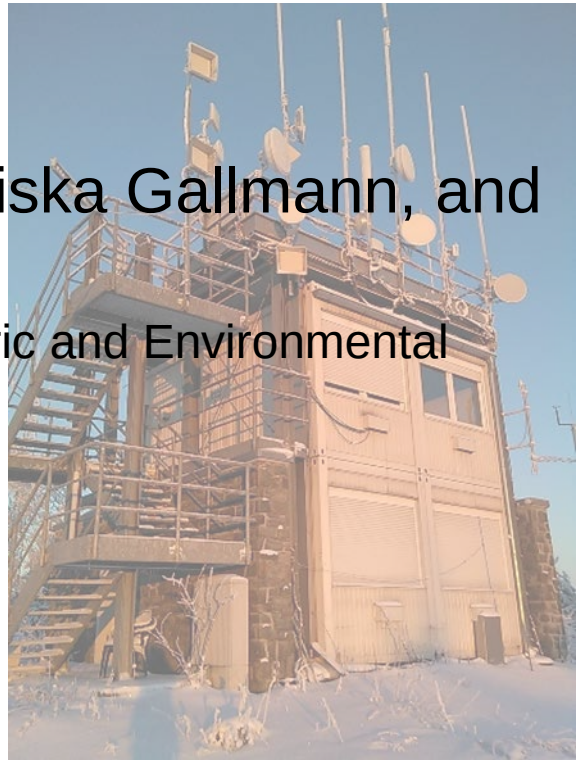
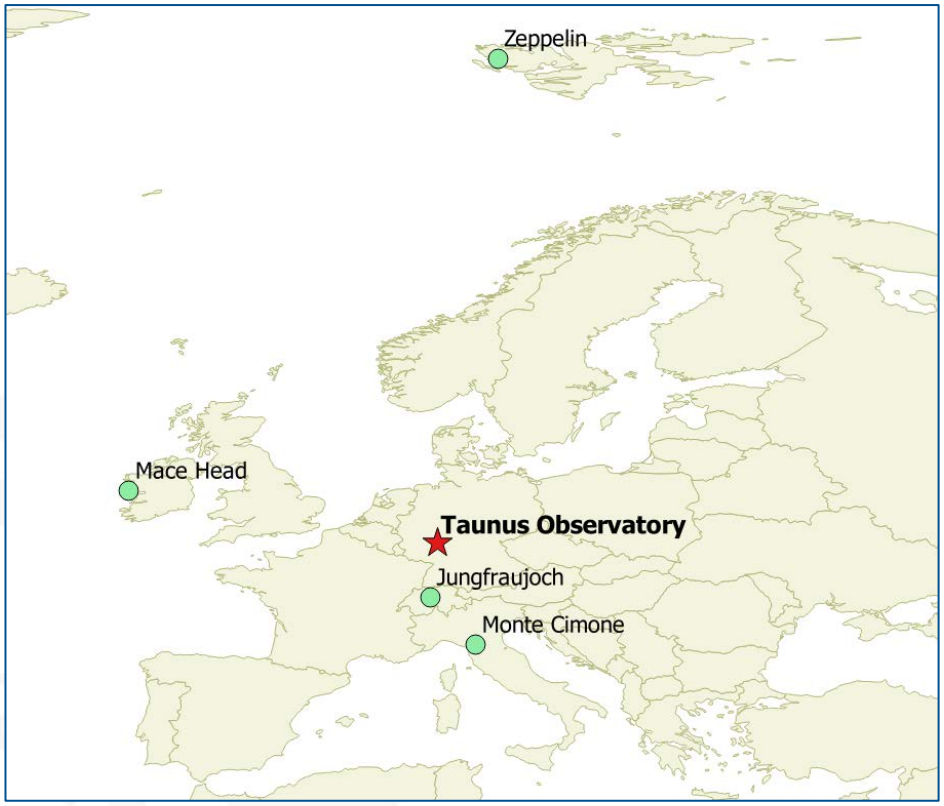
Establishing Regular Measurements of Halocarbons at Taunus Observatory

Tanja Schuck, Fides Lefrancois, Franziska Gallmann, and Andreas Engel

Goethe University Frankfurt, Institute for Atmospheric and Environmental Sciences

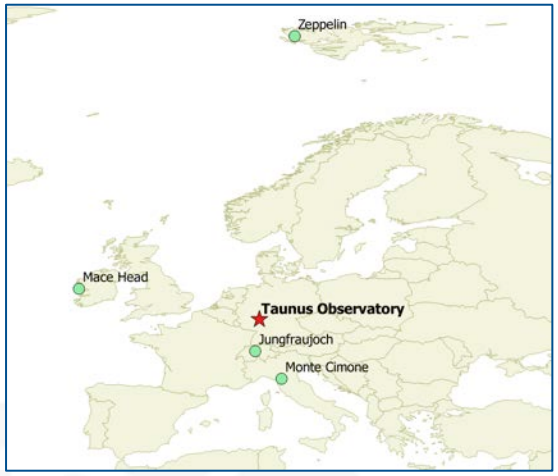


Taunus Observatory

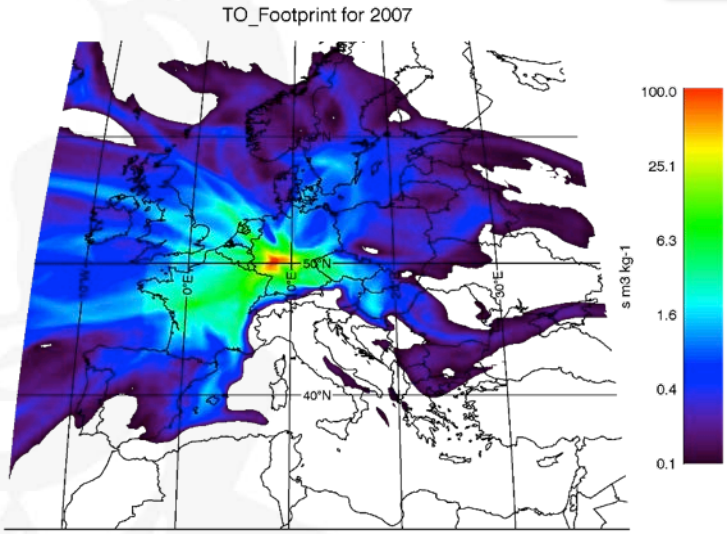


- Regular halocarbon measurements in Europe are made predominantly at clean air stations (NOAA and AGAGE network)
- Data from a semi-polluted site in central Europe will result in stronger constraints for emission estimates

Taunus Observatory



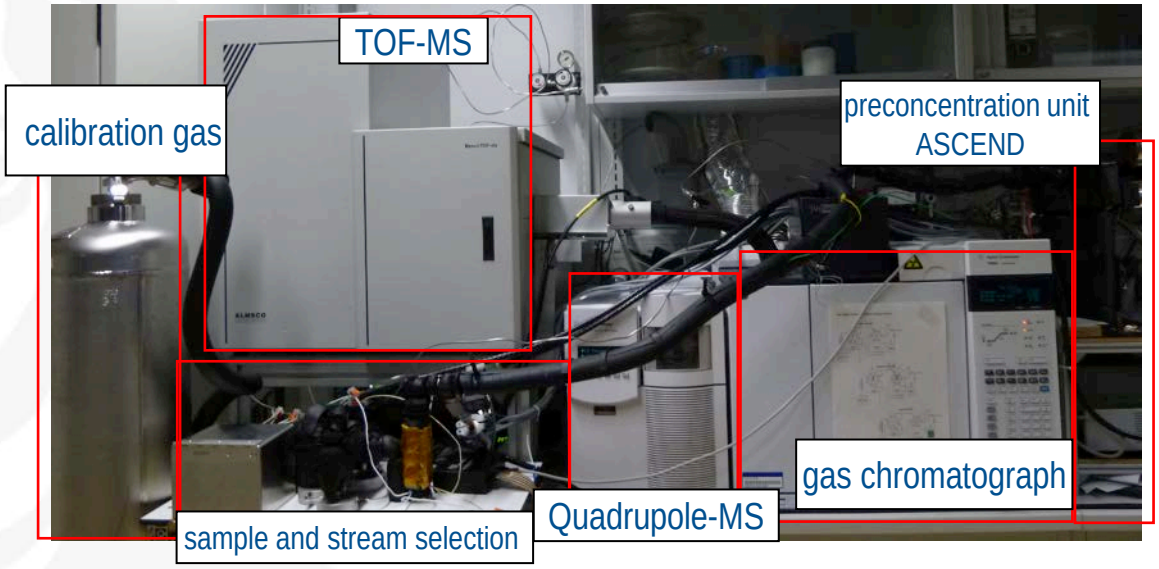
- Taunus Observatory is located at Kleiner Feldberg at 50.22°N, 8.44°W at 825m altitude.
- The site is influenced by emissions from the densely populated Rhein-Main region.
- Long-range transport is mainly from westerly directions, including marine background air from the North Sea.
- Regular measurements of halocarbons started October 2013.



courtesy Dominik Brunner

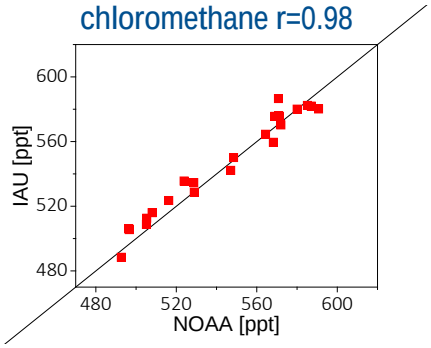
Current Status

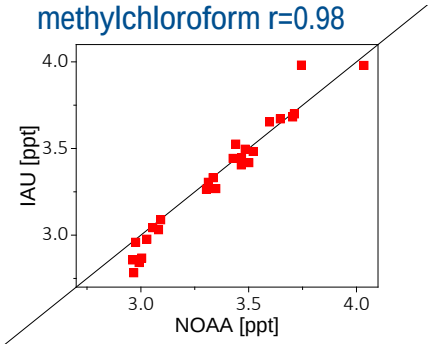
- Samples collected weekly in stainless steel canisters
- Analysis by GC-MS (Agilent 7980A) using a quadrupole MS (Agilent 5975C) and a TOF-MS (ALMSCO/BenchTOF) in parallel
- Sample drying with $Mg(ClO_4)_2$
- Cryo-trapping at -80°C (Stirling cooler), desorption at ≈ 200 °C
- Data quality assessment by taking double samples and having two analyses of each individual canisters

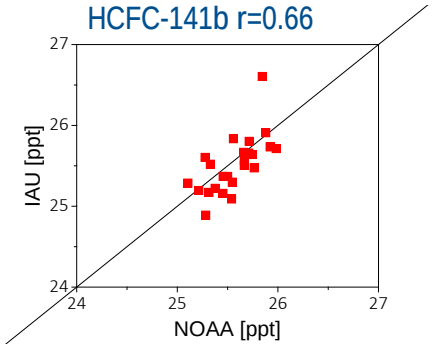


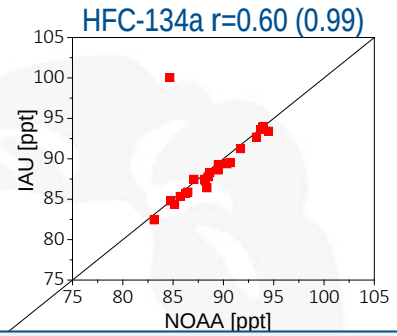
Hoker et al., Atmos. Meas. Tech. 2015

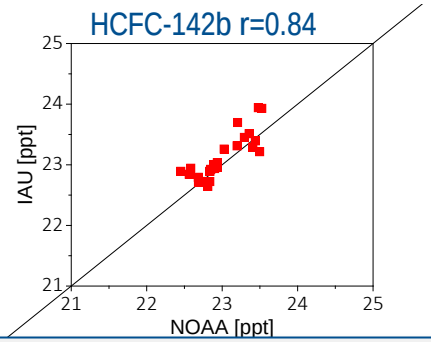
Sample Collection at Mace Head - Comparison with NOAA HATS data

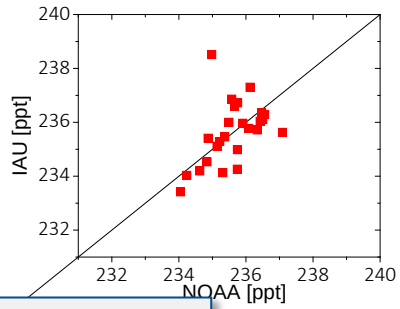






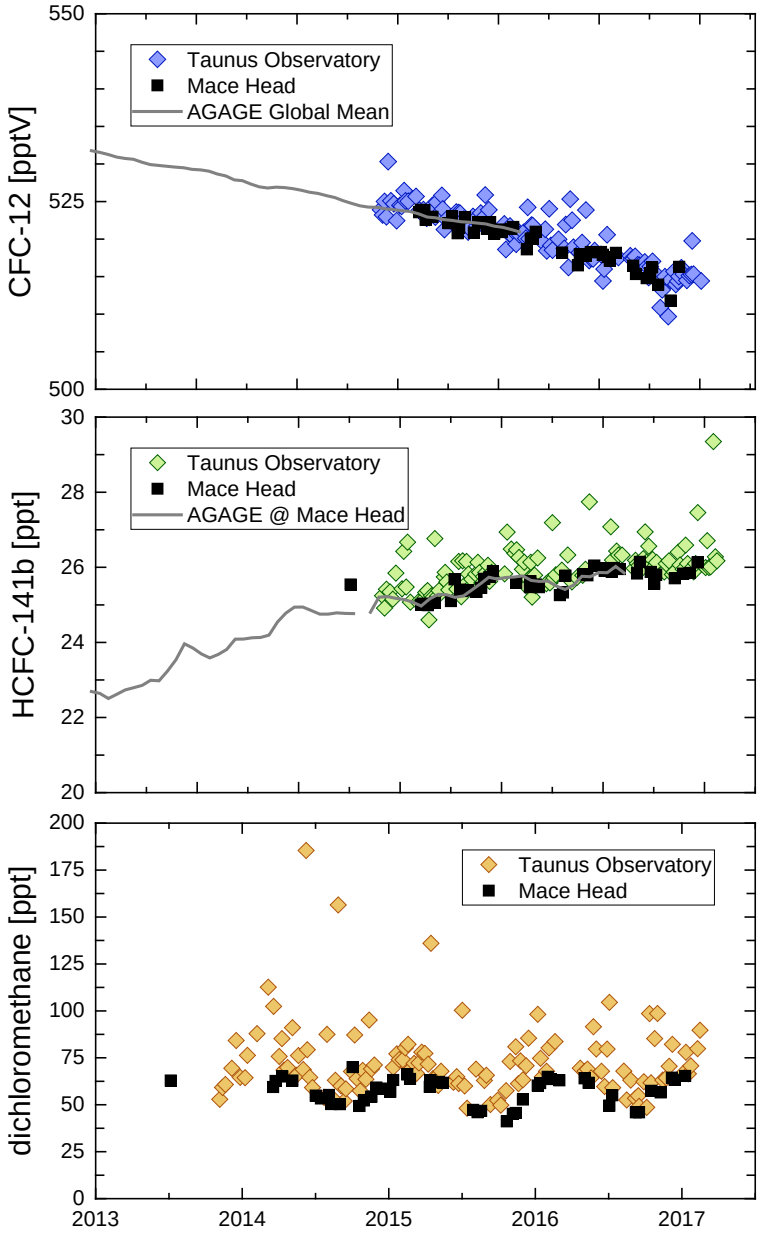


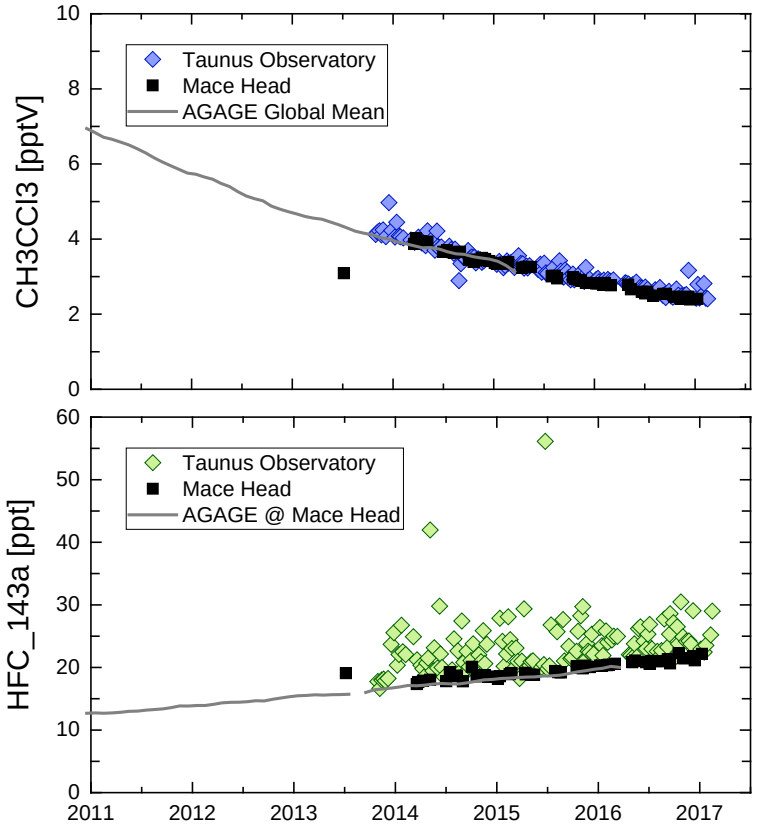




- sample collection at Mace Head twice per month (when wind is from clean air sector)
- comparison with NOAA data set @ Mace Head (sample collection for us and NOAA is under background conditions within less than half an hour)
- our calibration is on AGAGE scales, scale conversion necessary for most substances

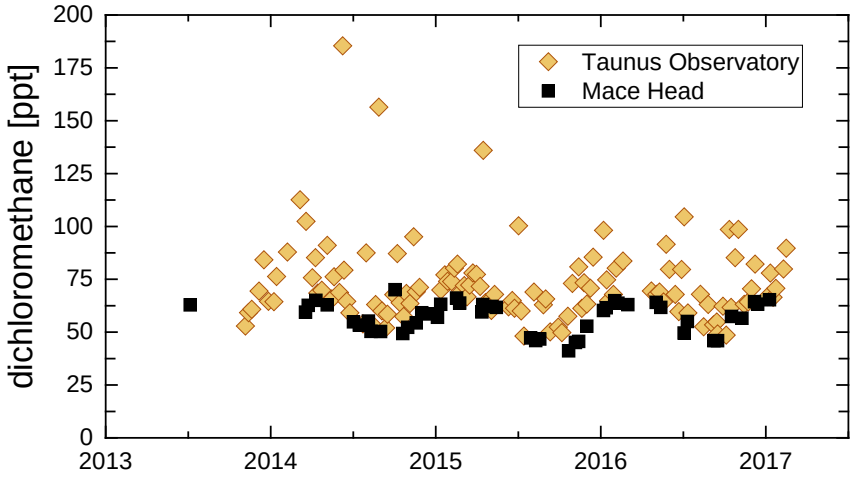
Time Series

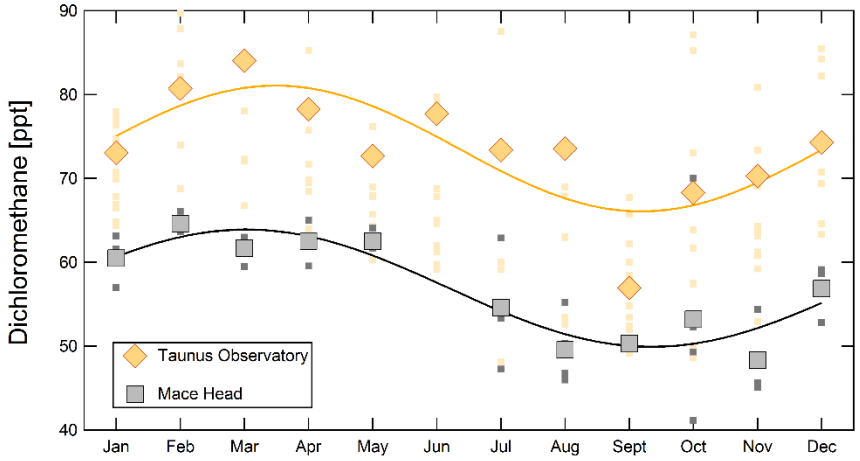


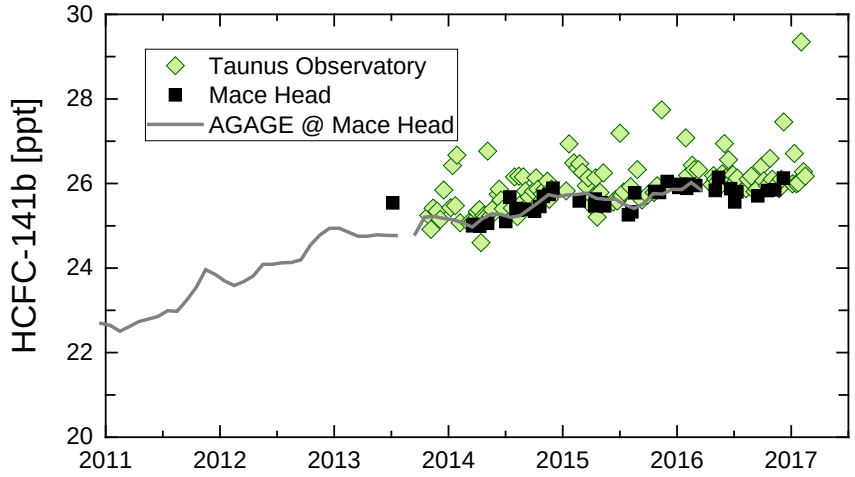


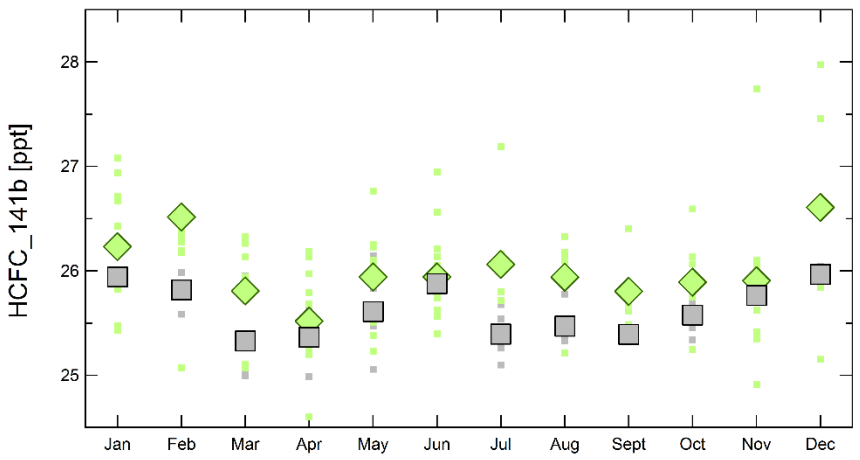
- mixing ratios at Mace Head nicely represent background
- good agreement with AGAGE data at Mace Head
- higher variability at Taunus Observatory with many polluted samples (includes data from all wind sectors, whereas Mace Head is from clean air sector only)

Seasonal Cycles



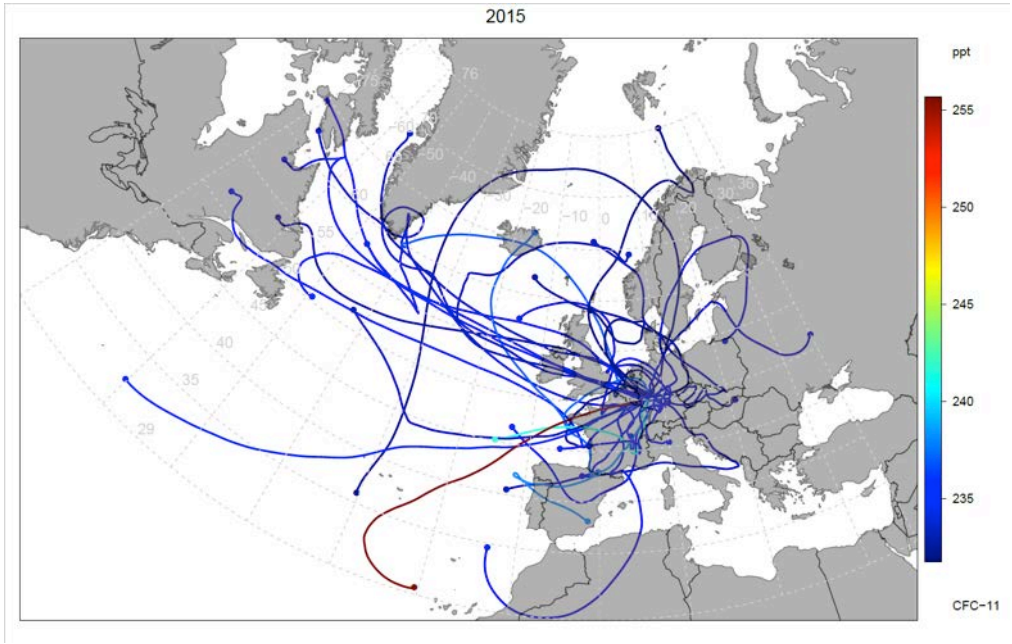




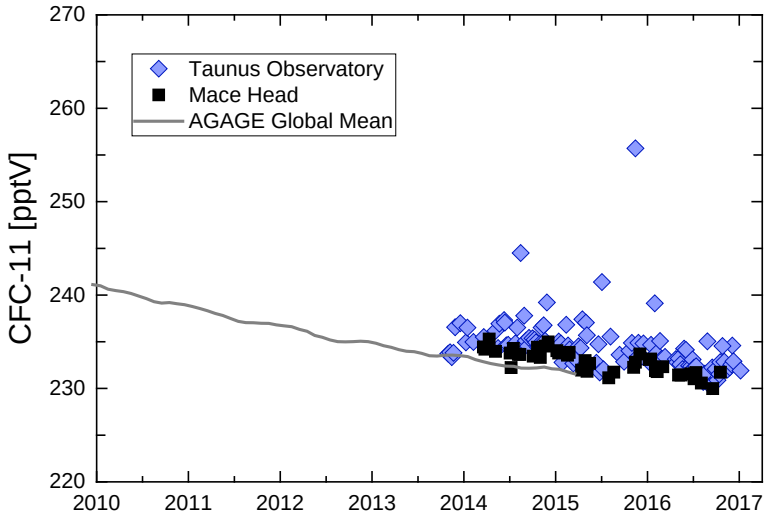


Trajectory Analysis

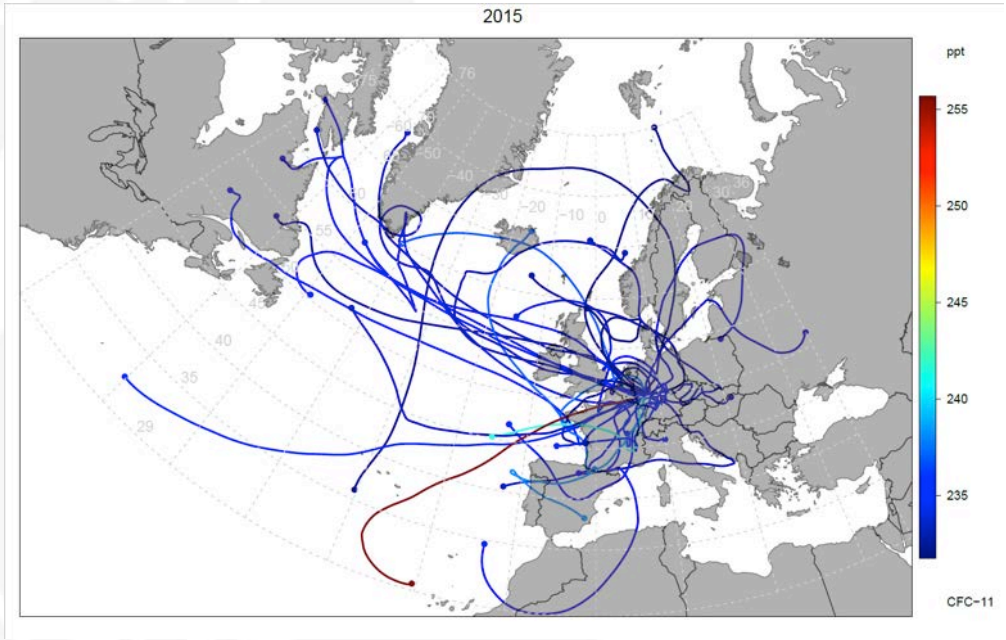
- Back trajectory calculations were performed for every single sample using
- HYSPLIT4
- 120 hours backward
- 1° x 1° GDAS1 dataset



Trajectory Analysis: CFC-11

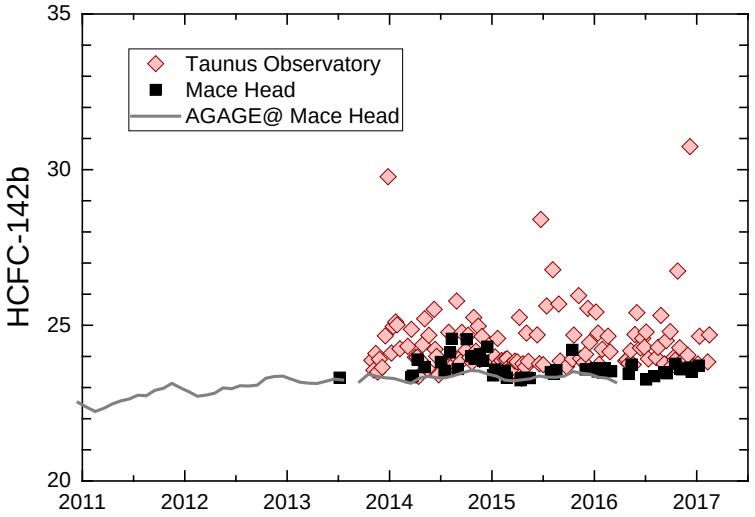


- use of CFC-11 is regulated
- atmospheric mixing ratios decrease
- variability at Taunus Observatory is low with few outliers

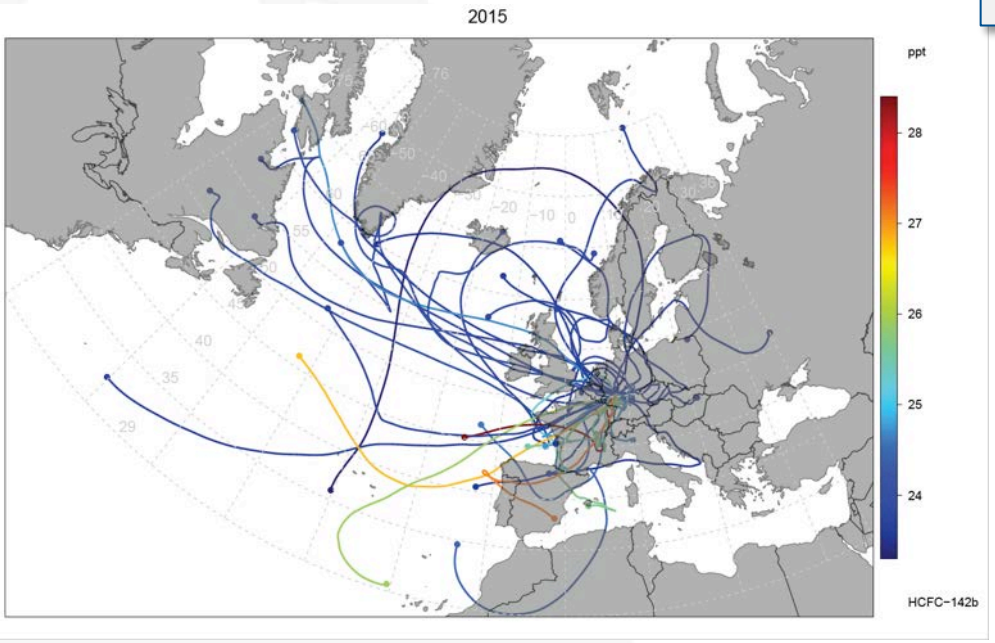


- HYSPLIT trajectories (120 hours backward) for samples collected in 2015
- color coded by CFC-11 mixing ratio
- elevated mixing ratios correlate with air mass origin from southwest

Trajectory Analysis HCFC-142b



- used as replacement for CFCs
- use is regulated
- mixing ratios have stabilized and are expected to decrease in the future
- over our observation period atmospheric mixing ratios have no significant trend
- variability at Taunus Observatory is high compared to Mace Head clean air samples

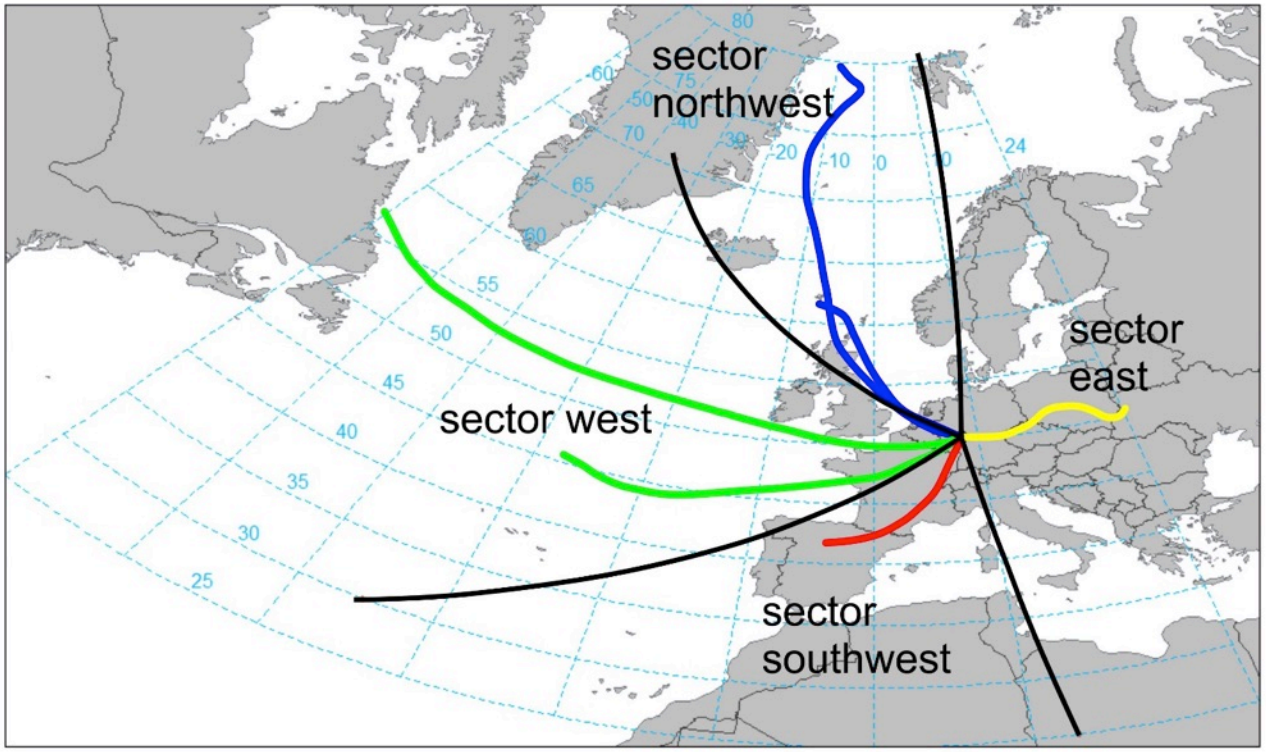


- HYSPLIT trajectories for samples collected in 2015
- color coded by HCFC-42b mixing ratio
- elevated mixing ratios correlate with air mass origin from southwest

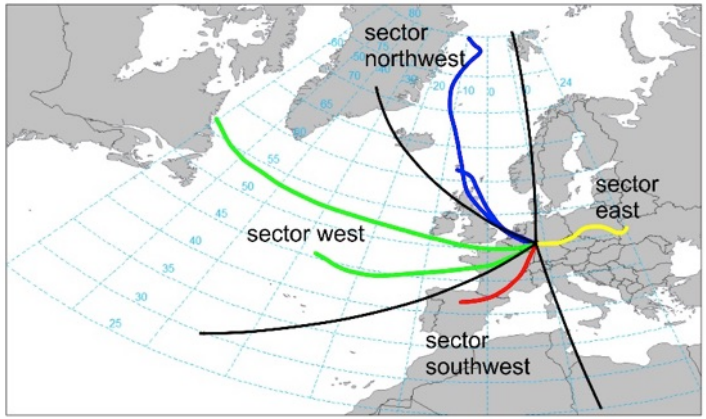
Trajectory Analysis

- HYSPLIT trajectories (120h backward) for each individual sample are grouped by the direction from with they approach Taunus Observatory (> 50% of time spent in respective sector)
- four main sectors were identified:

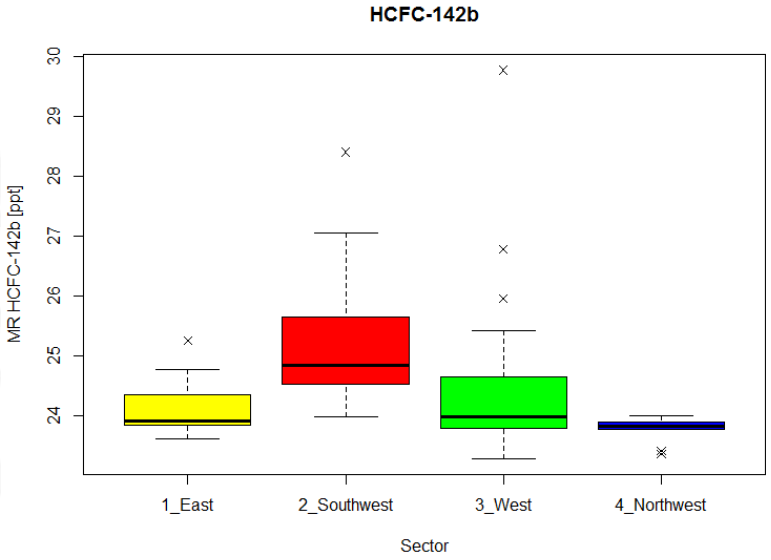
  northwest (slow and fast trajectories)
  west (slow and fast trajectories)
  southwest (slow trajectories)
  east (slow trajectories)

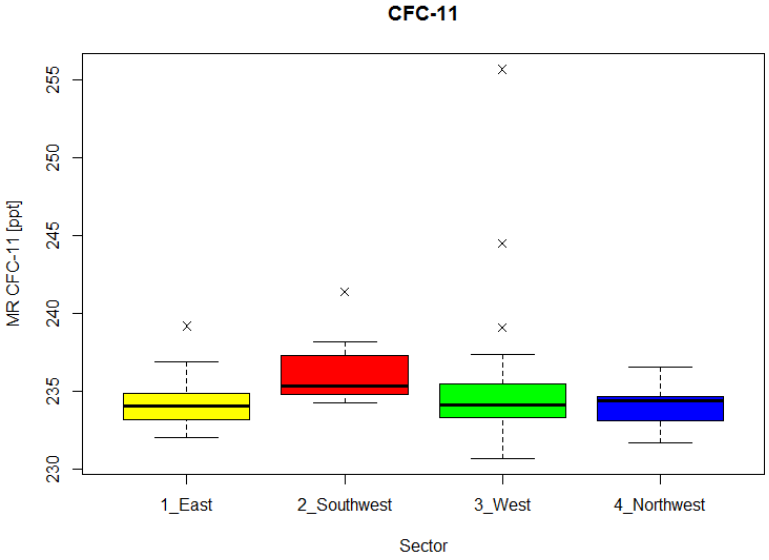


Trajectory Analysis

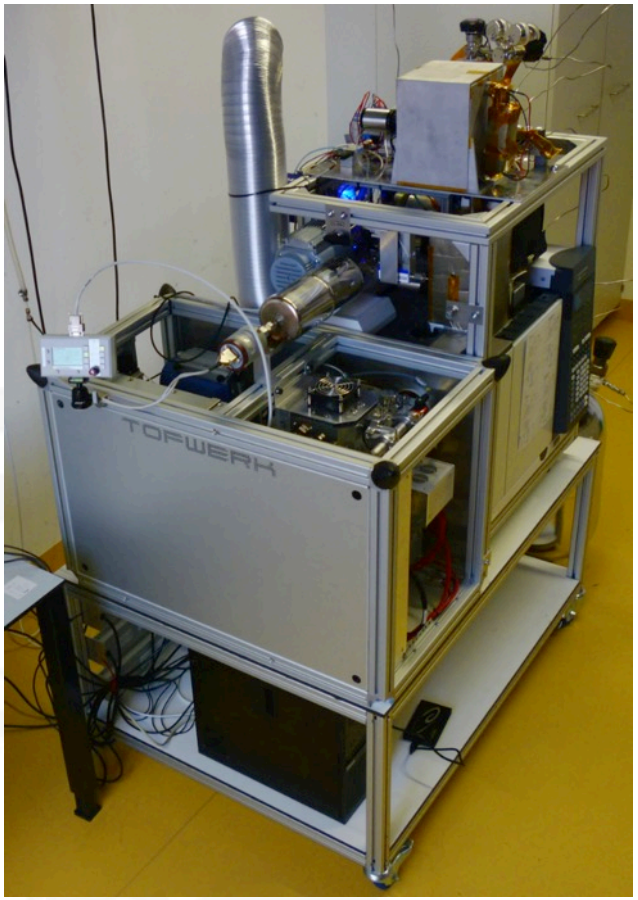


- For most substances investigated highest mixing ratios are measured in air masses arriving from the southwest sector.
- Background conditions are experienced when air mass transport towards the site is from the northwest.





Future Development: in-situ GC-TOF-MS



- In summer 2017, an in-situ GC-MS system will be installed.
- Measurements will be every 2h (following AGAGE protocol)
- The mass spectrometer to be deployed is a medium resolution time-of-flight mass spectrometer
- Large substance range: 90+ known species in the chromatogram
- High measurement precision:
  - 0.2-1.5% typical (multiple species)
  - 0.15% at best (CFC-12)
- Linear detector tested up to 5 ppb (25 ng) CFC-12 (~4 orders of magnitude)
- Open data format
- Complete mass scan will allow retrospective analysis (digital air archive)

Obersteiner et al., Atmos. Meas. Tech. 2016

Summary

- We started regular collection of air samples at Taunus Observatory in 2013
- Our measurement are linked to global networks through flask sampling at Mace Head (Ireland)
- Mace Head represents baseline for Taunus Observatory
- Trajectory analysis shows a distinct polluted / clean air sector
- Data from a medium-polluted site have the potential to better constrain European emission estimates
- Data from Taunus Observatory will be used for inversion modelling
- In summer 2017, an in-situ GC-TOF-MS system will be installed – rapid growth of the dataset
- Measurements will be every 2h (following AGAGE protocol) – now we have one data point per week
- Complete mass scan of the TOF-MS will allow retrospective analysis (digital air archive)

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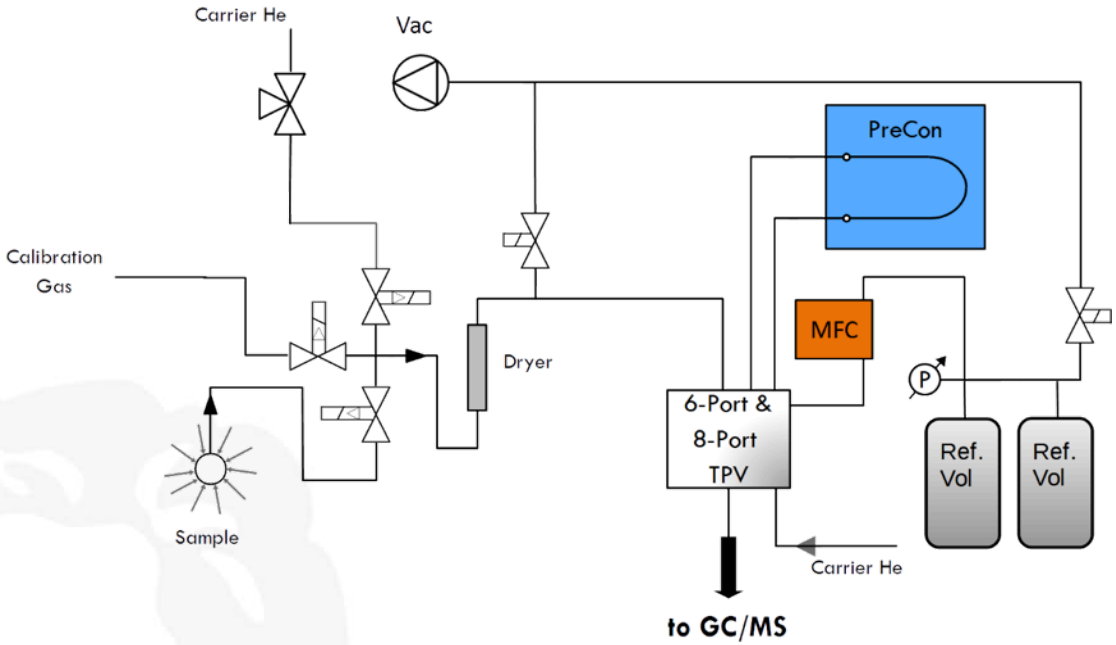
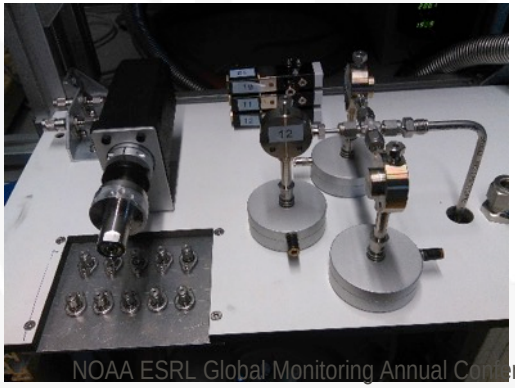
Thank you for your attention!

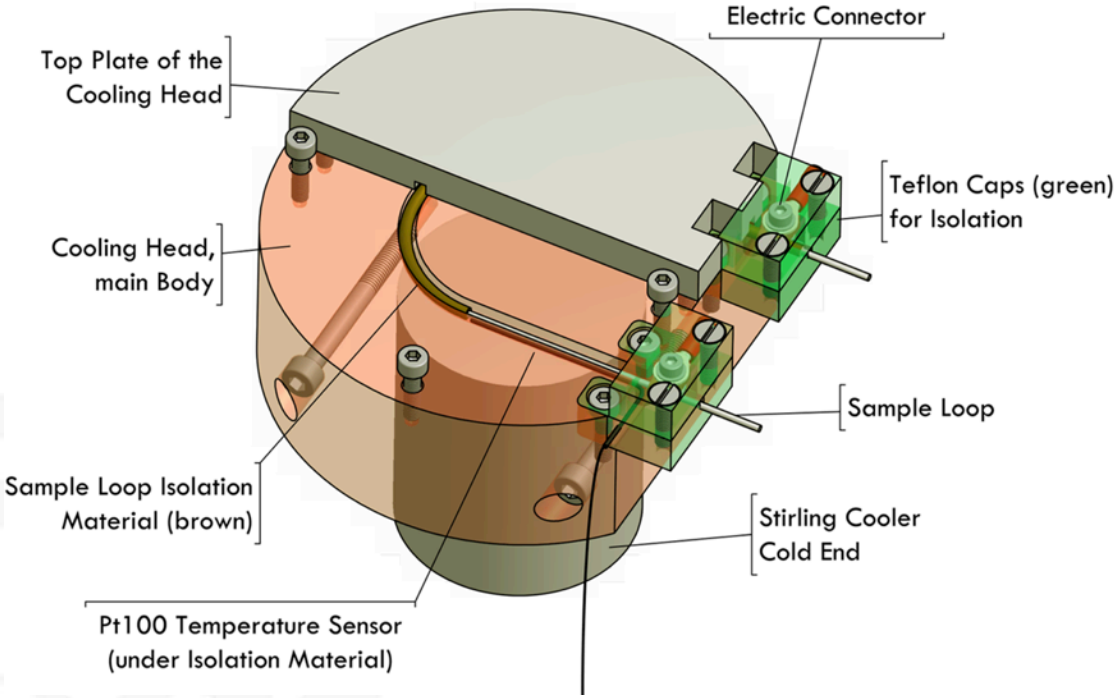
Instrumentation: Stream Selection Unit





- sample selection with multiposition Valve (Valco)
- stream selection (sample, blank, calibration gas) with pressure operated on/off valves (Valco)
- drying tube $Mg(ClO_4)_2$
- 2 x 2l reference volume for sample volume determination
- mass flow controller for sample flow regulation (Bronkhorst)

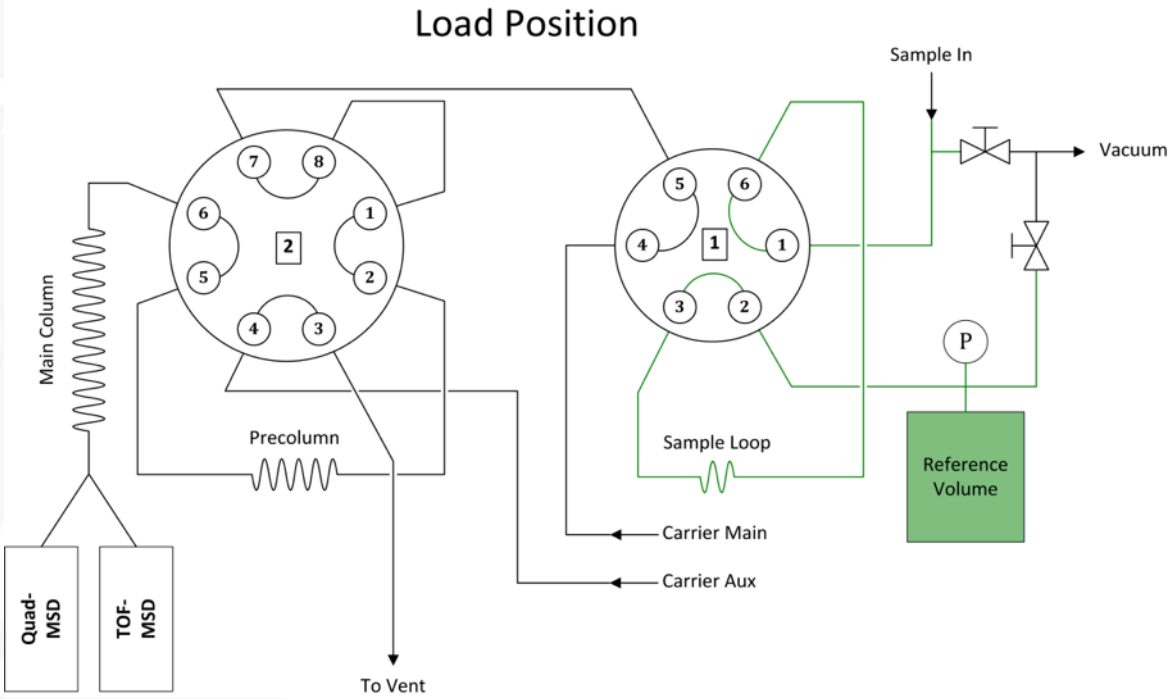
Instrumentation: Preconcentration Unit



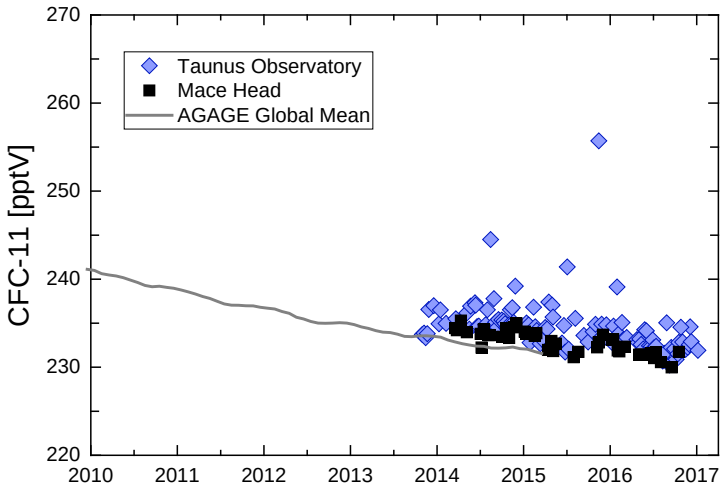
- sample enrichment is done on a sample loop filled with HayeSep D
- sample loop is embedded into a cooled aluminium block
- cooling works cryogen-free, based on a Stirling Cooler
- trapping at -80°C (flow 150 ml/min)
- desorption at ca. +200°C

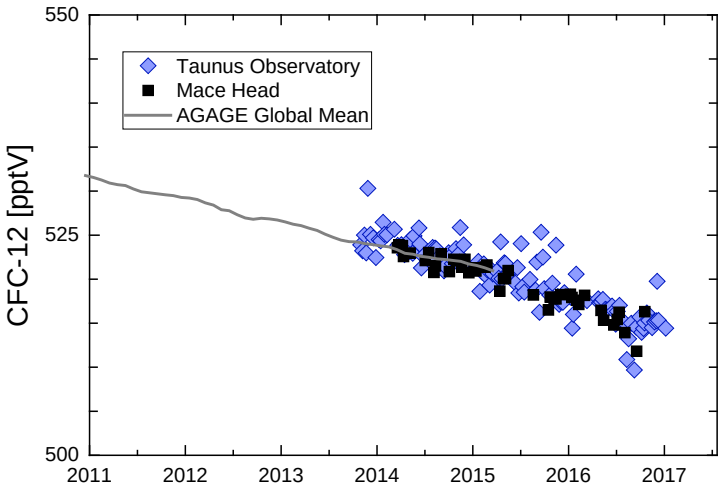
Instrumentation: Gas Chromatography

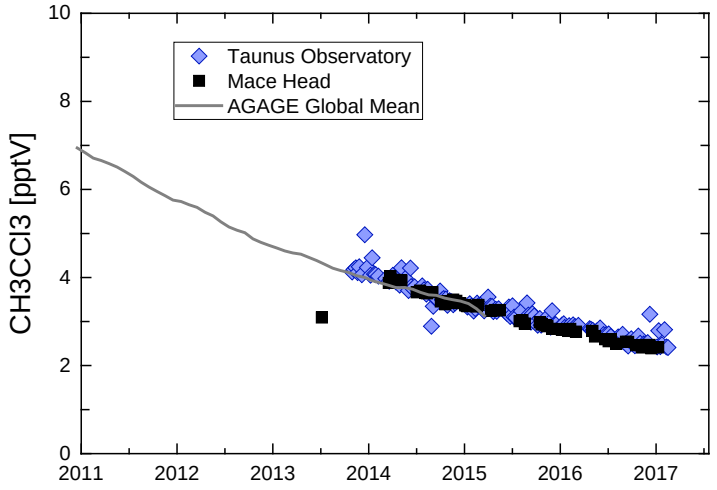
- column: 30m GasPro PLOT column (7.5m pre-column, 22.5m main column), inner diameter 0.32mm
- total duration: 17.95 min, backflush after 12.6 min
- oven temperature 50 – 200°C
- carrier gas: purified Helium 6.0



Time Series

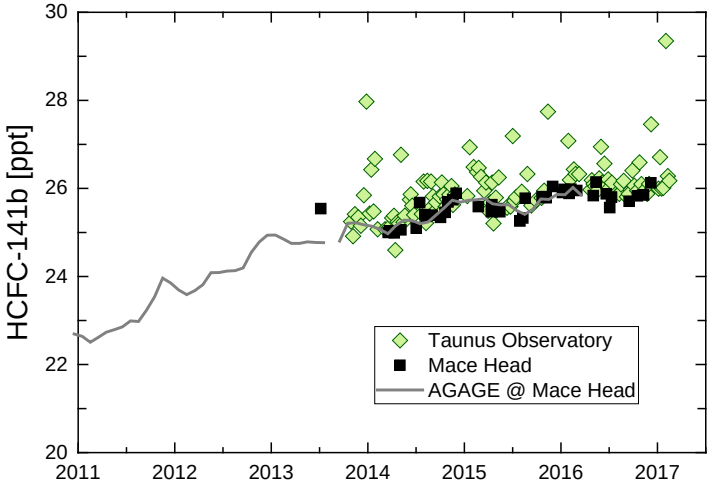


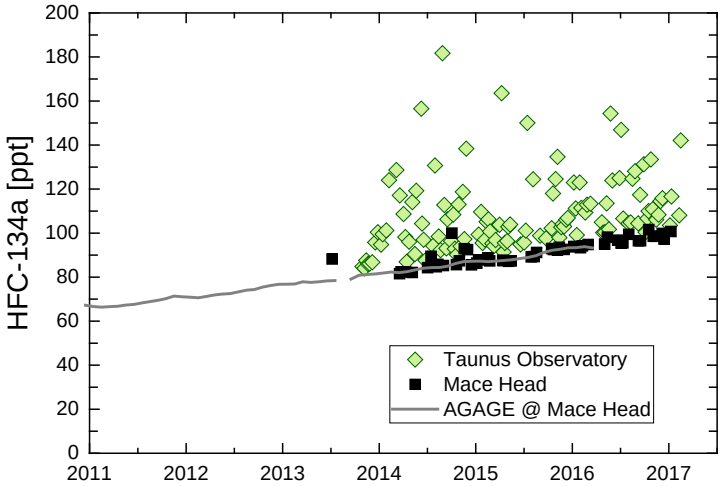


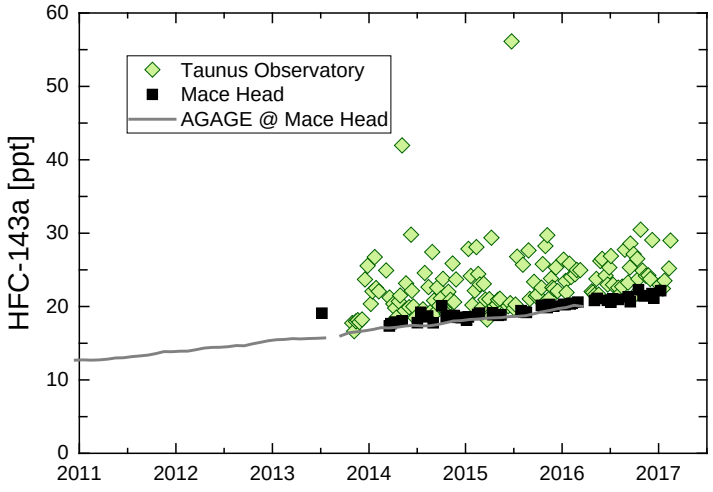


- mixing ratios of substances for which use is regulated decrease
- very similar mixing ratios at Mace Head and at Taunus Observatory
- low variability at Taunus Observatory with only few polluted samples (includes data from all wind sectors, whereas Mace Head is from clean air sector only)

Time Series

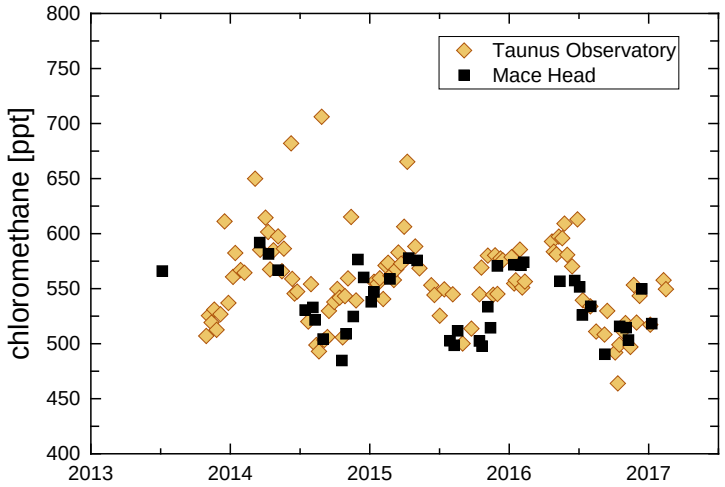


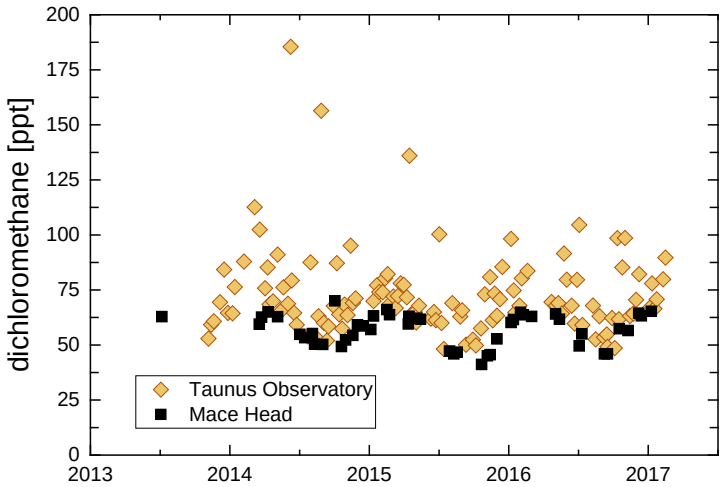


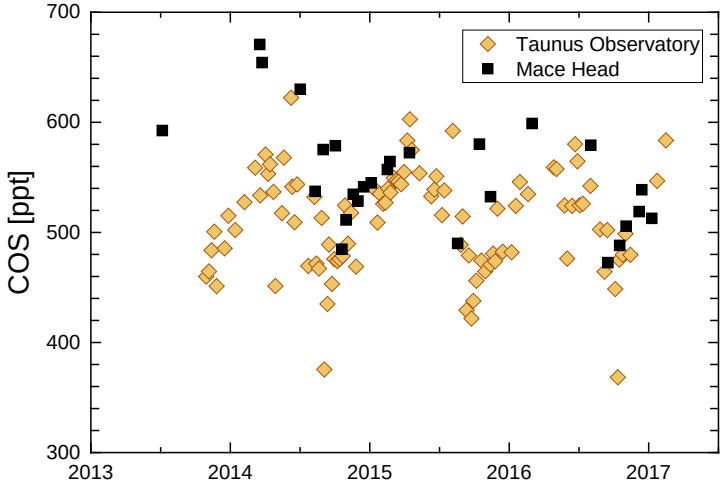


- mixing ratios of substances still widely uses increase at Taunus Observatory
- mixing ratios at Mace Head represent background
- good agreement with AGAGE data at Mace Head
- high variability at Taunus Observatory with many polluted samples (includes data from all wind sectors, whereas Mace Head is from clean air sector only)

Time Series







- similar seasonality of chloromethane and dichloromethane at Mace Head and Taunus Observatory
- higher variability at Taunus Observatory
- amplitude of seasonal cycle somewhat larger at Taunus Observatory
- lower mixing ratios of COS at Taunus Observatory