Atmospheric Monitoring – Student Presentation

Presenters: Cedric Wüthrich, Richard Zell

Corrections after the presentation written in red
The Family of Chlorofluorocarbons

- CFC-11 (FClCl)
- CFC-12 (FClF)
- CFC-13 (FCClF)
- CFC-114 (FClCl)
- CFC-113 (ClFCCl)
- CFC-115 (ClClF)

1st digit #C-1
2nd digit #H+1
3rd digit #F
Uses of Chlorofluorocarbons

Liquids for fridges

Tuning the ratio of chlorine and fluorine enables control of boiling point

Blowing agent (e.g. polyurethane)

\[
\left[ R_1\text{O} - \text{C} - \text{N} - R_2\text{N} - \text{C} - \text{O} \right]_n
\]

Propellant for spray-cans

Mechanism of Ozone Depletion

\[
\text{Cl}_2\text{F}_2 + h\nu \rightarrow \text{Cl}_2\text{F} + \text{Cl}^* \\
\text{Cl}^* + \text{O}_3 \rightarrow \text{ClO}^* + \text{O}_2 \\
\text{ClO}^* + \text{O}^* \rightarrow \text{Cl}^* + \text{O}_2 \\
\text{O}_3 + \text{O}^* \rightarrow 2\text{O}_2 \\
\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^* 
\]

Concentration of CFC-11 over the years

The Montreal Protocol on Substances that Deplete the Ozone Layer

Signed in 1987 by all UN-member states

Phasing out of CFC’s to protect the ozone layer

CFC regulation in Article 2A

Distinction between developed and non-developed countries

Kigali amendment on replacement chemicals

<table>
<thead>
<tr>
<th>Non-Article 5(1) Parties</th>
<th>Article 5(1) Parties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base level:</strong></td>
<td><strong>Base level:</strong></td>
</tr>
<tr>
<td><strong>January 1, 1992</strong></td>
<td><strong>July 1, 1999</strong></td>
</tr>
<tr>
<td>10 per cent of base level.</td>
<td>10 per cent of base level.</td>
</tr>
<tr>
<td><strong>January 1, 1996</strong></td>
<td><strong>January 1, 2010</strong></td>
</tr>
<tr>
<td>15 per cent of base level until 28 July 2000 (date of entry into force of the Beijing Adjustments).</td>
<td>15 per cent of base level.</td>
</tr>
<tr>
<td>New base level for basic domestic needs Effective July 28, 2000</td>
<td><strong>Non-Article 5(1) Parties</strong></td>
</tr>
<tr>
<td>Annual average production for satisfying basic domestic needs of Article 5(1) Parties for the period 1995 to 1997 inclusive.</td>
<td><strong>Article 5(1) Parties</strong></td>
</tr>
<tr>
<td>July 28, 2000</td>
<td><strong>January 1, 2003</strong></td>
</tr>
<tr>
<td>100 per cent of new base level for satisfying basic domestic needs until end of 2002.</td>
<td>80 per cent of new base level.</td>
</tr>
<tr>
<td><strong>January 1, 2005</strong></td>
<td><strong>January 1, 2007</strong></td>
</tr>
<tr>
<td>50 per cent of new base level.</td>
<td>15 per cent of new base level.</td>
</tr>
<tr>
<td><strong>January 1, 2010</strong></td>
<td><strong>January 1, 2010</strong></td>
</tr>
<tr>
<td>0.</td>
<td>Zero.</td>
</tr>
</tbody>
</table>

# Measuring the Atmosphere (1)

<table>
<thead>
<tr>
<th>Gas Name</th>
<th>Chemical Formula</th>
<th>Percent Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N(_2)</td>
<td>78.08%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O(_2)</td>
<td>20.95%</td>
</tr>
<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>0 to 4%</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.93%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO(_2)</td>
<td>0.0360%</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.0018%</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>0.0005%</td>
</tr>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>0.00017%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H(_2)</td>
<td>0.00005%</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N(_2)O</td>
<td>0.00003%</td>
</tr>
<tr>
<td>Ozone</td>
<td>O(_3)</td>
<td>0.000004%</td>
</tr>
</tbody>
</table>

Points to consider:
- Huge amount of species
- Low concentration, high impact
- Variation over the globe
- Dynamic system
- Chemical reactivity

Average of constituents of atmosphere up to 25 km (troposphere)

Amount of CO\(_2\) in the table is not accurate anymore

Measuring the Atmosphere (2)

Hewlett Packard 5840A dual channel GC,
EC (Electron Capture)-detector
N$_2$O, CCl$_2$F$_2$, CCl$_3$F, CH$_3$CCl$_3$, CCl$_4$

GAGE: Global Atmospheric Gas Experiment 1982–1992
Hewlett Packard 5880 three channel GC,
EC-, FI (Flame Ionization)-detector
N$_2$O, CCl$_2$F$_2$, CCl$_3$F, CH$_3$CCl$_3$, CCl$_4$, CH$_4$, CCl$_2$FCCIF$_2$

Measuring the Atmosphere (3)

AGAGE: Advanced Global Atmospheric Gas Experiment, since 1993
Measurement of long lived trace gases
Oceanic and mountainous measurement sites

GC-MS (Medusa system*)
Multiple GC-detectors:
Electron capture (EC), flame ionization (FI),
mercuric oxide reduction (MR), pulsed
discharge (PD)†


Medusa

Phase I: drying, concentrating on trap 1 (-165°C)

Phase II: volatile compounds are removed from T1 and refocused on T2, moved to MS

Phase III: remaining substances on T1 are refocused on T2 => MS


EPC: electronic pressure control
MFC: mass flow controller

For CF₄
Barbados and Zeppelin (1)

CFC-11 Concentration Barbados (ECD) 2017

CFC-11 Concentration Zeppelin (GC-MS) 2017

Sample Volume
GC-ECD: 4.5 mL

Sample Volume
GC-MS: 2 L
Barbados and Zeppelin (2)

CFC-11 Precision Barbados (GC-ECD) 2017

Precision Data for Zeppelin
GC-MS is missing

CFC-11 Precision Jungfraujoch (GC-MS) 2017

Data of Jungfraujoch taken
Sample Volume

Barbados GC-MD:
Median: 229.22 ppt
\( \sigma \) 0.08 \%
95% 229.22 ± 0.37 ppt
1.67 mL
99.7% 229.22 ± 0.55 ppt
2.48 mL

Zeppelin GC-MS:
Median: 230.04 ppt
\( \sigma \) 0.2 \%
95% 230.04 ± 0.92 ppt
1.84 L
99.7% 230.04 ± 1.38 ppt
2.76 L

Assumption:
1 ppt corresponds to the sample volume

Precision value for Zeppelin assumed from Prinn2018
## MS-Spectra of CFC’s (1)

### Table: Atoms, Nominal Mass, and Relative Abundance

<table>
<thead>
<tr>
<th>Atom</th>
<th>Nominal Mass</th>
<th>Rel. Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>~1</td>
</tr>
<tr>
<td>C</td>
<td>12 / 13</td>
<td>0.99 / 0.01</td>
</tr>
<tr>
<td>F</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Cl</td>
<td>35 / 37</td>
<td>0.76 / 0.24</td>
</tr>
</tbody>
</table>
MS-Spectra of CFC’s (2)

\[
\begin{align*}
\text{CCl}_2\text{F}_2 & \xrightarrow{-\text{Cl}} \text{CClF}_2 & \xrightarrow{-\text{Cl}} \text{CF}_2 \\
120/122/124 & \quad 85/87 & \quad 50
\end{align*}
\]

Base Peak [M-Cl]^+
MS-Spectra of CFC’s (3)

CCl₃F → -Cl → CCl₂F → -Cl → CClF
136/138/140/142 → 101/103/105 → 66/68

Base Peak [M-Cl]^+
MS-Spectra of CFC’s (4)

CCl₂FCCIF₂ → CI⁻F⁻ CCl₂F
186/188/190/192 → 101/103/105

-CCl₂F → CF₂
85/87 → 50

CCl₂F → CI⁻ F⁻
66/68 → 85/87

CIF → CI⁻ F⁻
66/68 → 31

#1

Base Peak [M-CClF₂]⁺
MS-Spectra of CFC’s (5)

\[
\begin{align*}
\text{C}_2\text{H}_3\text{Cl}_3 & \xrightarrow{-\text{Cl}} \text{C}_2\text{H}_3\text{Cl}_2 & \xrightarrow{-\text{Cl}} \text{C}_2\text{H}_2\text{Cl} \\
132/134/136/138 & \quad 97/99/101 & \quad 62/64 \\
\text{-CH}_3 & \quad \text{Cl}_3 \\
117/119/121/123 & \quad \text{Cl}_2 & \quad 82/84/86
\end{align*}
\]

Base Peak [M-Cl]^+
MS-Spectra of CFC’s (6)

CCl$_4$ → -Cl → CCl$_3$ → -Cl → CCl$_2$

152/154/156/158/160 → 117/119/121/123 → 82/84/86

Base Peak [M-Cl]$^+$

#5
Satellite Measurement with IR-Spectroscopy (1)

Two geometries to measure different spheres

Nadir (Troposphere)

Limb (Stratosphere)

Satellite Measurement with IR-Spectroscopy (2)

Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS)

Two detectors enable measurement from 750–4400 cm\(^{-1}\)

Opinion about advantages and disadvantages:
- Spatial resolution
- Instantaneous measurement
- Detection of short lived species
- Price
- Satellite orbits
- Additivity effects of interference biases
- Global background concentration contains artifacts
- Precision?

Solar Occultation:
Transmission measured, ratio with the exoatmospheric measurement

Satellite Measurement with IR-Spectroscopy (3)

VMR: Volume Mixing Ratio


12.5–29.5 km altitude, average over whole latitude
What is happening in China?

CFC-11 is still used as foaming agent for polyols by manufacturers, according to EIA (Environmental Investigation Agency)


Measurement

CCl₃F: 137.36 g/mol

\[ \rho = 15 \times 10^{-6} \text{g m}^{-3} : 137.36 \text{ g mol}^{-1} = 1.09 \times 10^{-7} \text{mol m}^{-3} \]

\[ n = \frac{p}{R \times T} \Rightarrow \rho = 40.36 \text{mol m}^{-3} \]

\[ \chi_{source} = 1.09 \times 10^{-7} \text{mol m}^{-3} : 40.36 \text{mol m}^{-3} = 2.70 \times 10^{-9} \]

At source: \( \chi = 2.70 \text{ ppb} \)

\[ \chi_{station} = \frac{\chi_{source}}{5 \times 10^6} = 5.40 \times 10^{-16} \]

At station: \( \chi = 0.54 \text{ ppq} \)

ECD: 0.07% peak height precision, 0.017 ppt over background needed for detection

MS: 0.2% precision, 0.48 ppt over background for detection
Strategy to Measure in China

- Need to find hotspot
- Generate “heatmap” of China
- In-situ measurement on airplane
- Concentrations should be high enough / ECD-detectors are able to detect ppt

Advantages over stationary measurements:
- Mapping possible
- Less reliant on atmospheric models
- Spatial resolution

From HCFC-22 to CFC-11

\[
\begin{align*}
\text{CHCl}_3 & + 2 \text{HF} \xrightarrow{\text{SbCl}_4 \text{F}} \text{CHClF}_2 & + 2 \text{HCl} \\
\text{CCl}_4 & + 2 \text{HF} \xrightarrow{\text{SbCl}_4 \text{F}} \text{CHClF}_2 & + \text{HCl} + \text{Cl}_2 \\
\text{CCl}_4 & + \text{HF} \xrightarrow{\text{SbCl}_5, 100 \, ^\circ \text{C}, \text{pressure}} \text{CCl}_3 \text{F} & + \text{CCl}_4 + \text{CCl}_2 \text{F}_2
\end{align*}
\]

Is EIA right?

- Sites reported by EIA partially match the concentration map of Rigby et al.
- Emissions unlikely stem mostly from banks / release from old buildings etc.
- The numbers of close stations are low, measurements allow only regions to be determined
- Investigative journalism vs. analysis / wind-models

Point to discuss: What is the possible ideal measurement techniques?

WHY DON'T THE GREENHOUSE GASES ESCAPE THROUGH THE HOLE IN THE OZONE LAYER?