed of mostly regional sites (plus two baseline stations - Mace Head and Jungfraujoch)



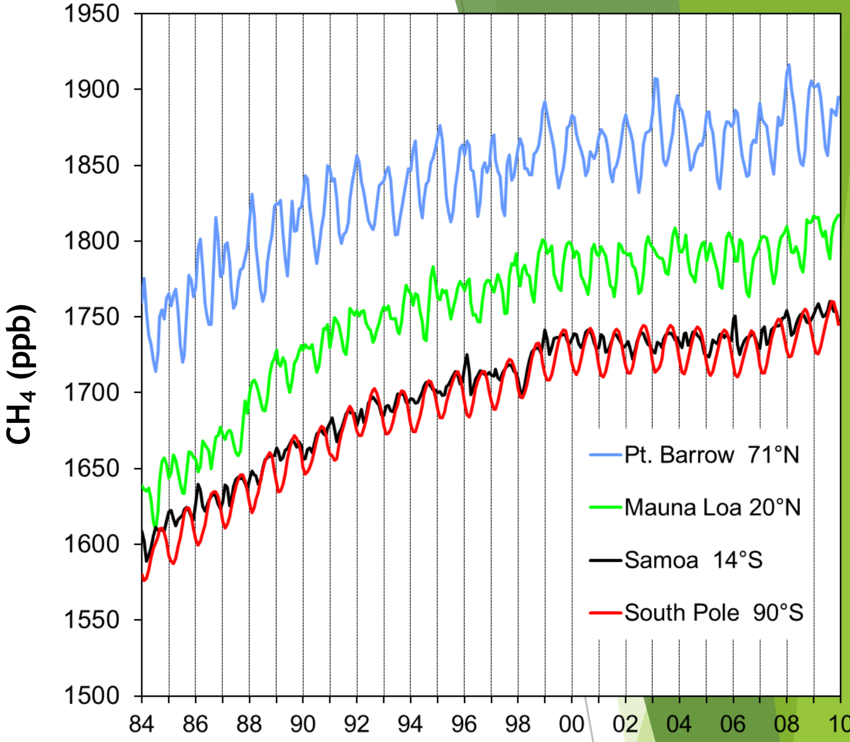
Enhanced tall tower network: UK DECC and GAUGE

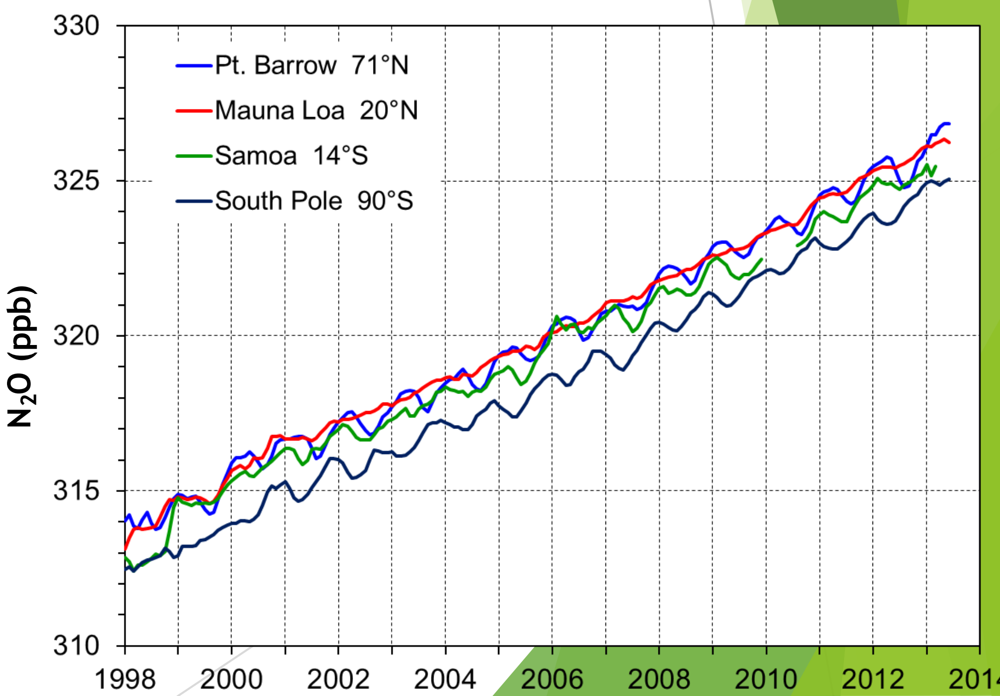


CO_2, CH_4, CO, N_2O and SF_6

Site location

- Hemispherical gradient:
  - Lower concentrations in southern hemisphere
  - Differences in seasons
- Localised issues:
  - Strong pollution sources that blanket measurements.
  - Topography
  - Dominant air masses

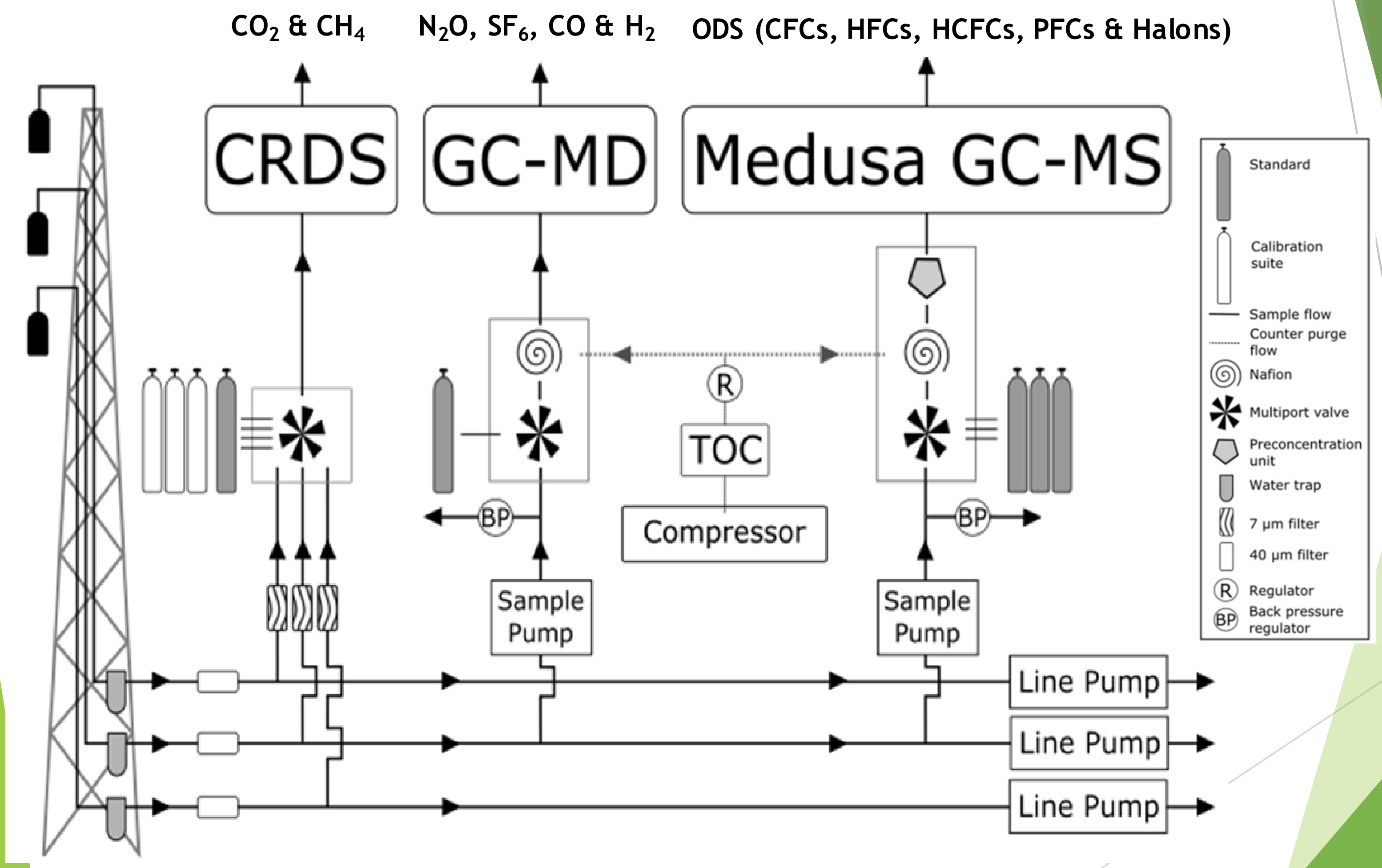




Site setup

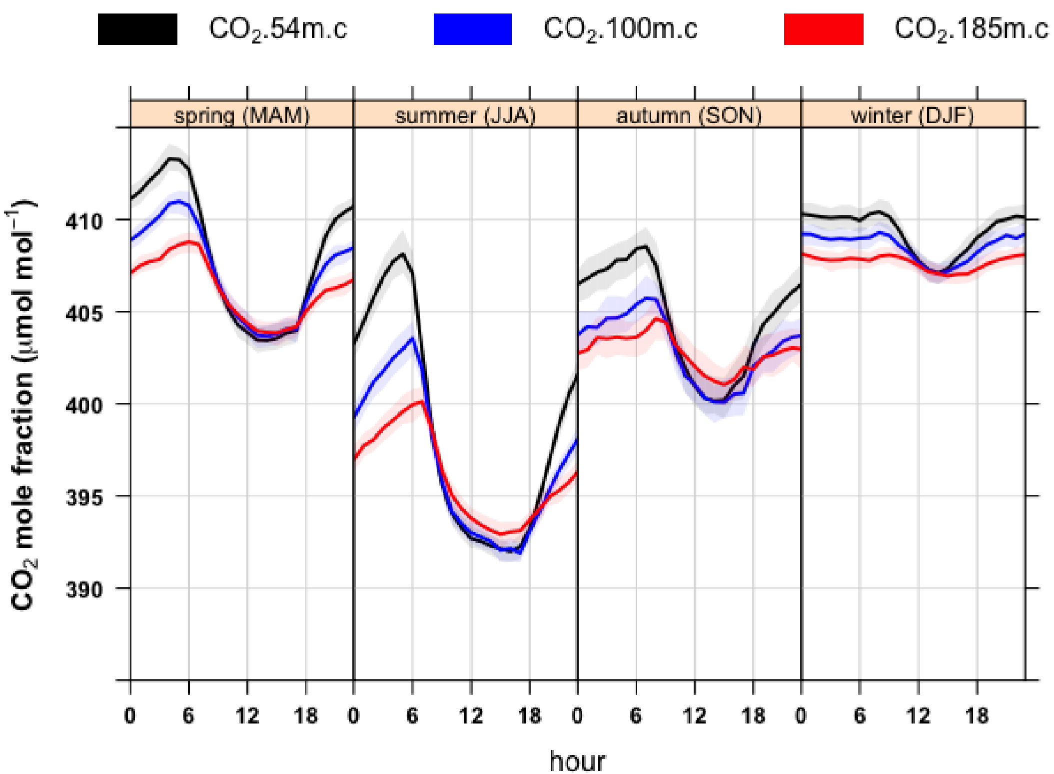
- Something need to consider when interpreting data and modelling data.
- Even small issues can cause significant changes in mole fraction measurements.
- Things to consider:
  - # inlets
  - Inlet heights
  - How H_2O is dealt with
  - Instrumentation used

Example site setup: Tacolneston, Norfolk



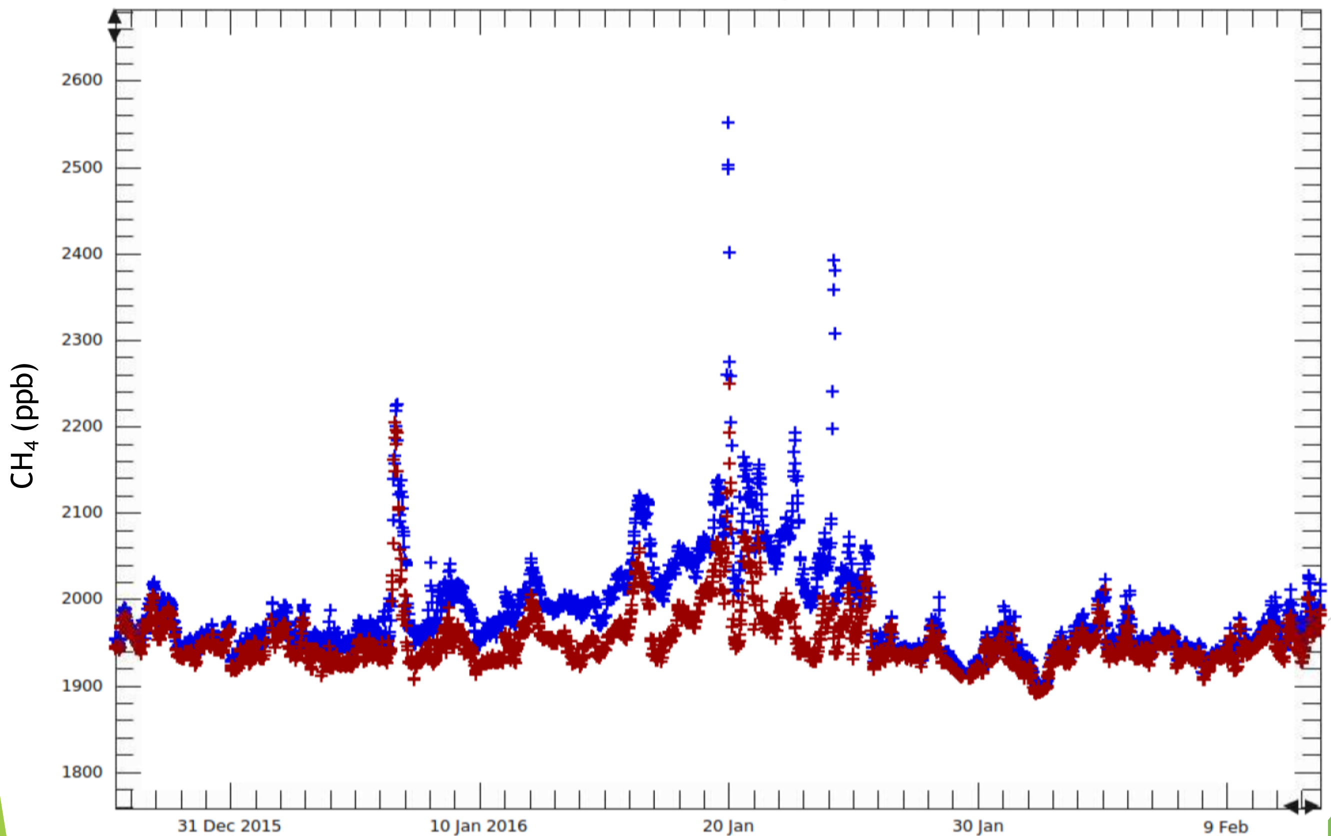
Number of inlets

- Why important?
  - Can show nocturnal planetary boundary layer movements
  - If questionable data from one inlet, can look at another
  - Amount of continuous data from one inlet
  - Complex logistics



Sample inlet height

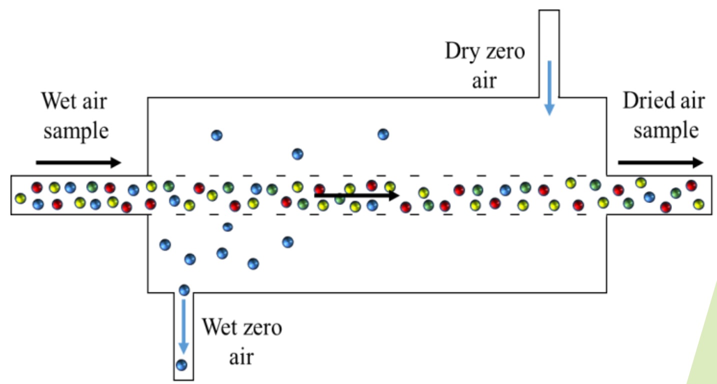
- Why important?
  - Areal footprint that observe
  - Localised pollution sources



H_2O

- GHG mole fractions reported as dry mole fractions.
- H_2O one of the biggest issues with measurements.
- How to correct for it?
  - Chillers/ice traps

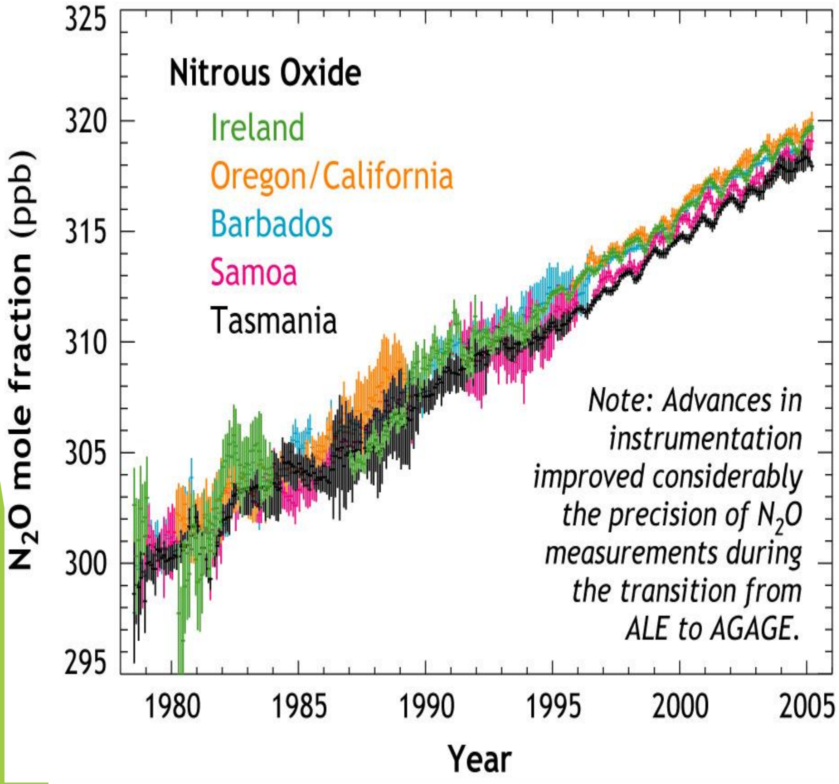
  - Nafion drier



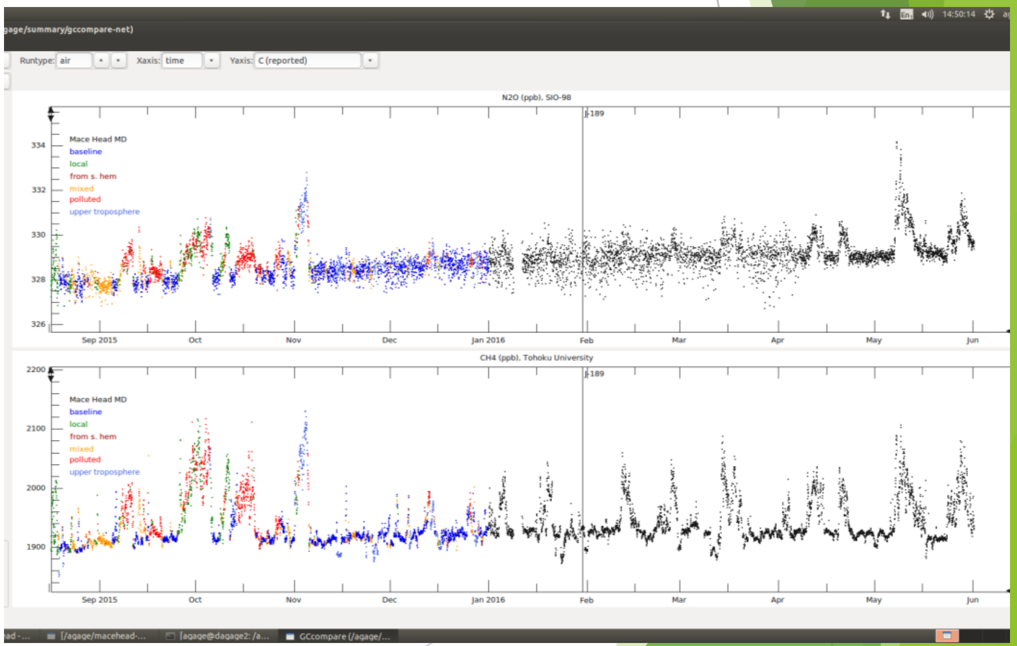
  - Magnesium perchlorate driers

  - Correction coefficients

Measurement Precision



Cleaned valve rotor



Meta data information

- Information on dataset when download it from data source
- Why important to think about?
  - Site location
  - Instrumentation used
  - Inlet height
  - Type of measurement (discreet or continuous)
  - Site type
  - How deal with H_2O

Meta data example

```
66 1001
O'Doherty, Simon; Stanley, Kieran; Stavert, Ann; Young, Dickon
GB05L, "ACRG, University of Bristol, School of Chemistry, Cantocks Close, BS8 1TS, Bristol, United Kingdom", UNIVBRIS, , "Cantocks Close,, BS8 1TS, Bristol, United Kingdom", , , ,
Stanley, Kieran
GAW-WDCGG-node UK_DECC
1 1
2012 01 01 2016 06 06
0
Days from the file reference point (start_time)
7
1 1 1 1 1 1 1
9999.999999 9999.999 999.999 9.999 9999.999 999.999 9.999
end_time of measurement, days from the file reference point
dinitrogen_oxide, ppb
dinitrogen_oxide, ppb,Statistics=expanded uncertainty 3sigma
numflag dinitrogen_oxide, no unit
SF6, ppt
SF6, ppt,Statistics=expanded uncertainty 3sigma
numflag SF6, no unit
0
45
Data definition:              EBAS_1.1
Set type code:                TI
Station code:                 GB0055R
Platform code:                GB0055S
Timezone:                     UTC
Startdate:                    20120301151435
Timeref:                      00_00
Revision date:                20160606113900
Component:                    greenhouse_gas
Unit:                         ppt
Matrix:                       air
Period code:                  1y
Resolution code:              10mn
Sample duration:              1mn
Laboratory code:              GB05L
Instrument type:              online_gc
Instrument manufacturer:      Agilent
Instrument model:             7890A_uECD
Instrument name:              Agilent_GC-uECD_7890_MD_RGL
Instrument serial number:     CN11171049
Method ref:                   GB05L_ACRG_DECC_MD
Orig. time res.:              10mn
File name:                    GB0055R.20120101.20160606.greenhouse_gas.air.12m.10mn.GB05L_ACRG_DECC_MD.nas
Station GAW-ID:               RGL
Station latitude:             51.997558
Station longitude:            -2.54003
Station altitude:             204m
Station land use:             Warm Temperate
Station setting:              Regional
Station GAW type:             R
Station WMO region:           6
Originator:                   O'Doherty, Simon, s.odoherty@bristol.ac.uk, University of Bristol, ACRG, Atmospheric Chemistry Research Group, Cantocks Close,, BS8 1TS, Bristol, United Kingdom
Originator:                   Stanley, Kieran, k.m.stanley@bristol.ac.uk, University of Bristol, ACRG, Atmospheric Chemistry Research Group, Cantocks Close,, BS8 1TS, Bristol, United Kingdom
Originator:                   Young, Dickon, , University of Bristol, ACRG, Atmospheric Chemistry Research Group, Cantocks Close,, BS8 1TS, Bristol, United Kingdom
Originator:                   Stavert, Ann, , University of Bristol, ACRG, Atmospheric Chemistry Research Group, Cantocks Close,, BS8 1TS, Bristol, United Kingdom
Submitter:                    Stanley, Kieran, k.m.stanley@bristol.ac.uk, University of Bristol, ACRG, Atmospheric Chemistry Research Group, Cantocks Close,, BS8 1TS, Bristol, United Kingdom
Data level:                   1
Version:                      1
Version description:          initial revision, manually inspected
Height AGL:                   90m
Inlet type:                   Hat or hood
Inlet description:            Downward facing with hood, 90 m, stainless steel, flow ~20 l/min
Volume std. temperature:      273.15K
Volume std. pressure:         1013.25hPa
  start_time    end_time      N20 N20 prec numflag      SF6 SF6 prec numflag
```

Data locations

- WDCGHG: http://ds.data.jma.go.jp/gmd/wdcgg/
- CDIAC: http://cdiac.ornl.gov/
- EBAS: http://ebas.nilu.no/
- NOAA GMD: http://www.esrl.noaa.gov/gmd/dv/ftpdata.html
- ObsPack GlobalView: http://www.esrl.noaa.gov/gmd/ccgg/obspack/
- AGAGE: https://agage.mit.edu/data
- ICOS: not online yet but watch this space!

Summary

- Most interested in troposphere for GHG measurements.
- GHGs only make up a very small portion of the atmosphere.
- Measurements key to helping inform climate change mitigation policy.
- Large number of stations measuring GHGs over the World.
  - But large areas where very few measurements taken.
- Key to understanding measurements:
  - Station location
  - Type of station
  - Instrumentation used
  - Site setup
  - H_2O issue
- All necessary information in data headers - ALWAYS READ!!!
- Lot of work goes into measurements: make sure you properly acknowledge the work that goes into the numbers you use.

Thank you

Time for the exciting stuff!