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Fundamentals of atmospheric monitoring

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11 June 2019

Flux Measurements Winter School, Vuwani, South Africa

Overview

- Atmospheric observation networks
- Site specifications
- Instruments: Gas chromatography
- Instruments: Non-dispersive infrared spectroscopy
- Instruments: Cavity ringdown spectroscopy
- Atmospheric measurement peripherals
- Processing data
- Quality assurance / Quality control

Why measure atmospheric constituents?

Atmospheric monitoring sites are established with the purpose of providing the best possible information on atmospheric constituents that drive

- climate change
- stratospheric ozone depletion
- surface radiation

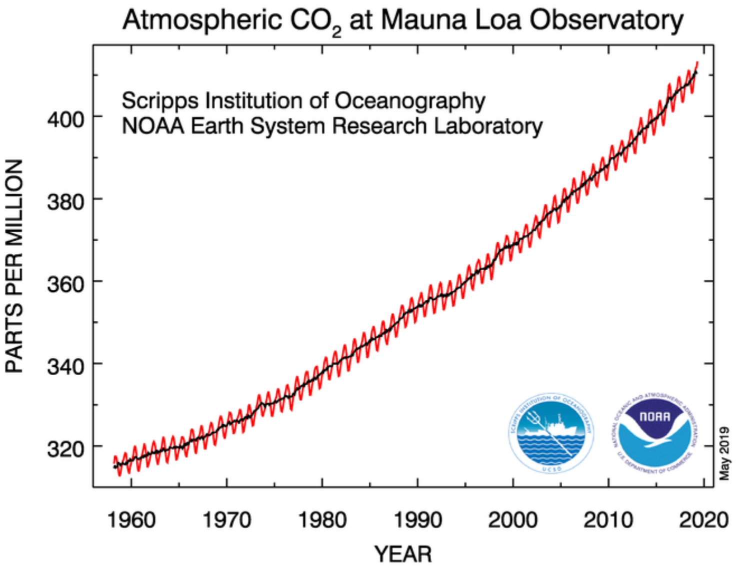
World Meteorological Society - Global Atmospheric Watch

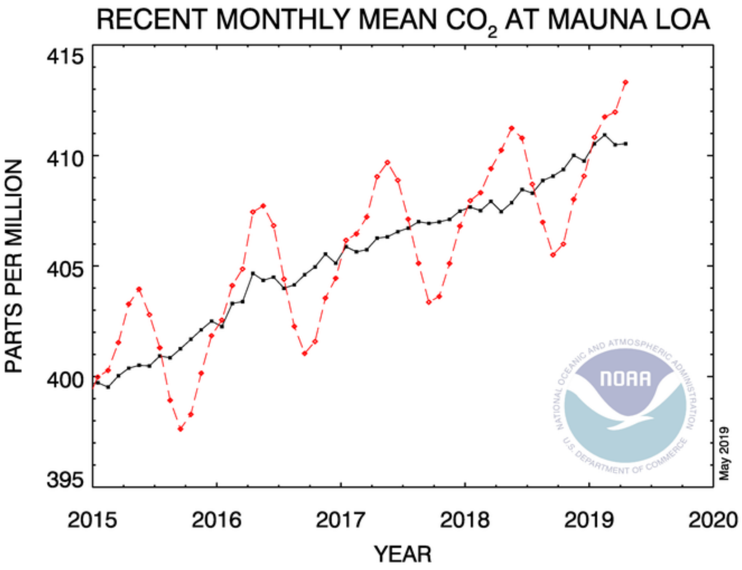
https://www.wmo.int/pages/prog/arep/gaw/measurements.html

Example - Mauno Lao – NOAA

- Chosen as a site because it was:
  - Far from the continent
  - Relatively undisturbed air
  - Minimal influences from vegetation and human activity
- First started monitoring CO_2 in 1958

Example - Mauno Lao - NOAA

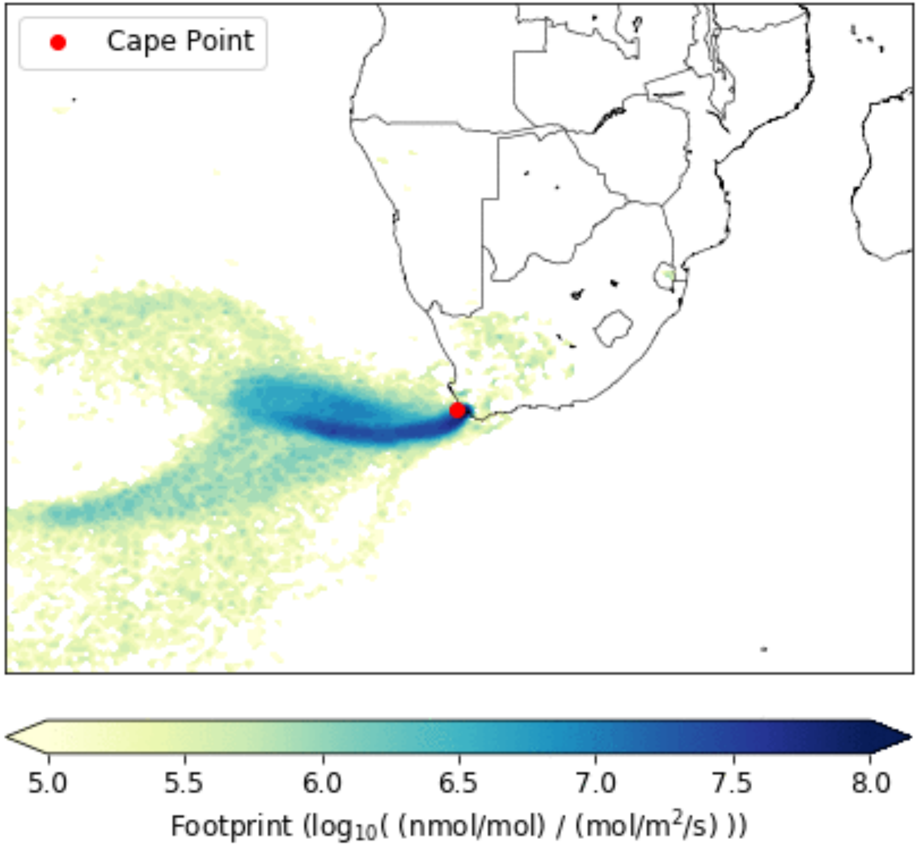




https://www.esrl.noaa.gov/gmd/ccgg/trends/index.html

Cape Point – GAW site

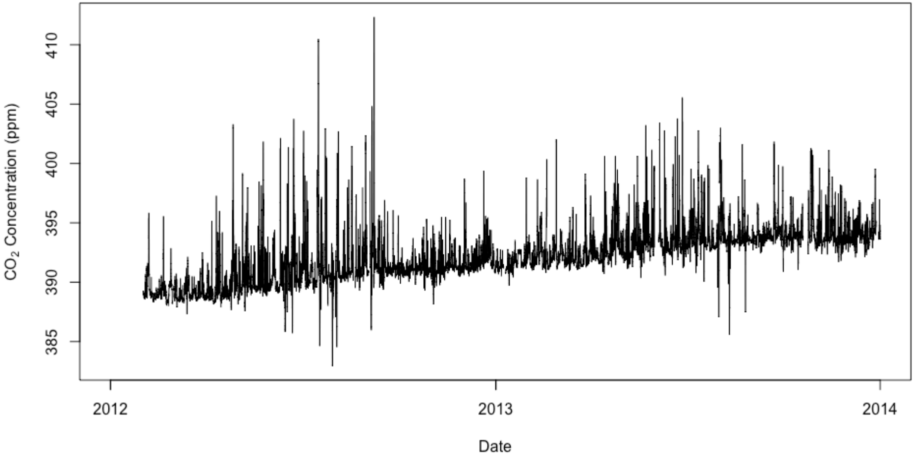
Cape Point - Footprint



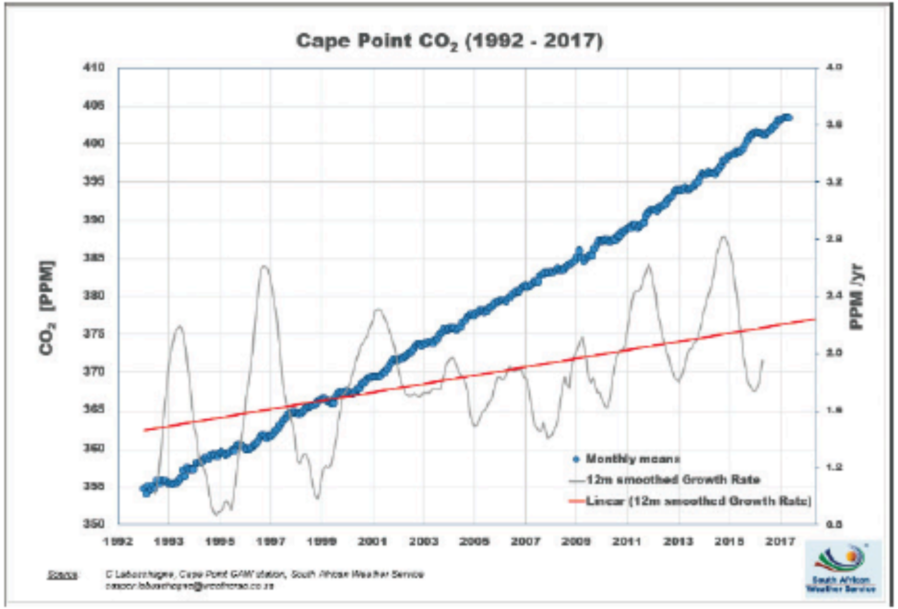
Cape Point – GAW site

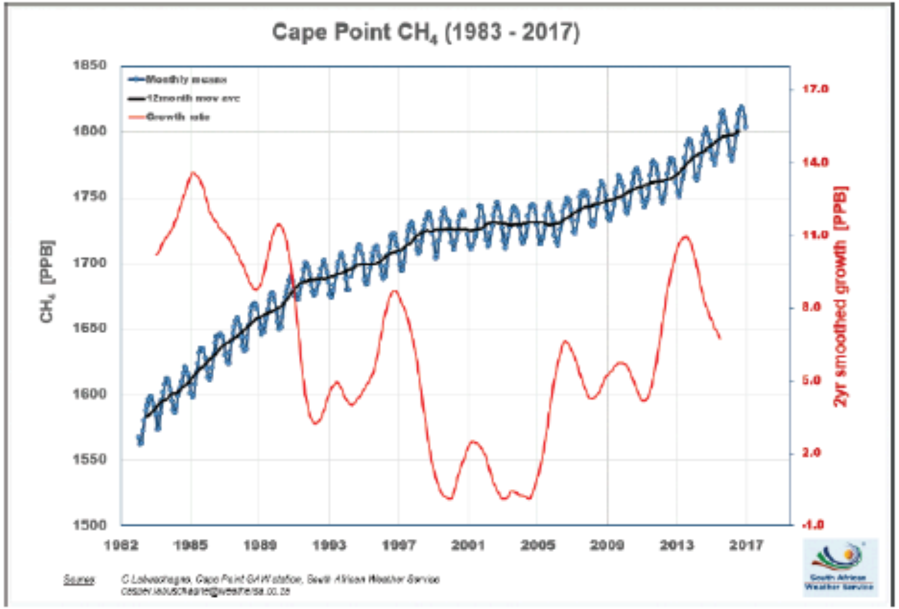
- Site established in 1977 to measure CO and CFC-11
- Measurements of CH_4 (methane) started in 1982 and N_2O (nitrous oxide) in 1983. Longest CH_4 record in the Southern Hemisphere.
- Started measuring CO_2 in 1991.
- Other constituents include surface ozone (O_3) and Sulphur dioxide (reactive gases), and stratospheric ozone depleting gases CFC-11, CFC-12, CFC-113, and methyl chloroform, as well as aerosols and total gaseous mercury.

Cape Point – CO_2 Data Record



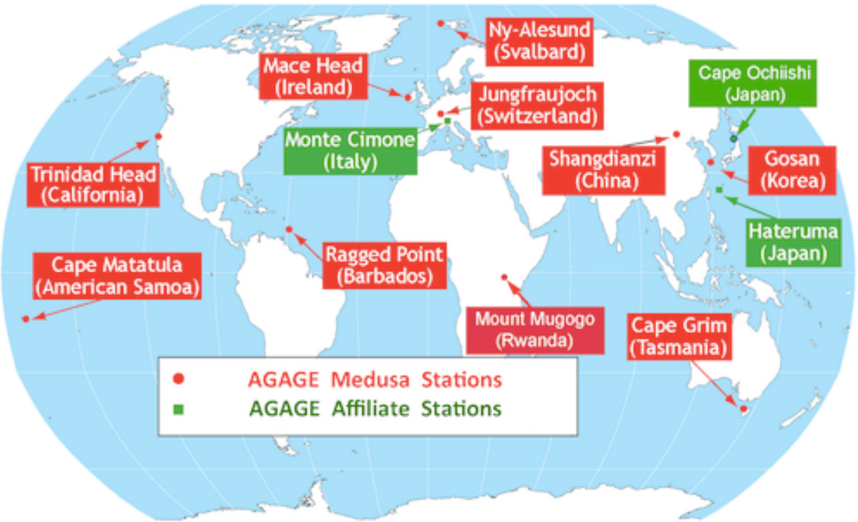
Cape Point – CO_2 and CH_4 Data Record





Labuschagne et al., 2018, "A review of four decades of atmospheric trace gas measurements at Cape Point, South Africa", Clean Air Journal, doi: 10.17159/2410-972X/2018/v28n2a10

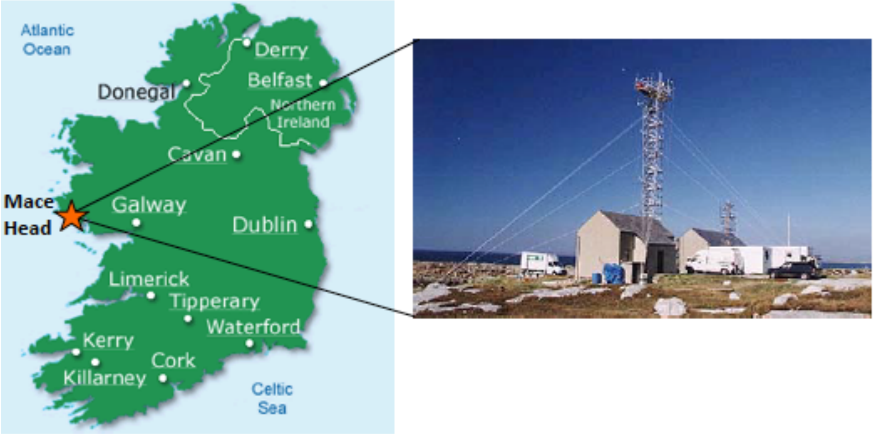
AGAGE (Advanced Global Atmospheric Gases Experiment) Network

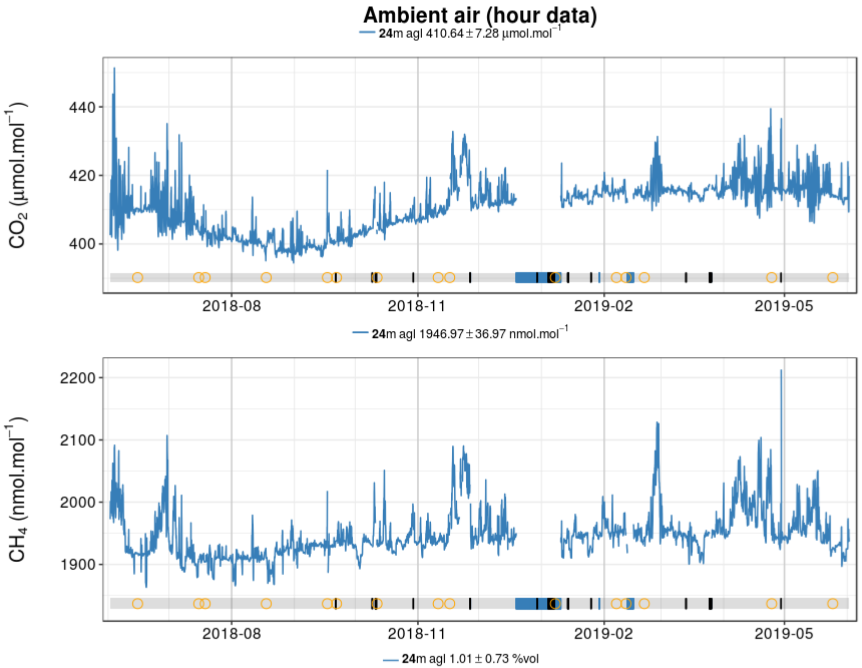


https://cgcs.mit.edu/research/agage

- Measuring since 1978
- Major objective: Measure the ozone-depleting gases (such as CFC-11, CFC-12, CCl_4, CH_3CCl_3, N_2O).
- Many of these are very potent greenhouse gases.
- CH_4 and CO_2 measurements have been added more recently.

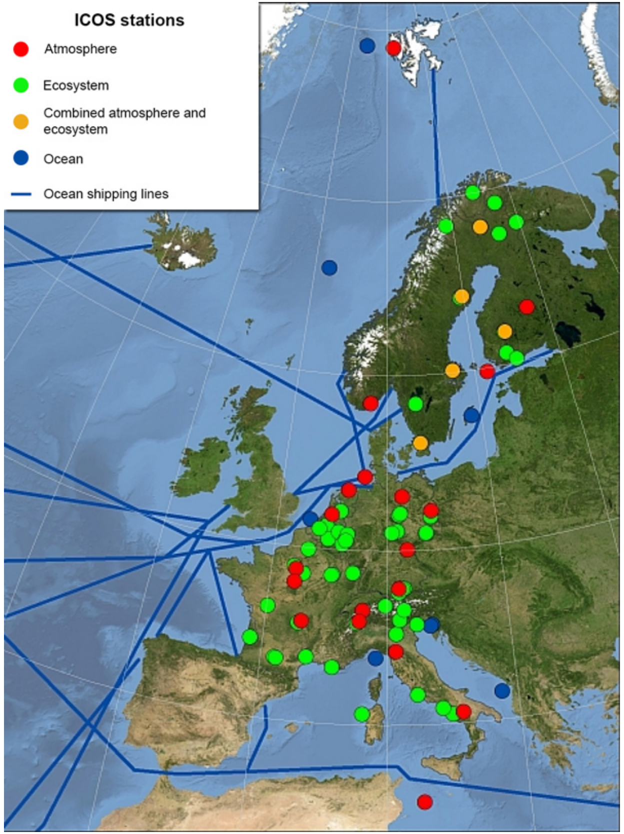
Mace Head, Ireland AGAGE site





https://icos-atc.lsce.ipsl.fr/?q=MHD

ICOS RI Network



https://icos-atc.lsce.ipsl.fr/universcience/icos_en.php

Site specifications

- Low levels of pollution from local sources. Should be at least 40km from anthropogenic sources.
- Representative of a large area (typically at least 10 000km^2 footprint).
- Careful scrutiny of back trajectories can help identify which regions will be sampled by the site.
- Location based on whether the site needs to be a coastal (targeting marine air-masses), continental (targeting continental air-masses) or mountain site (will target free tropospheric air during the night).
- Initial measurements of meteorological variables like wind speed and direction at the site can assist in determining how well modelled meteorological data replicates these parameters.
- Avoid complex terrain if possible. Mountain sites are hard for transport models.

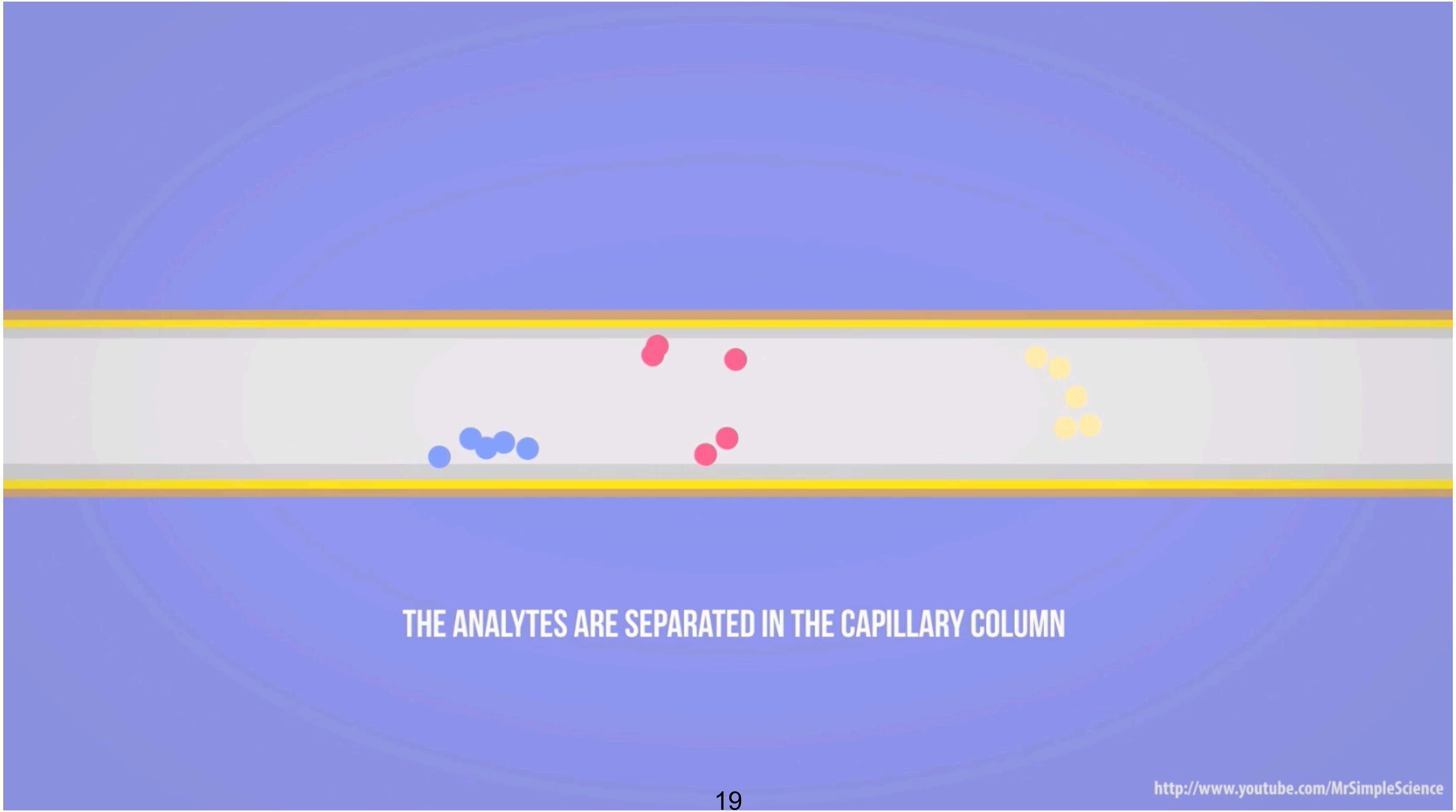
Site specifications

- Height of the tower is important.
- Coastal and mountain sites should be tall enough to avoid contamination by local sources.
- Continental stations, targeting mixed layer air over land, should have a top level at least 90m tall, and have additional measurement levels at 10m (above vegetation) and 50 – 70m, 100, 200 for taller towers.
- Logistic constraints should be considered, as these sites need to be accessible for calibration and instrument maintenance.
- Need reliable power source.
- Network connectivity.
- Temperature-controlled housing for instruments.

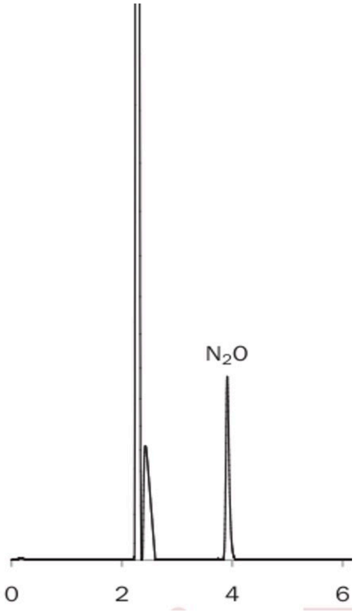
Ridge Hill, UK

Instruments – Gas Chromatography

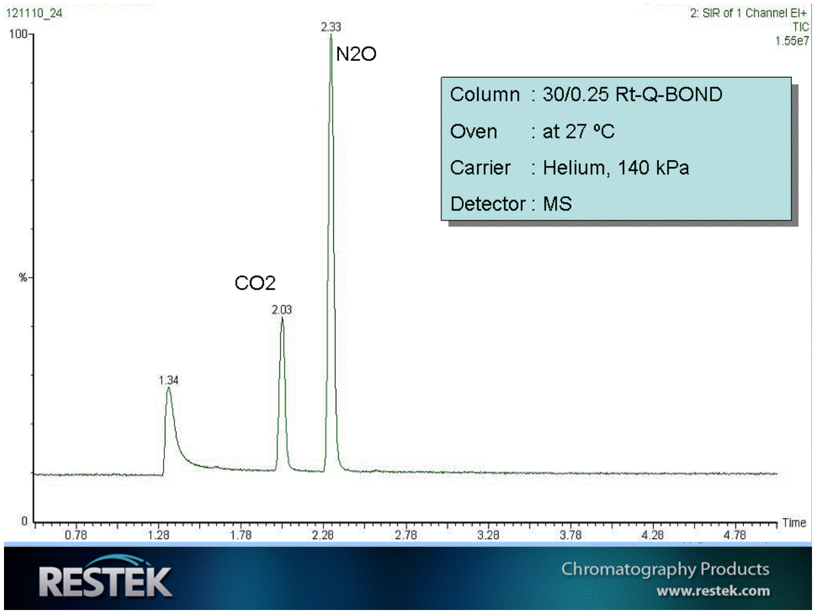
- An air sample is injected onto the head of the chromatographic column.
- The sample is transported through the column by the flow if an inert gas, such as argon. The choice of gas is based on the detector.
- The column temperature must be controlled to within tenths of a degree. (very important!!) This means that the room temperature should be cool and as constant as possible.


THE ANALYTES ARE SEPARATED IN THE CAPILLARY COLUMN
http://www.youtube.com/MrSimpleScience

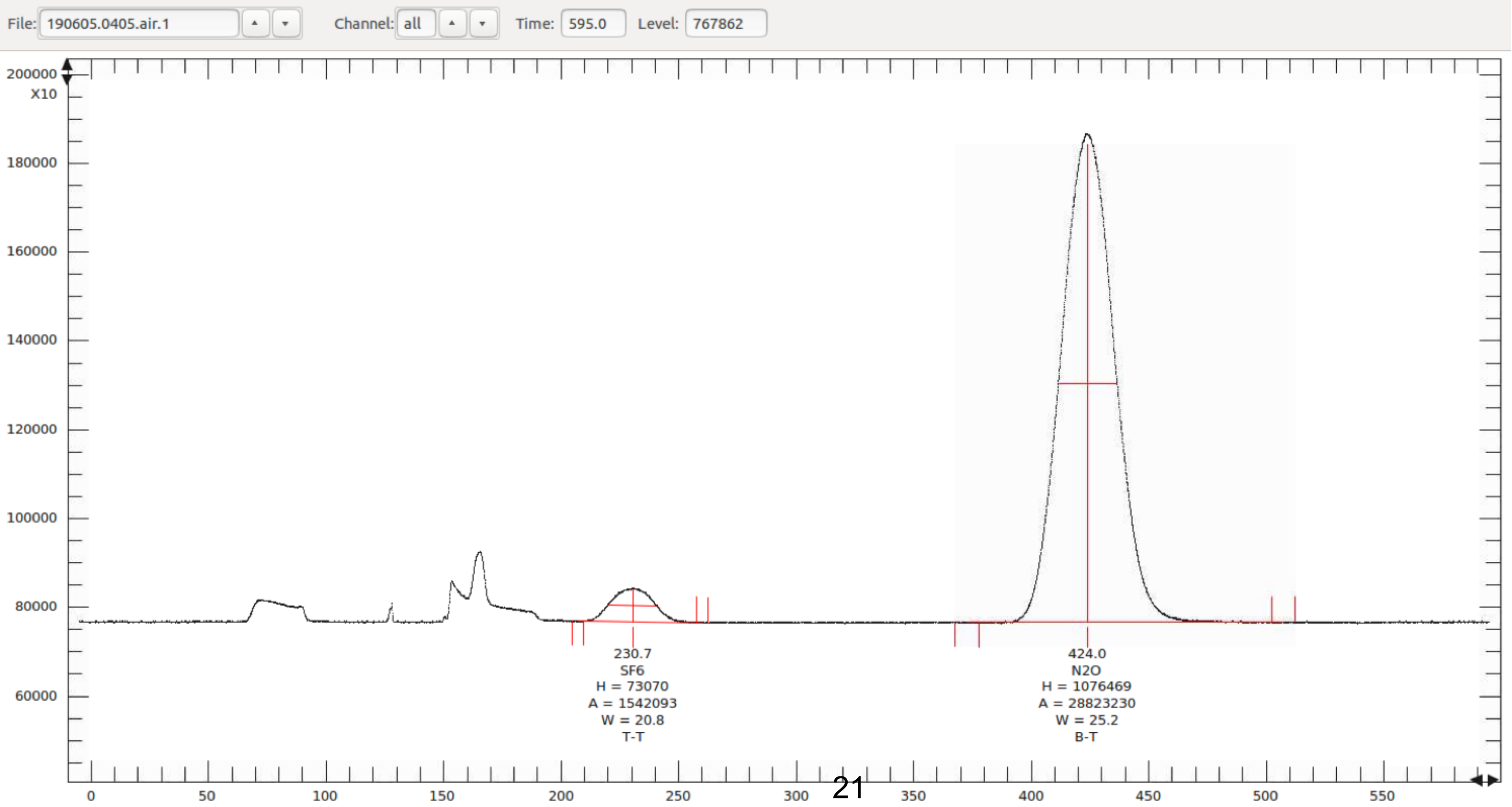
Gas Chromatogram



Nitrous oxide on Alumina BOND / Na2SO4 Column: 30m x 0.53mm Rt Alumina BOND / Na2SO4; Helium, 4 mL/min; Oven: 40ºC; sample: 60µl; Detector: PlasmaDetek PED; sample: 5.4 ppm



Gas Chromatogram



MEDUSA Gas Chromatography with Mass Spectrometry

- Phase 1: Sample gas introduced. Stripped of water. Analytes are preconcentrated by adsorption at low temperature on a trap.
- Phase 2: CF_4 and NF_3 (most volatile) and residual bulk air (N_2, O_2, Ar, and Kr) are transferred to a second cold microtrap for refocusing. These are separated on a precolumn before transfer to main column for MSD detection.
- Phase 3: The remaining compounds are desorbed from Trap1, residual water is removed, and refocused on Trap2 to the main column for separation before being detected by the MSD.

Infrared gas analyzers

www.licor.com

www.yokogawa.com

- Non-dispersive infrared (NDIR) spectroscopy.
- The absorption intensity is governed by the Lambert-Beer's law :

$$I = I_0 e^{-ckl}$$

Where I: the intensity of the transmitted light, I_0 is the intensity of the incident light, c is the concentration of the gas, k is the absorption coefficient of the gas, and l is the light path length.

- Requires a reference gas, usually nitrogen, and is therefore also referred to a differential gas analyzer.

Cavity ringdown spectroscopy

www.picarro.com

www.lgrinc.com

- This type of analyzer can measure more than one species.
- ICOS requires < 50 ppb precision for CO_2 and <1 ppb for CH_4
- High accuracy measurements require:
  - Pressure control of the molecules
  - Temperature control of the molecules
  - Precise control of the wavelength of light utilized
  - Optimal absorption technique with no systematic errors

Concentration and isotope analyzers

- Analyzers are available which measure both the concentrations of the gas and the isotope ratios of the gases.
- This is useful for attributing the sample to specific sources.
- E.g. Picarro G2131-*i*

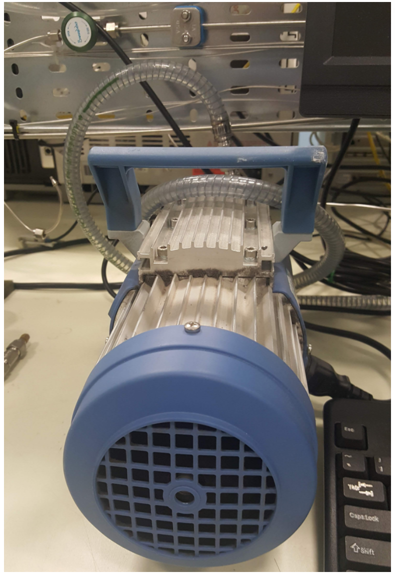
Plumbing

- Tubing should be durable and non-reactive, such at PTFE (Teflon).
- Connectors need to be durable and leak proof.
- A filter either at the inlet or inline should be in place to prevent water and particles getting into the analyzer.

www.swagelok.com

Pumps

- Gas analyzers require a pump to mo
  the sample through the system.
- Picarro comes with a vacuum diaphragm pump.
- Needs to be a low-leak.
- Vital component to get the cavity pressure to the required.
- May require an external pump to reduce residence time of sample in the tube.



Valves

- Used for switching between sampling heights or running reference/calibration gases.
- Picarro have valve sequencer software pre-installed which allow for automated switching between sampling lines.
- Measurements that are taken during valve switches should be discarded for flagged.

www.vici.com

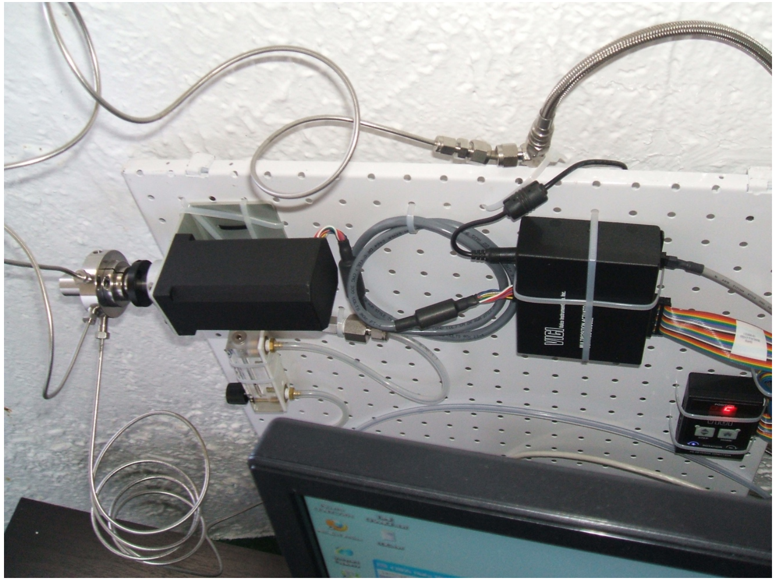
Calibration standards

- Intercomparability between measurement sites is very important.
- WMO/ICOS recommend tiered measurement standards are used at most sites, at least two levels, but preferably three.
- Primary standards: e.g. those maintained by the Central CO_2 calibration Laboratory (CCL NOAA) established either through gravimetric or manometric means. Used for absolute calibration.
- Secondary standards link back to primary. Ambient clean air that has been measured on an instrument at the CCL.

- Secondary/Tertiary and are used for regular calibration. Can have several of these at different concentrations to perform non-linearity corrections.
- Tertiary/Quaternary standards can be a working standard to correct for drift. Also contains ambient air which is measured frequently.

Regulators and Rotameters

- Rotameters are used to measure the flow rate of the gas through the system. Electronic flow sensors are available as well.
- Good quality regulators are required for linking the gas standards to the instrument. These need to provide a stable flow rate, and need to be leak resistant.
- When gas cylinders are changed, check for leaks around the regulator.



Additional Measurements

ICOS requires the following additional meteorological measurements:

- Wind speed
- Wind direction
- Temperature
- Relative humidity
- Barometric pressure

www.gillinstruments.com

Processing Data

- Data processing needs to be meticulous and as automated as possible.
- It also needs to be transparent and well documented.
- Instruments produce fairly high frequency data (although not as frequent as eddy-covariance towers). These data need to be processed into averaged values, usually every hour. Calibration measurements need to be separated.
- Don't just rely on spreadsheets to do this. It's worth spending time or money on good processing software. Speak to your collaborators – they may have some software already.

Processing data

- Any data that are removed due to potential contamination or instrument failure need to be carefully documented. Rather flag the data than permanently delete it.
- Make sure to maintain a log book! (preferably electronic, which is accessible on and off site)
- Back up your data!
- Ensure your data are in the correct format for which ever repository you store your data on.

Quality Assurance / Quality Control

- Ensure standards are calibrated once every two years (WMO recommendations).
- Scrutinize the data regularly, at least graphically. It is a good idea to regularly inspect data statistics like the mean and standard deviation over short periods of time.
- Also regularly inspect the “engineering data”, such as the instrument temperature, pressure and flow rates.
- If data are reprocessed, be sure to document this and version control.
- If using a GC, you will need to keep track of peak retention time and peak width.
- Redundancies in the system can help to identify problems. For example, leaks can potentially be detected if you use two sampling lines (when you swap between the lines you can detect if one line is producing anomalous readings)

Additional Reading

- Casper Labuschagne, Brett Kuyper, Ernst-Günther Brunke, Thumeka Mokolo, Danie van der Spuy, Lynwill Martin, Ernst Mbambalala, Bhawoodien Parker, M. Anwar H. Khan, Michael T. Davies-Coleman, Dudley E. Shallcross & Warren Joubert (2018) A review of four decades of atmospheric trace gas measurements at Cape Point, South Africa, Transactions of the Royal Society of South Africa, 73:2, 113-132, DOI: 10.1080/0035919X.2018.1477854
- Laurent, O. ICOS Atmospheric Station Specifications, Version 1.3.