Utrecht University

Institute for Marine and Atmospheric research Utrecht

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No 742798

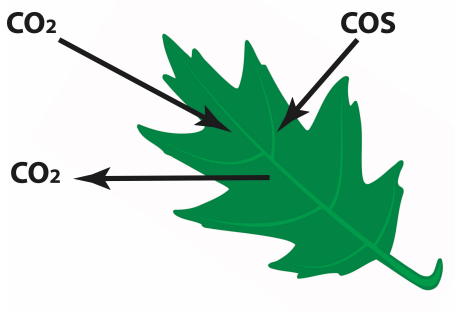
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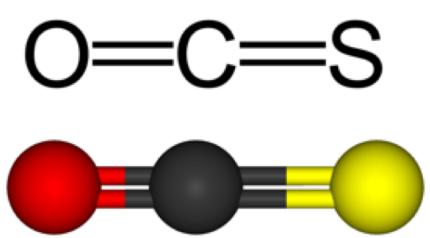
Isotopic Measurements of Carbonyl Sulfide

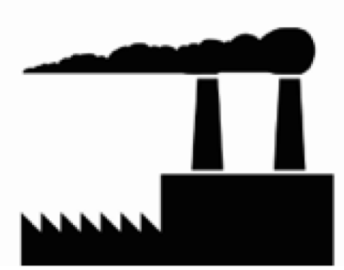
The first results from outside air measurements in the Netherlands

Sophie L. Baartman[1], Maarten Krol[1,2] & Thomas Röckmann[1], Maria Elena Popa[1], Shohei Hattori[3], Kazuki Kamezaki[3], Naohiro Yoshida[3]

[1]Utrecht University, Netherlands, [2]Wageningen University, Netherlands [3]Tokyo Institute of Technology, Japan





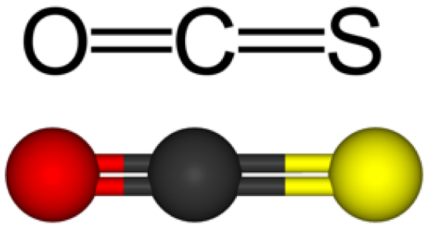


Paper manuscript: Sophie L. Baartman, Maarten Krol, Thomas Röckmann, Shohei Hattori, Kazuki Kamezaki, Naohiro Yoshida, Maria Elena Popa
A new CF-IRMS method for measuring sulfur isotope ratios of carbonyl sulfide from small air samples



Carbonyl sulfide

- Most abundant sulfur containing gas in atmosphere
- Average tropospheric mixing ratio: 500 ppt
- Lifetime of about 2 years
- Transported into stratosphere
- Four stable sulfur isotopes



^{32}S	^{33}S	^{34}S	^{36}S
95.02%	0.75%	4.21%	0.02%



Data from Angert et al. (2019), Kamezaki et al. (2019), Hattori et al. (2020) & Davidson et al. (2021)

Photolysis

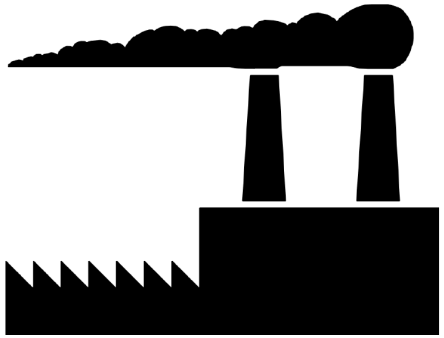
Oxidation

Carbonyl Sulfide

$\delta^{34}S$ = 10.5 ‰ to 13.2 ‰



$\delta^{34}S$ = 13 ‰ to 19 ‰



$\delta^{34}S$ = 3 ‰ to 8 ‰

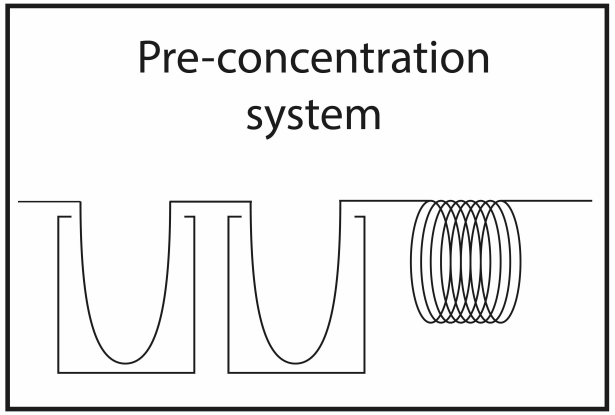




$^{34}\varepsilon$ = -1.9 ± 0.5 ‰

Methods





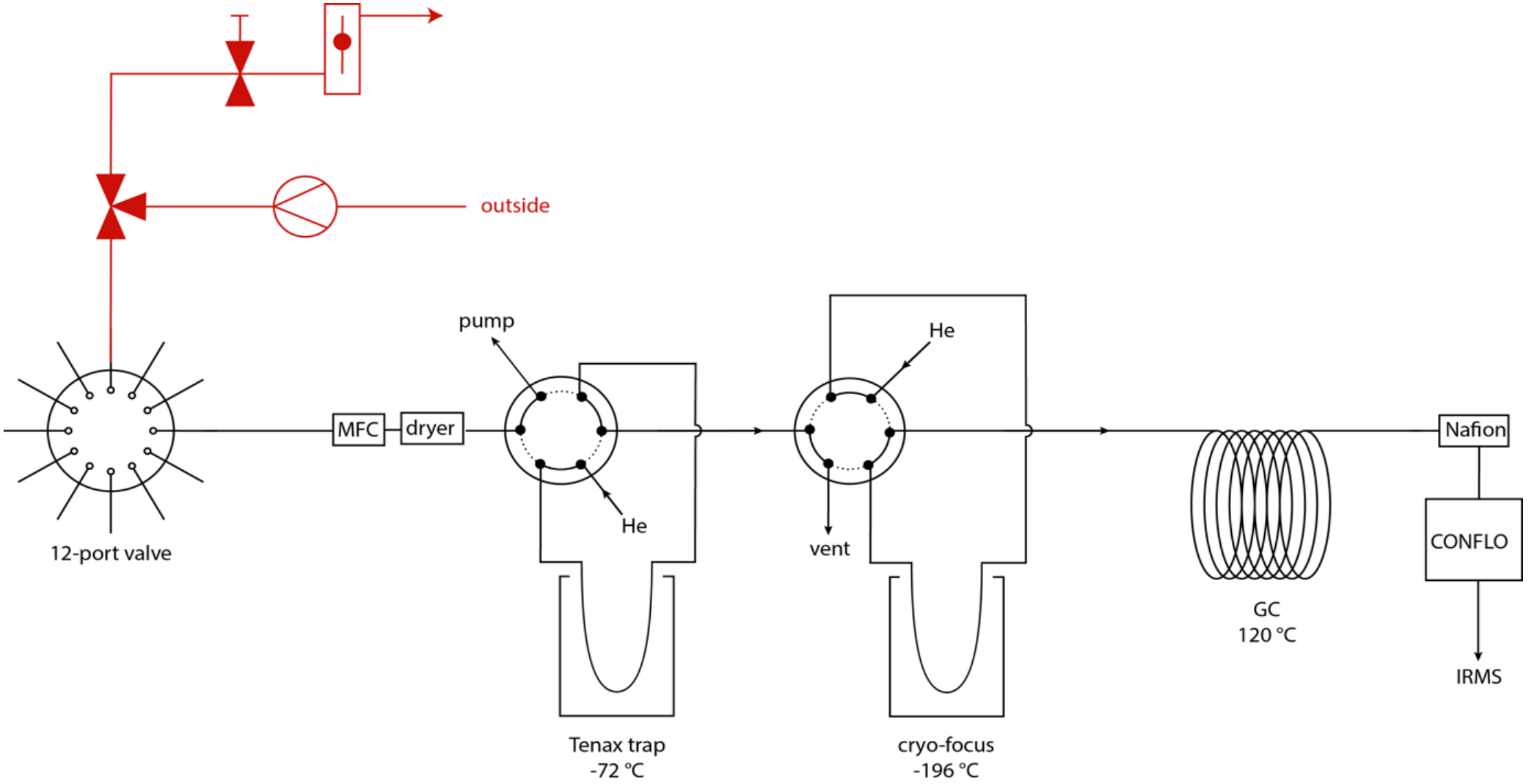


Raw data → Data correction → Isotope ratios

- Measure S^+ fragments with CF-IRMS
- 2 – 4 L samples
- Current 4 L 500 ppt precision
  - ^{33}S: 2.1‰
  - ^{34}S: 0.9‰
- System includes option to measure outside air at Utrecht



Detailed measurement set-up



Pre-concentration system in black and outside air sampling system in red

Methods – tunnel measurements

- Samples collected in Leidsche Rijntunnel, Utrecht
- Evacuated canisters opened while driving



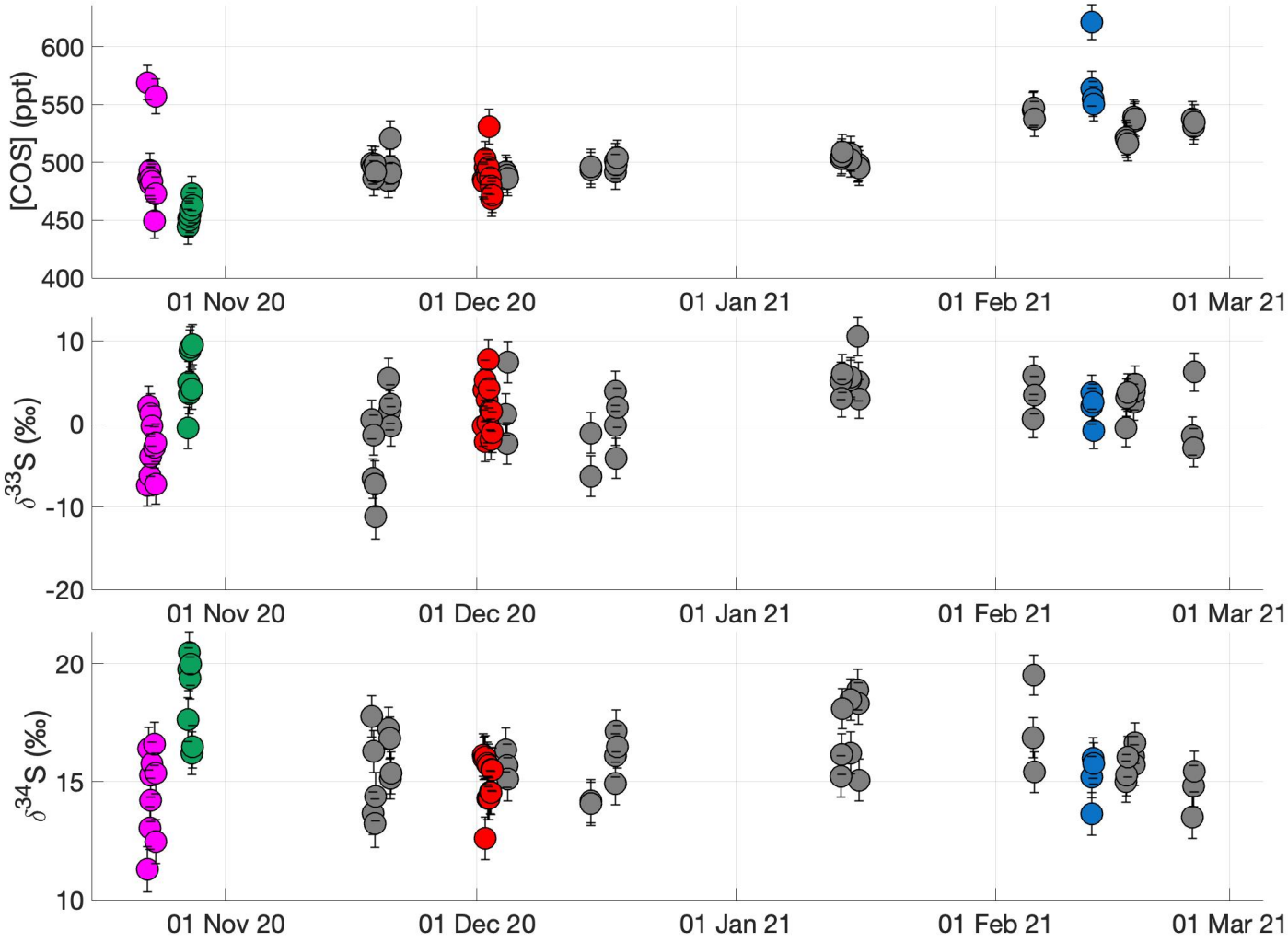
Rijkswaterstaat, 2021 https://www.rijkswaterstaat.nl/wegen/wegenoverzicht/a2/leidsche-rijntunnel-a2



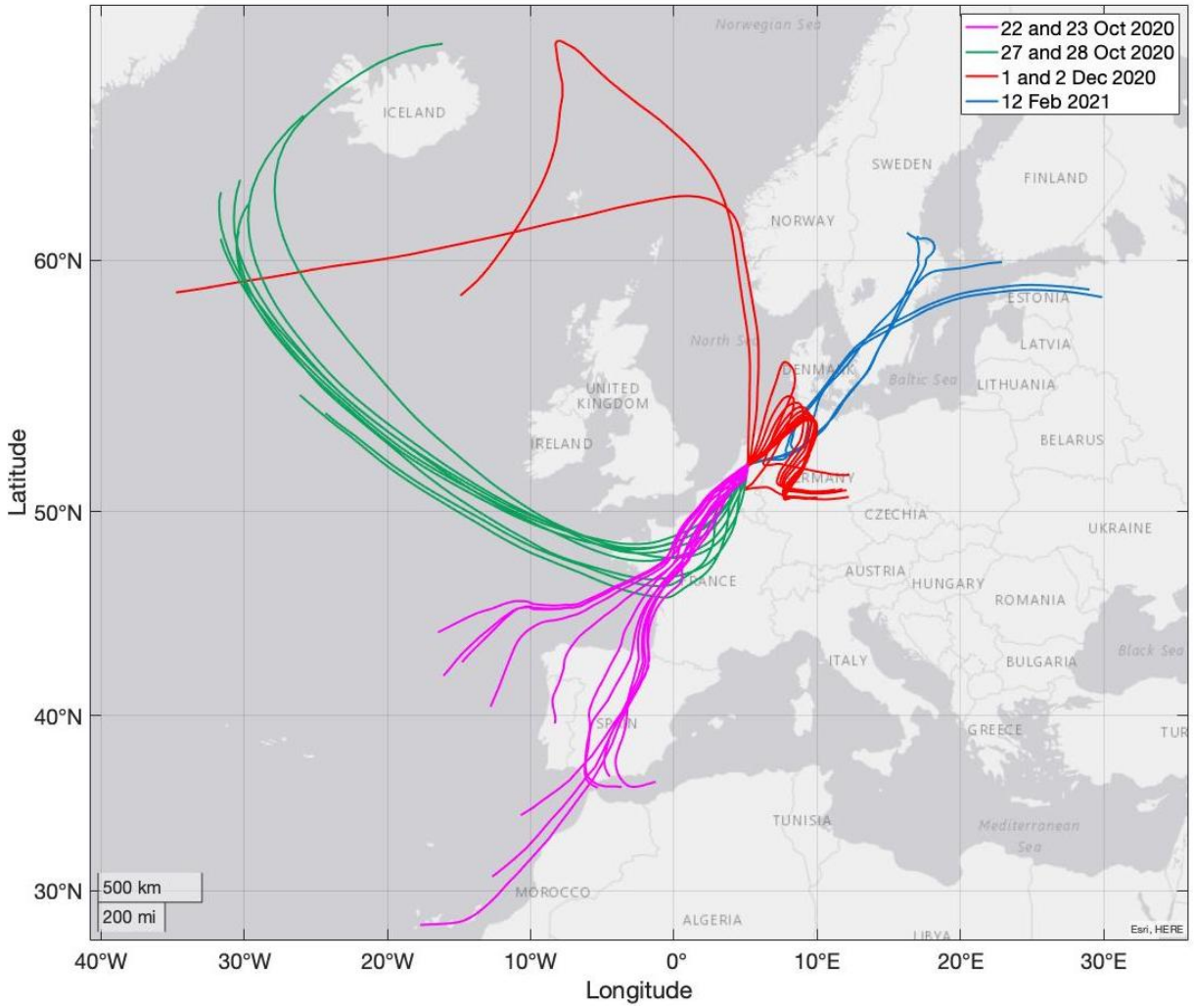
Results - outside air

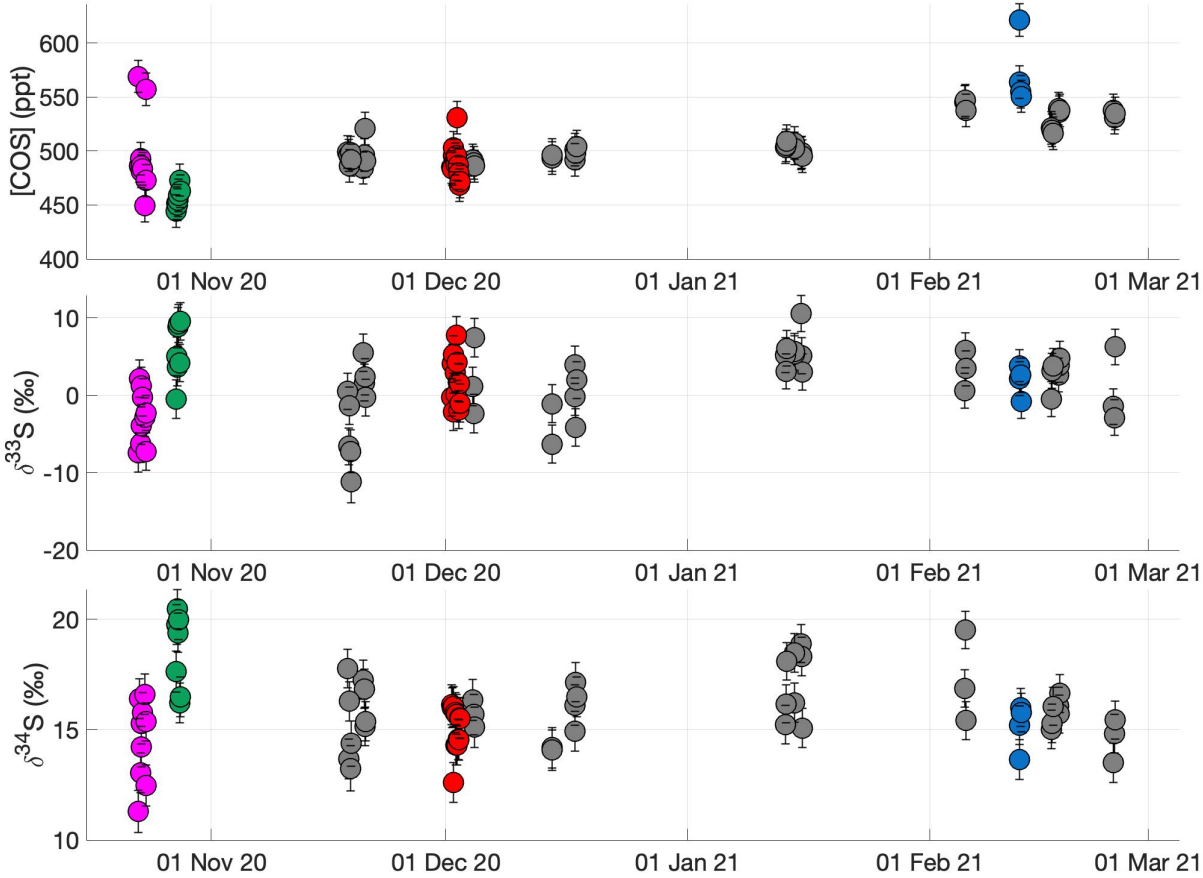
- Average [COS] = 488 ± 15 ppt
- Maximum [COS] = 620 ± 15 ppt
- Average $\delta^{34}S$ = 15.9 ± 0.9 ‰
- Average $\delta^{33}S$ = 1.5 ± 2.1 ‰

- [COS] + 40 ppt in winter than in fall
- No seasonal trend $\delta^{34}S$ yet obs.





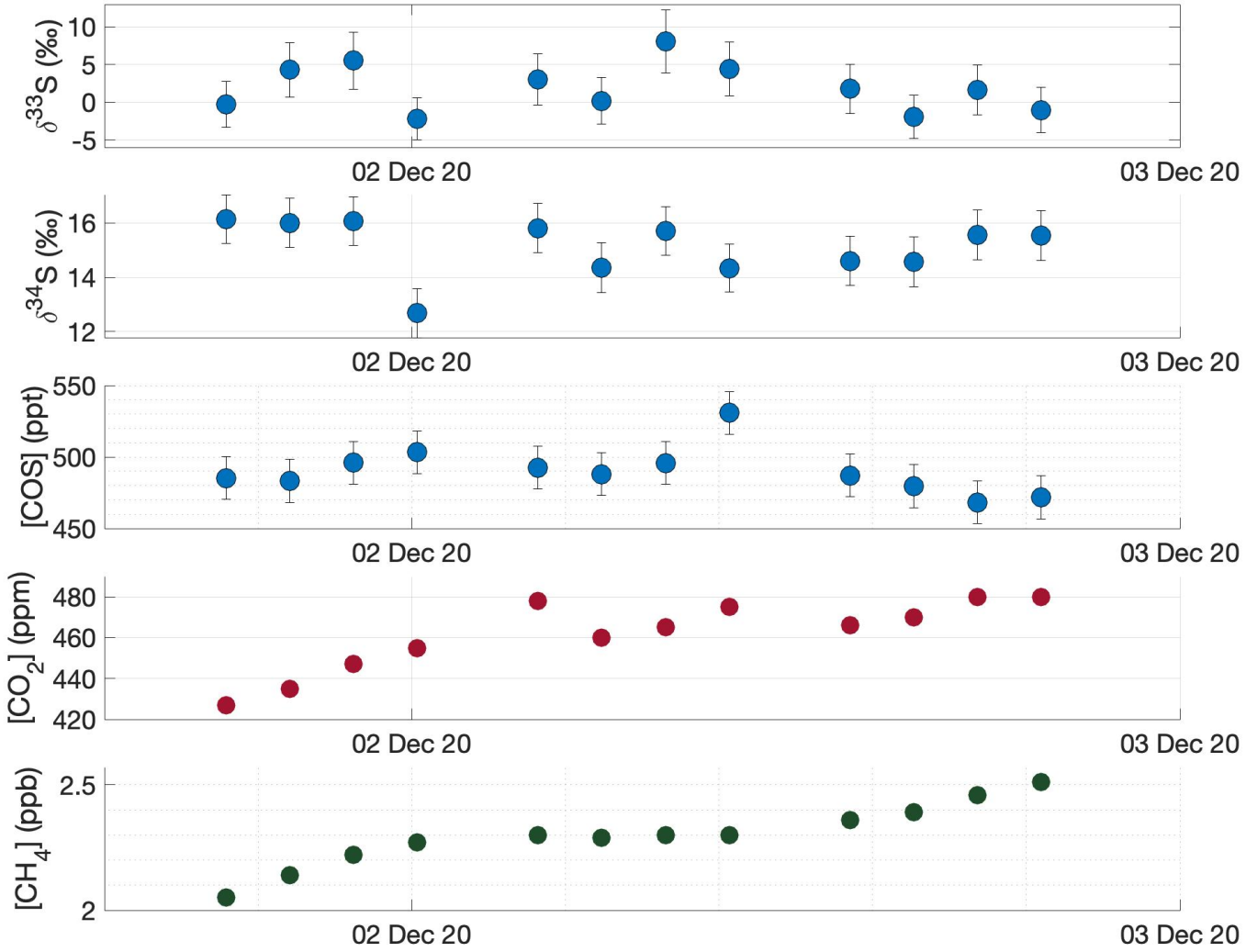

22 and 23 Oct 2020
27 and 28 Oct 2020
1 and 2 Dec 2020
12 Feb 2021
ICELAND
SWEDEN
FINLAND
NORWAY
ESTONIA
LATVIA
LITHUANIA
BELARUS
UNITED KINGDOM
IRELAND
CZECHIA
UKRAINE
AUSTRIA
HUNGARY
ROMANIA
ITALY
BULGARIA
GREECE
TUNISIA
MOROCCO
ALGERIA
500 km
200 mi
Esri, HERE
60°N
50°N
40°N
30°N
40°W
30°W
20°W
10°W
0°
10°E
20°E
30°E
Latitude
Longitude


[COS] (ppt)
600
550
500
450
400
01 Nov 20
01 Dec 20
01 Jan 21
01 Feb 21
01 Mar 21
$\delta^{33}S$ (‰)
10
0
-10
-20
$\delta^{34}S$ (‰)
20
15
10



Results pollution plume

- Pollution plume from industrial area in Germany
- Build-up of CO_2 and CH_4 but not in COS
- Not much change in isotopes either

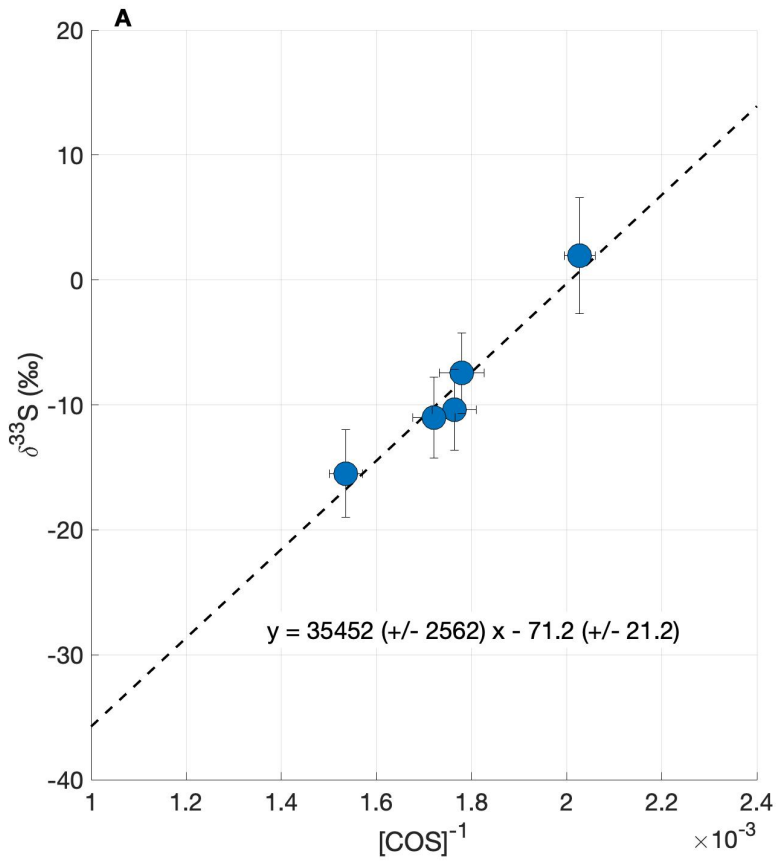


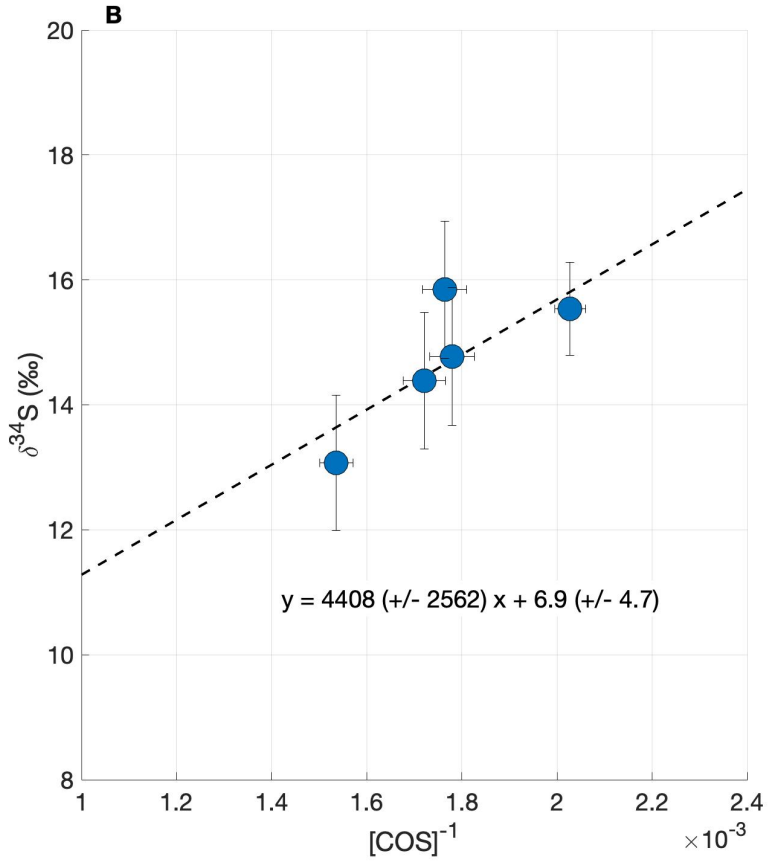


Traffic emissions

- Depleted in ^{33}S and ^{34}S
- $COS:CO_2$ = 0.4 ppt/ppm
- European COS traffic emissions 0.19 Gg S a^{-1}
- Global emission estimate 0.8 – 8 Gg S a^{-1}

(Fried, 1992; Chin & Davis, 1993; Watts, 2000; Lee & Brimblecombe, 2016)







Conclusion

- New CF-IRMS system for S^+ isotopes from COS
- Precision for 4L samples: $\delta^{33}S$ = 2.1 ‰ $\delta^{34}S$ = 0.9 ‰
- Small contribution anthropogenic emissions
- Traffic emissions: depleted in $\delta^{33}S$ and $\delta^{34}S$, small source in Western Europe

- For more information → come to the chat session!

