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THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Automated monitoring of organic ozone depleting substances and greenhouse gases

Markes International's ODS and GHG portfolio

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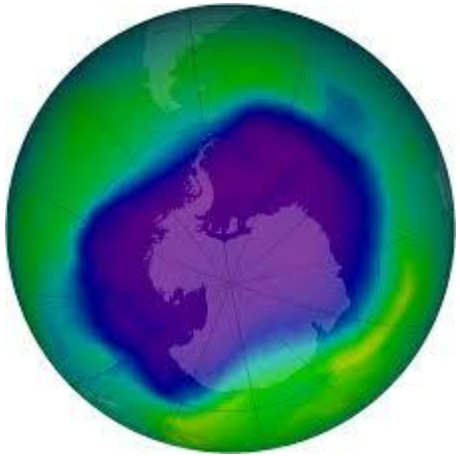
Agenda

- Background to ODS and GHGs
  - Global activities
  - Future monitoring networks
- Considerations for monitoring
- Instrument overviews
- Data comparison

MONTREAL PROTOCOL



ODS = Ozone depleting substance
A compound that contributes to stratospheric ozone depletion.
Categorized by their ozone depletion potential (ODP)

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GHG = Greenhouse gas
Gases that trap heat in the atmosphere.
Categorized by their global warming potential (GWP)

Species have 12 – 14000 x high GWP than CO_2

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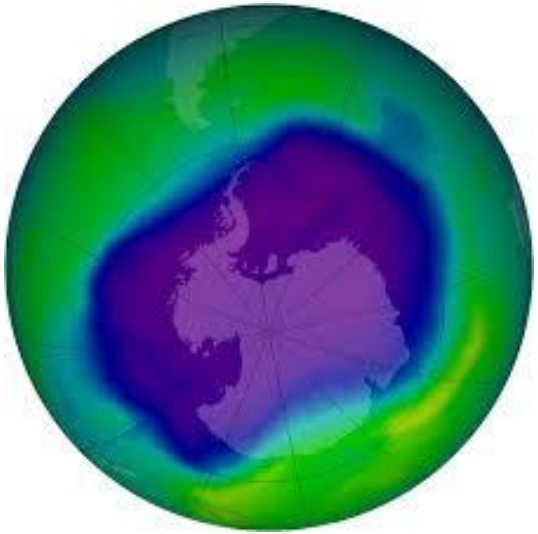
“Top-down” atmospheric measurements ensure emissions are captured.
Vital for countries to really reach net zero.



Where is monitoring needed? What range of concentration levels are these compounds typically present at?

Background stations

>500 ppt to

<0.01 ppt

Urban areas

>1 ppb to

<70 ppt

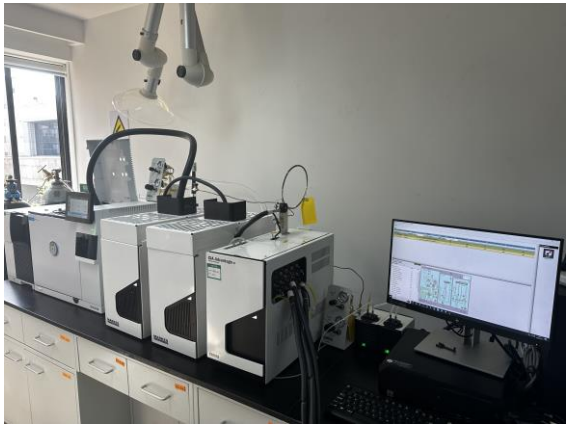
Industrial areas

>1 ppm to

<1 ppb

Considerations for monitoring

How will the sample be collected?



Considerations for monitoring

How will the sample be collected?

Monitoring station with online sampling

- High frequency data
- Remote / urban / industrial locations possible

Requires:

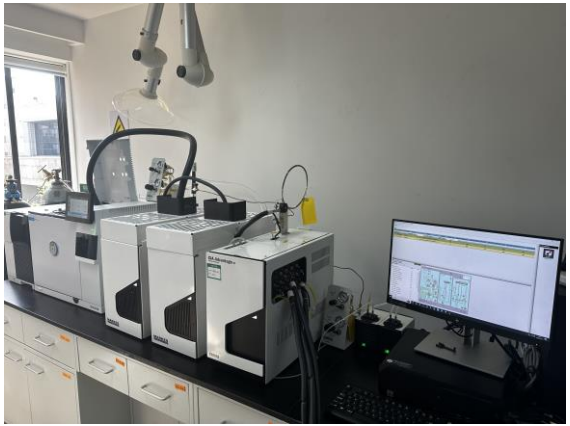
- Infrastructure
  - Carrier gases, electricity generators, data transmission
- Specialist software
- Reliable analytical systems

Considerations for monitoring

How will the sample be collected?

Flask / canister sampling with laboratory analysis

- Low frequency data
- Background / urban / industrial locations possible with a single system



Requires:

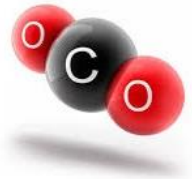
- Infrastructure
  - Carrier gases
- Software
- Reliable and flexible analytical systems

Considerations for the analysis

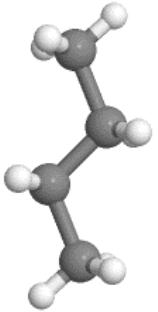
Volatility, interferents and concentration range.

Ultra volatile target species.

Water, CO_2 and hydrocarbons all interfere with the analysis of ODS & GHGs



- Water must be removed from the sample
- CO_2 requires removal and management chromatographically
- Hydrocarbon co-elutions need to be understood by the chromatographer in case they impact quantitation



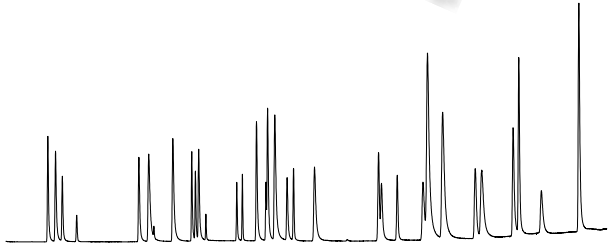
High concentrations during pollution events.

How is monitoring be carried out?

TD-GC-MS

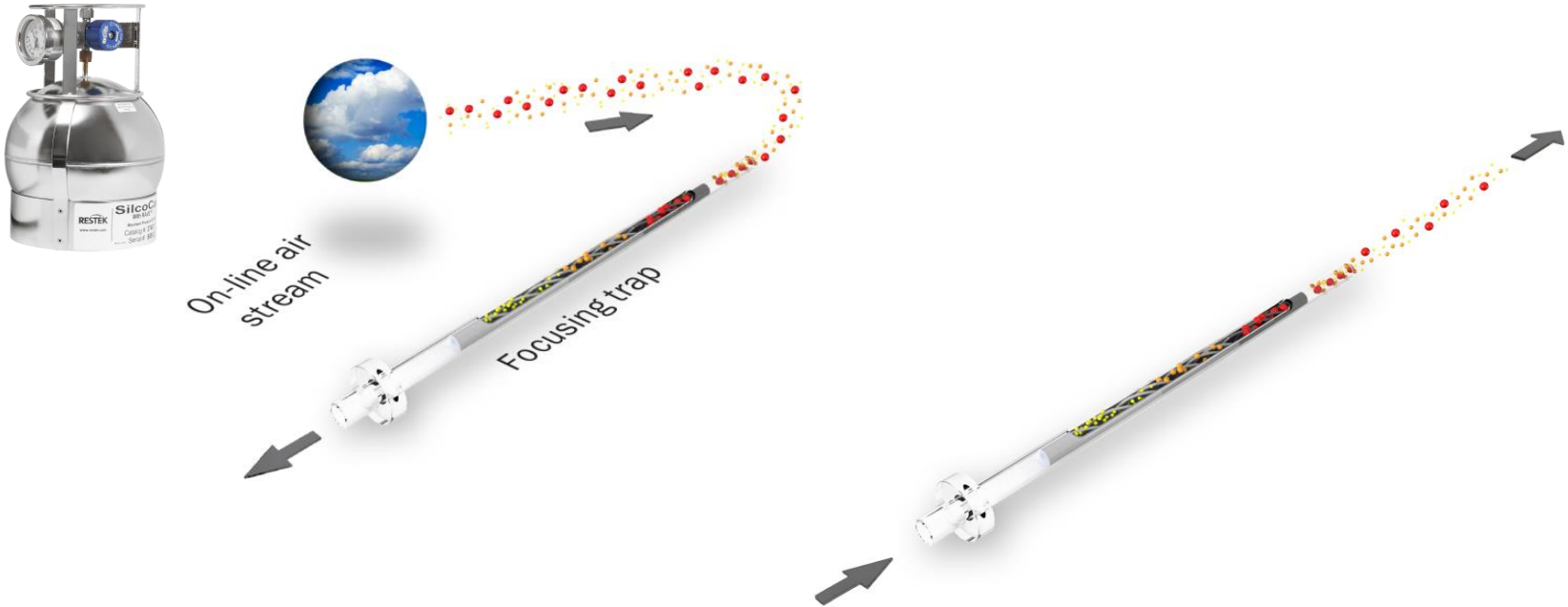
- Preconcentration is essential for this application
- Mass spectrometry is needed for these compounds of interest

- Sampling must be canister or online for the full list of Montreal species.
  - Sorbent tubes can be used for a reduced list.



How can we monitor?

Pre-concentration and GC-MS



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NuVo 200

An application specific instrument.

Urban area and industrial monitoring of ODS & GHGs

How it works

NuVo 200

NuVo 200 is comprised of three parts:

- Canister autosampler, CIA-Advantage-xr
- NuVo 200 HT
- NuVo 200 LT

The two focusing traps of the NuVo work together to trap ultra-volatile species and manage CO_2

- Trapping temperatures down to -100 °C
- Cryogen-free

NuVo 200 LT
Focusing trap

NuVo 200 HT
Focusing trap

CIA *Advantage*-xr
Canister autosampler

How it works

NuVo 200

Possible to run with multiple carrier gas types (Multi-gas)

- Helium
- Hydrogen
- Nitrogen

Water removal provided by Nafion dryer

- *Not compatible with Kori-xr or other -xr series instruments*

Samples from pressurized and unpressurized sources

- Online and canister
- Laboratory and field station

NuVo 200 LT
Focusing trap

NuVo 200 HT
Focusing trap

CIA *Advantage*-xr
Canister autosampler

Why did we develop the NuVo 200?

Two targets and one interferent

NF_3 CF_4 CO_2

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NF_3 **CF_4** **CO_2**

- Boiling point: -129 °C
- Impossible to trap on standard online / canister -xr systems

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- Maximum trapping volume 25 mL on Markes –xr systems

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CO_2

- Boiling point: -78 °C
- Significant interferent when trapping below -30 °C

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CF_4

- Maximum trapping volume 25 mL on Markes –xr systems

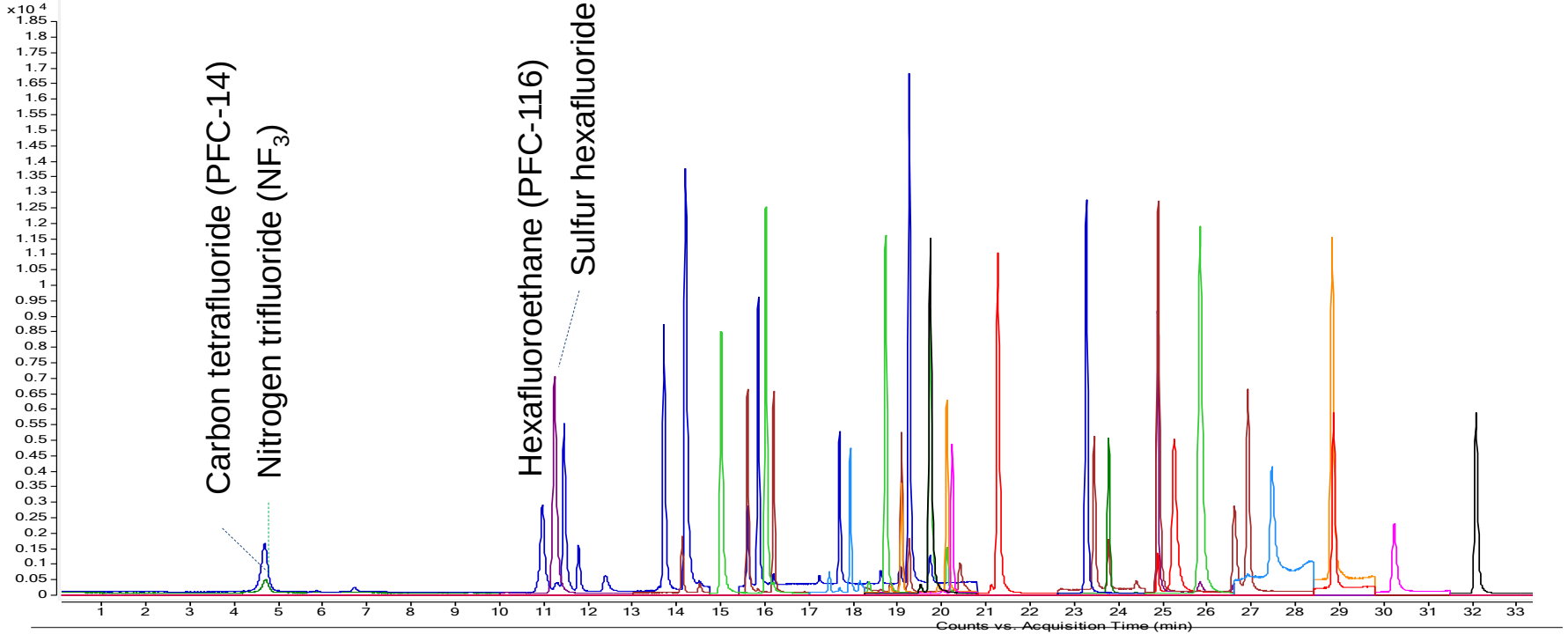
CO_2

- …nt: -78
- Significant interferent when trapping below -30 °C

The NuVo balances retention of the two priority compounds without the analysis being compromised through the presence of CO_2

Confident reporting

Managing interferents. No interference from CO_2 or water at atmospheric levels



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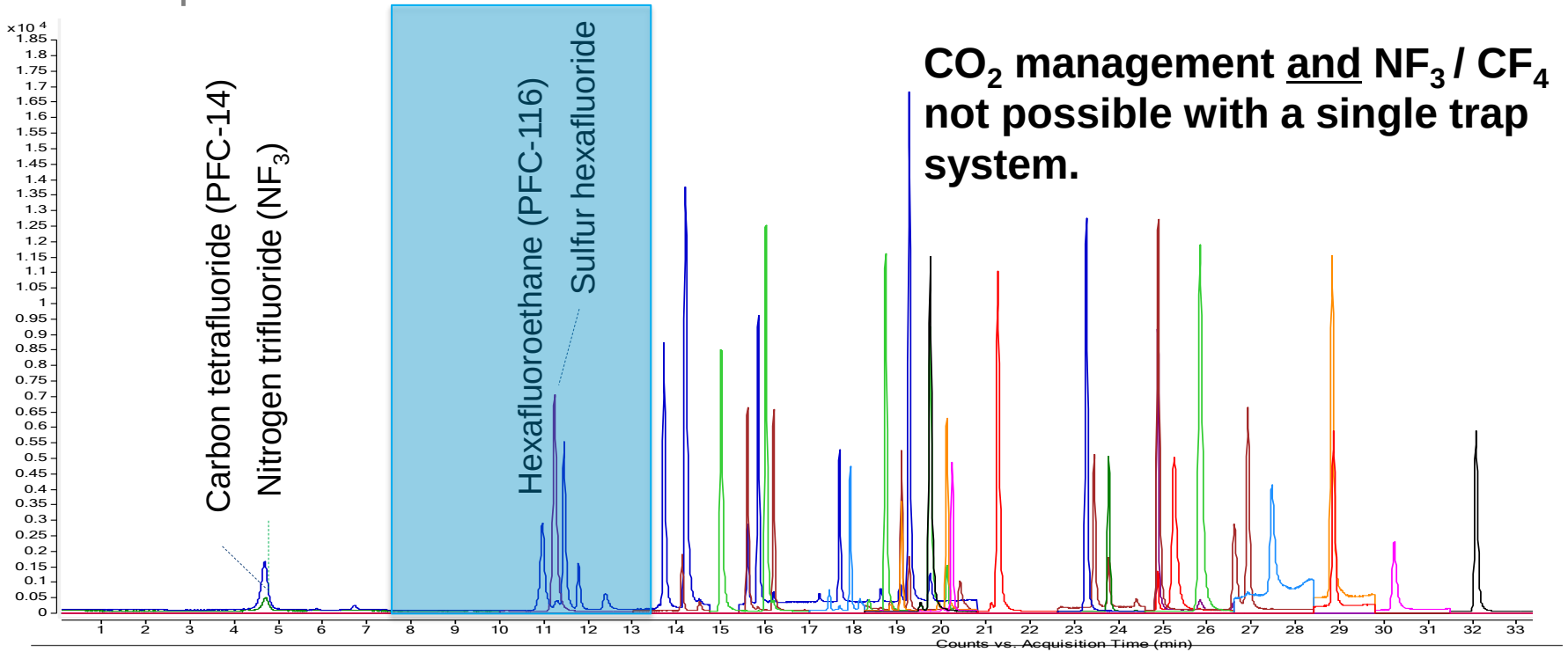
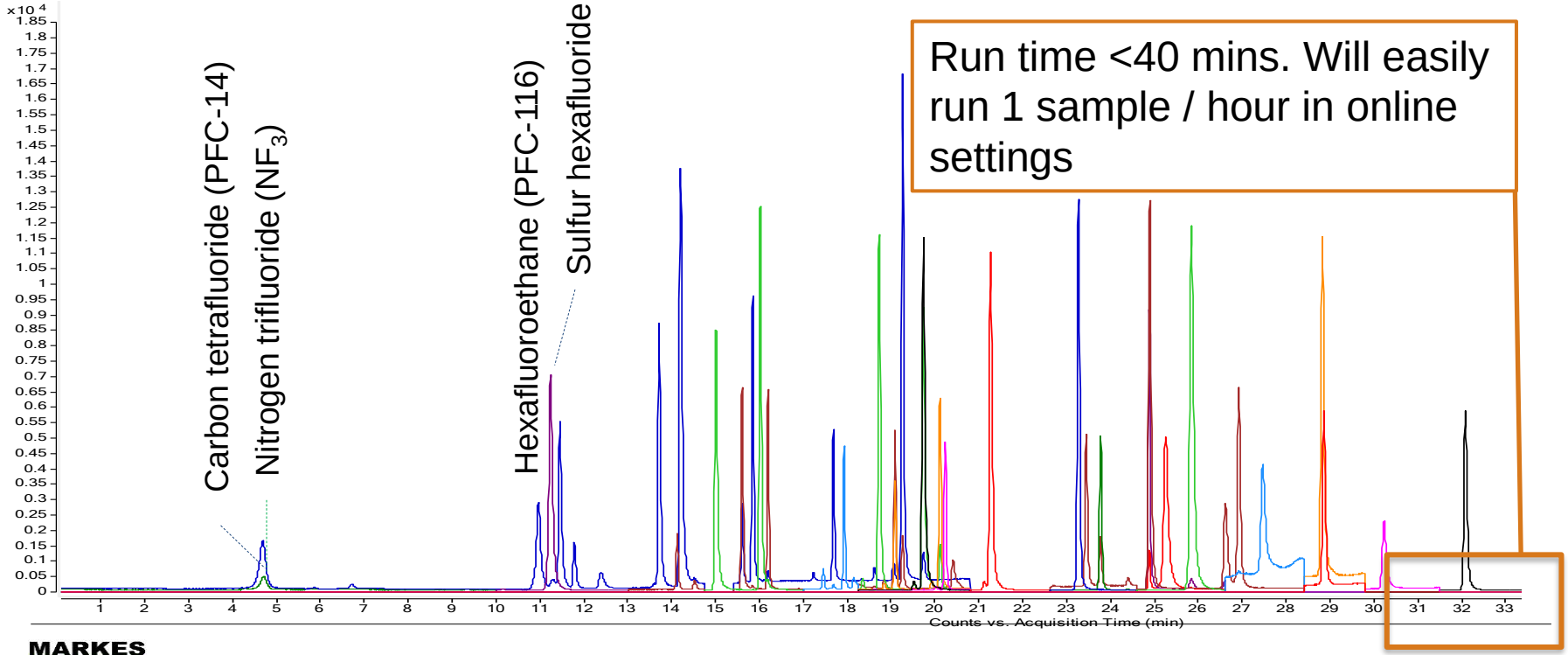


CO_2 management <u>and</u> NF_3 / CF_4 not possible with a single trap system.

Confident reporting

Stable and high throughput. Excellent for online measurements



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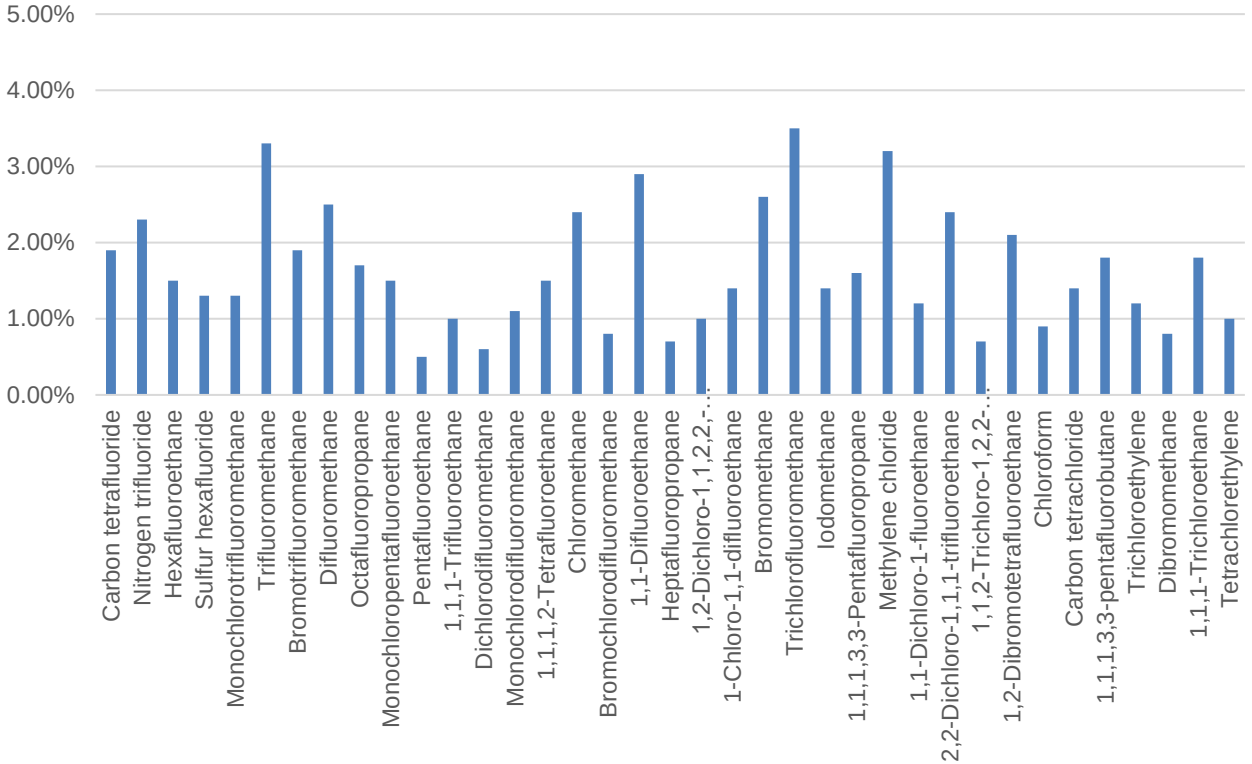
Reliable results

Repeatability n = 7; 600 mL, 10 ppt standard, 100% RH, 0.04% CO_2

All compounds showed good repeatability.

Below 5% criteria.

n = 25 replicates average RT stability was ±0.01 minutes



Confident reporting

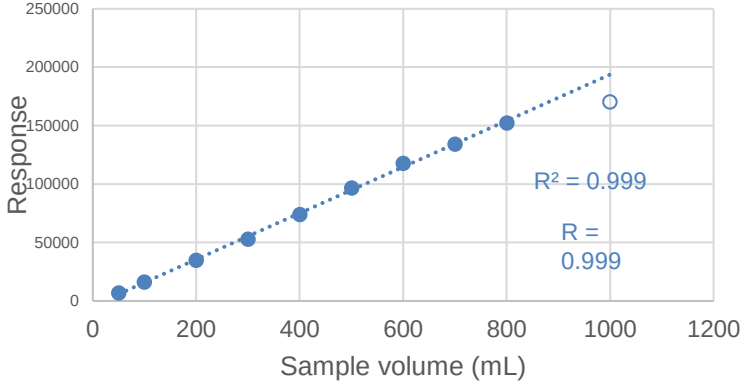
Breakthrough, linear range and carryover

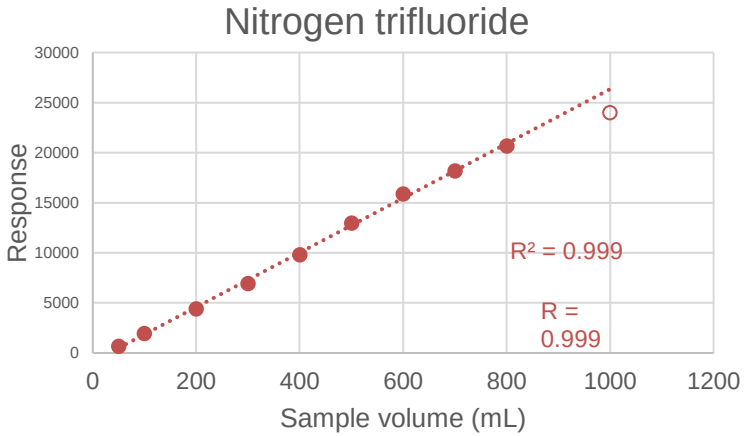
Breakthrough of over 800mL for key compounds CF_4 and NF_3

Linearity

- Two canister calibration – 18 levels
  - 3 ppt – 375 ppt
- All compounds:
  - R^2 above 0.99

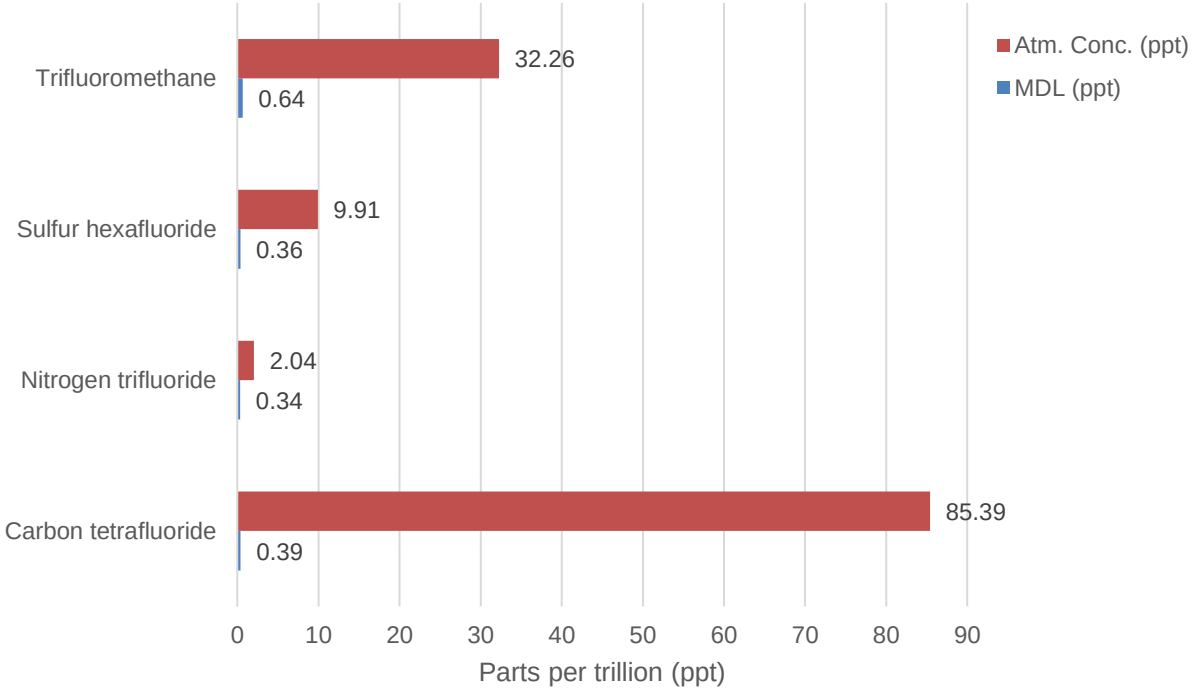
Carryover less than 1% for majority of species





Confident reporting

Method detection limit: 10 ppt, 100% RH, atmospheric CO_2 level



- Method detection limits for these key species are below the background atmospheric concentrations
- Important for seeing pollution events

Urban and industrial monitoring

NuVo 200

- Confident reporting
  - Manage interferents (H_2O and CO_2) as standard
  - Highly sensitive
- Reliable
  - Excellent recovery from high concentration samples
  - Internal standard addition
- Flexible
  - Suitable for laboratory or field measurements.
  - Compatible with all major GCMS.

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Medusa

Background monitoring

Medusa overview

Medusa Preconcentration System

Trapping:

- Compounds trapped at -165 °C (without cryogen)
- Dual trap design
- Linear response over wide range of sample volumes
- 2 L sample typical (sampling and analysis = 2 hours)

Managing interferents:

- Nafion
- Temperature variation to minimise bulk gases
- CO_2 managed through chromatography and dual trapping

Medusa overview

Medusa Preconcentration System

Operated by GCWerks SW only

Calibration

- Ambient air samples alternately sampled against a standard to account for MSD response drift.
- Air → standard → Air → standard
  - Sandwich calibration.

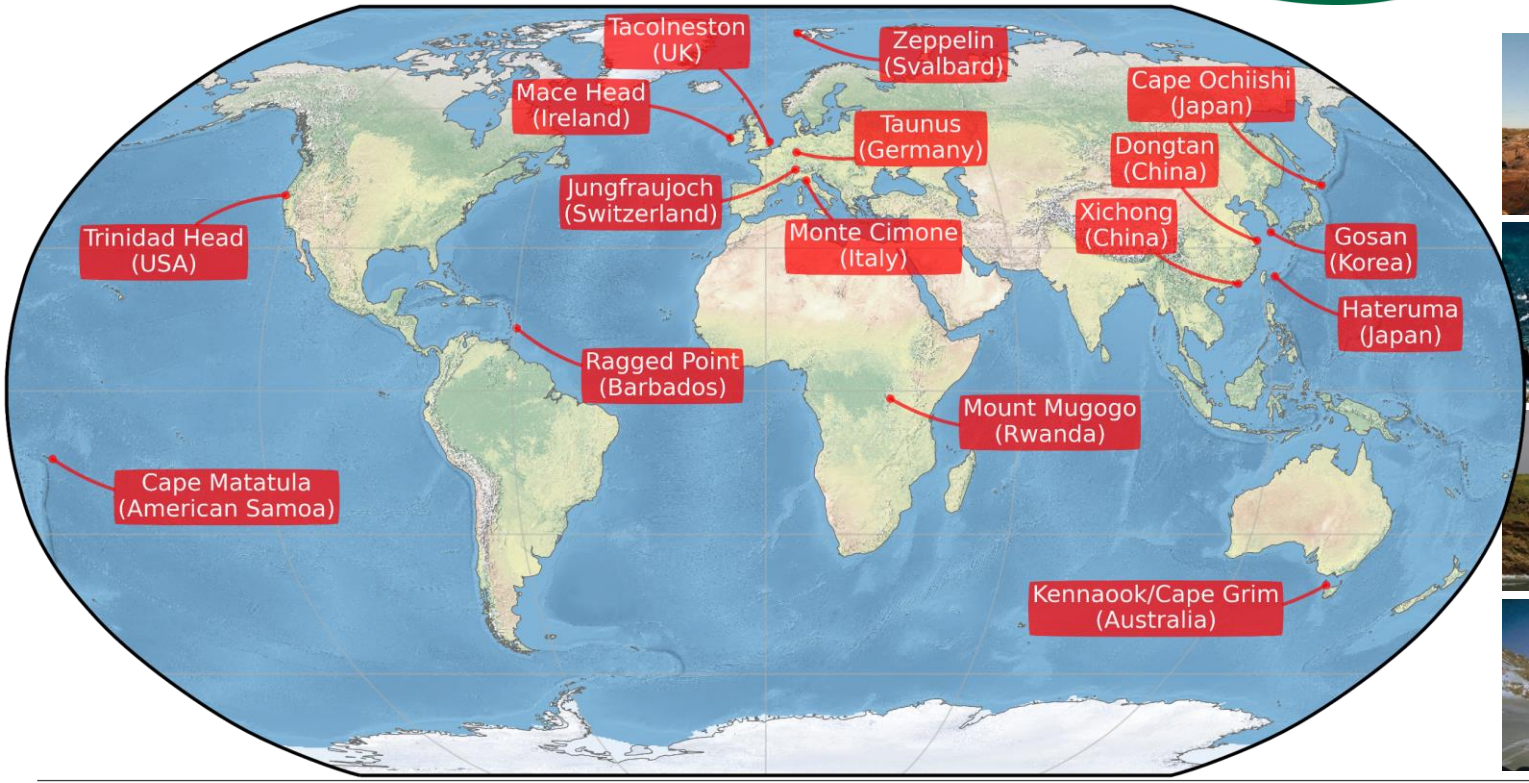
Proven performance

Markes International Medusa

- The Medusa is the only instrument routinely used to measure NF_3 in ambient air samples at background levels (2 – 4 ppt).
- Multiple instruments in use globally by the AGAGE network and NOAA
- Markes have been producing Medusa systems since 2020 in collaboration with the AGAGE network.

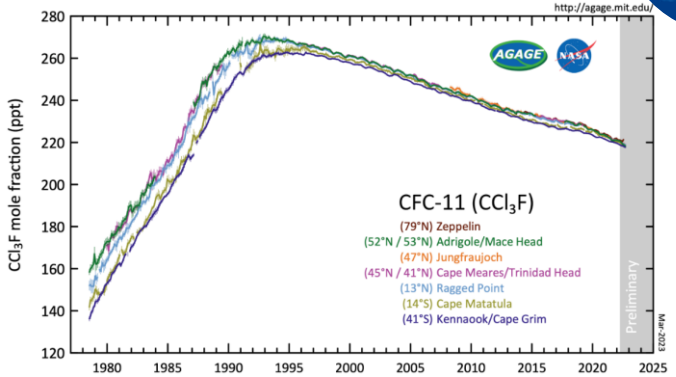
Top-down measurements

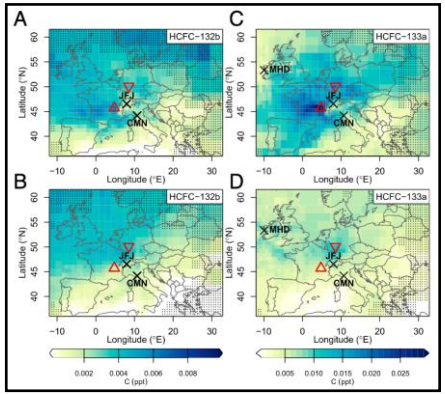
Medusa Preconcentration System

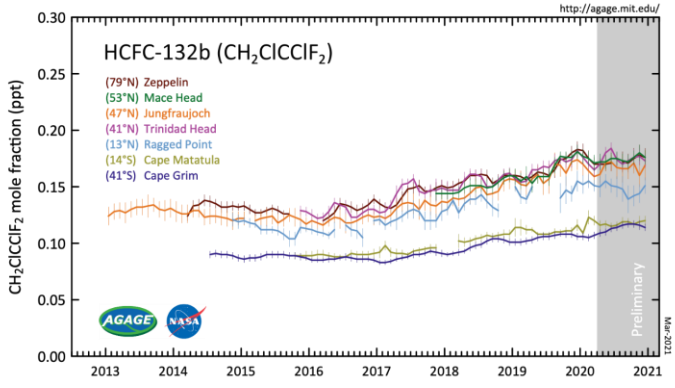


The importance of background site measurements

- Data spanning over 45 years collected for many species by various networks
- Medusa measurements since 2008
- Regional variations can be modelled
- New species added







Vollmer et al., 2021. *Proc Natl Acad Sci USA*, doi:10.1073/pnas.2010914118

Ultimate system for background measurements

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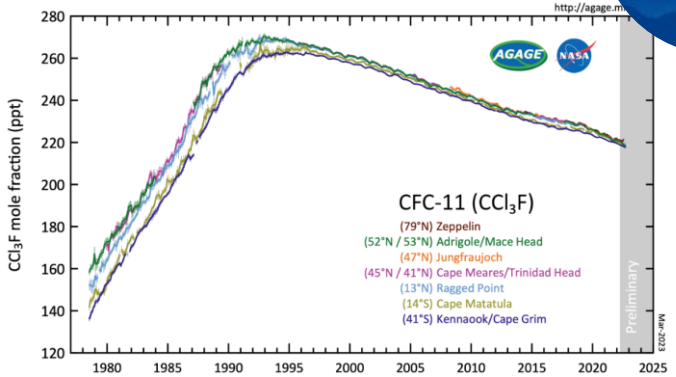

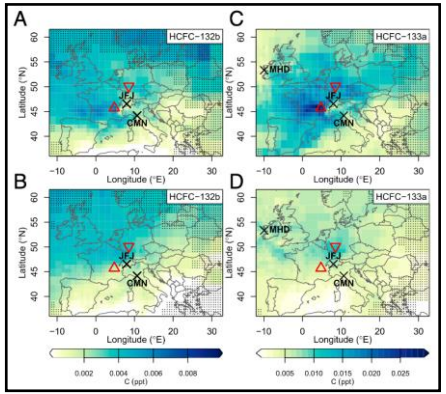

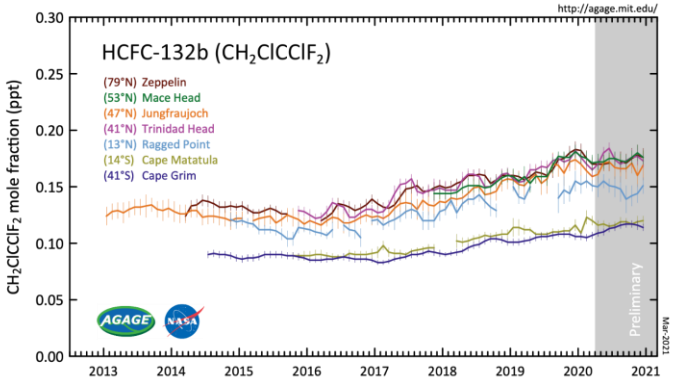

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Comprehensive sample introduction and preconcentration for GC–MS

Designed for scientists monitoring ODS and halocarbon GHG in air, Markes' portfolio of pre-concentration instruments for GC–MS monitor key species in any environment, from ppm to sub-ppt method detection limits.

Flexible:	Adapting to different monitoring needs
Reliable:	Manage interferents
Convenient:	Designed for laboratories and field stations

Thank you for your attention

Any questions?

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NuVo 200

Medusa

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