GGMT 2022 @ Wageningen

[Poster 11] Development of a dynamic dilution system for COS in air mixture at ambient levels

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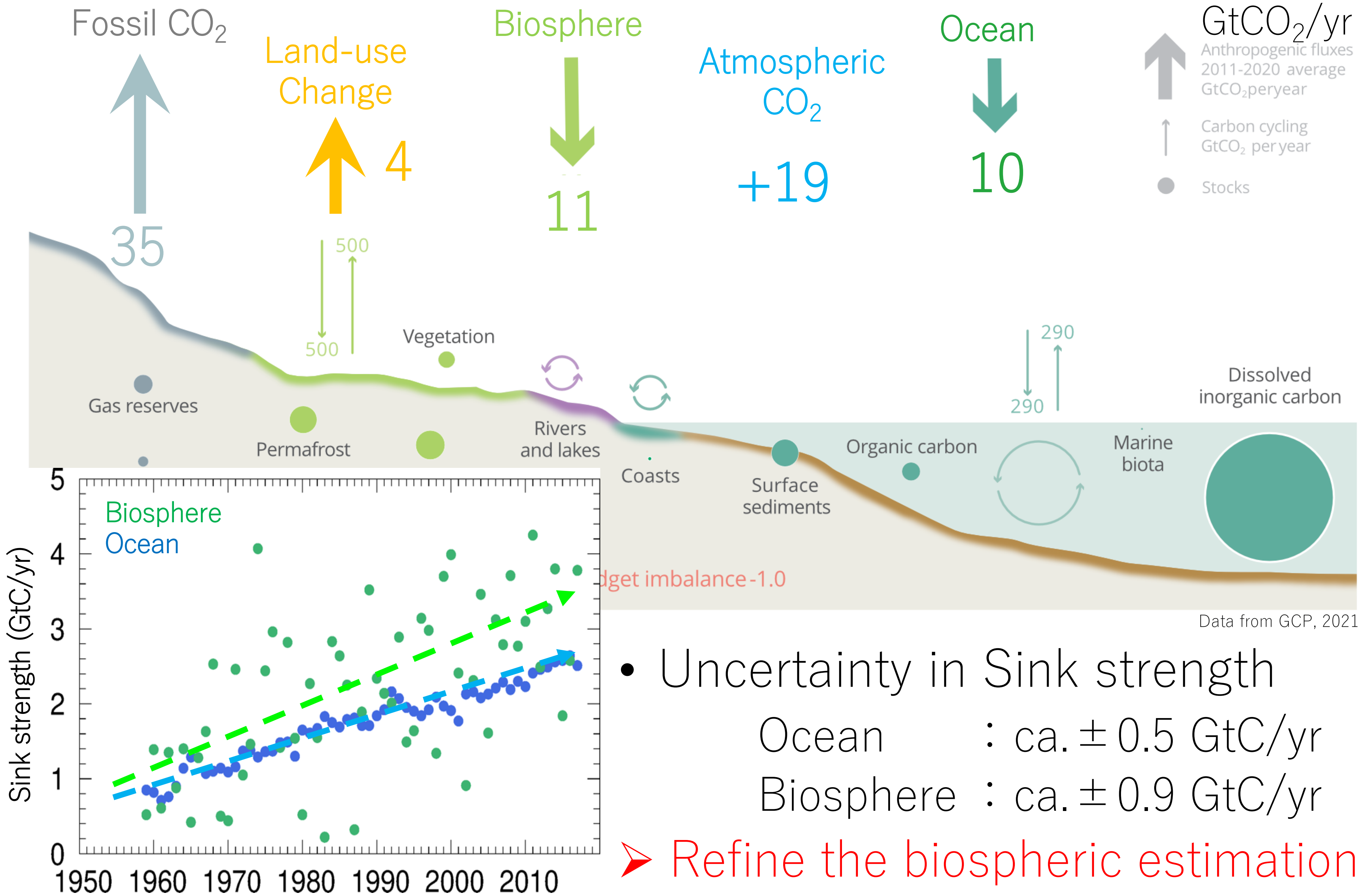
Future climate projections and global CO_2 cycle



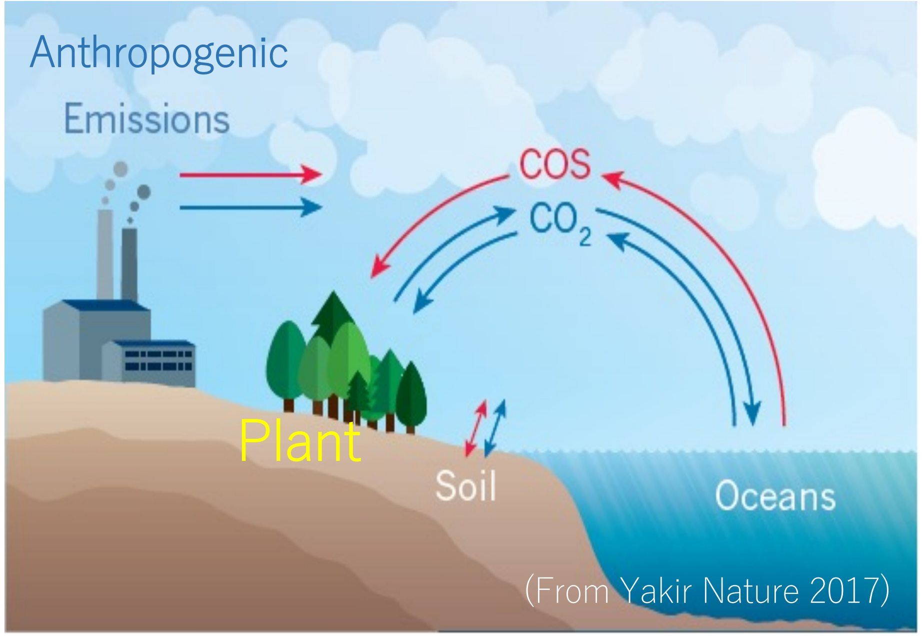
- Uncertainty in Sink strength

  Ocean ： ca. ± 0.5 GtC/yr

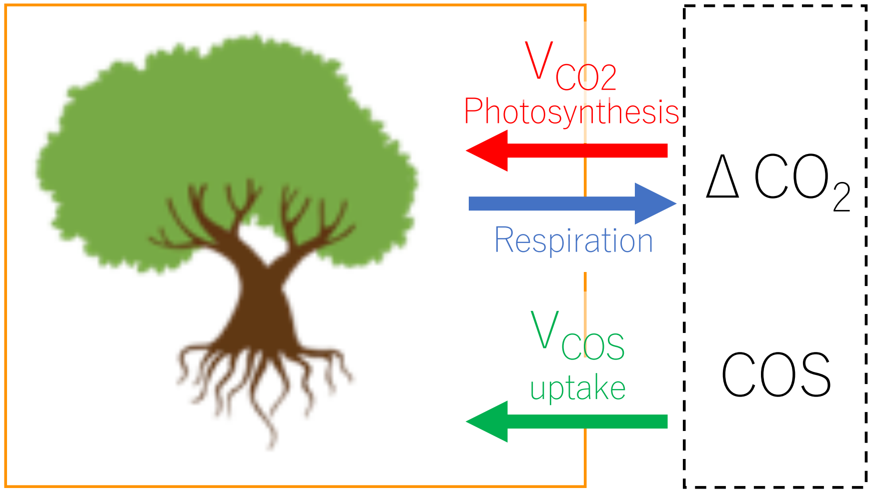
  Biosphere ： ca. ± 0.9 GtC/yr

➢ Refine the biospheric estimation

Carbonyl sulfide as a new carbon cycle tracer



Global cycle of CO_2 and COS



Main concept of COS as the tracer

Measurable

- Carbonyl sulfide(COS)
  - ✓ Most abundant S-compound
  - ✓ 350-600 ppt (CO_2 × 10^{-6})
  - ✓ Similar Source and Sink of CO_2
- Gas exchange by plants

Ratio of the absorption velocity

$$V_{CO2} / V_{COS} = \alpha$$

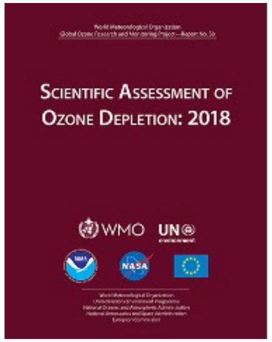
$$GPP = \alpha \times \Delta COS$$

Photosynthesis CO_2 fixation
GPP : Gross Primary Production

➢ COS can be a GPP tracer

Problems in long-term observation of COS

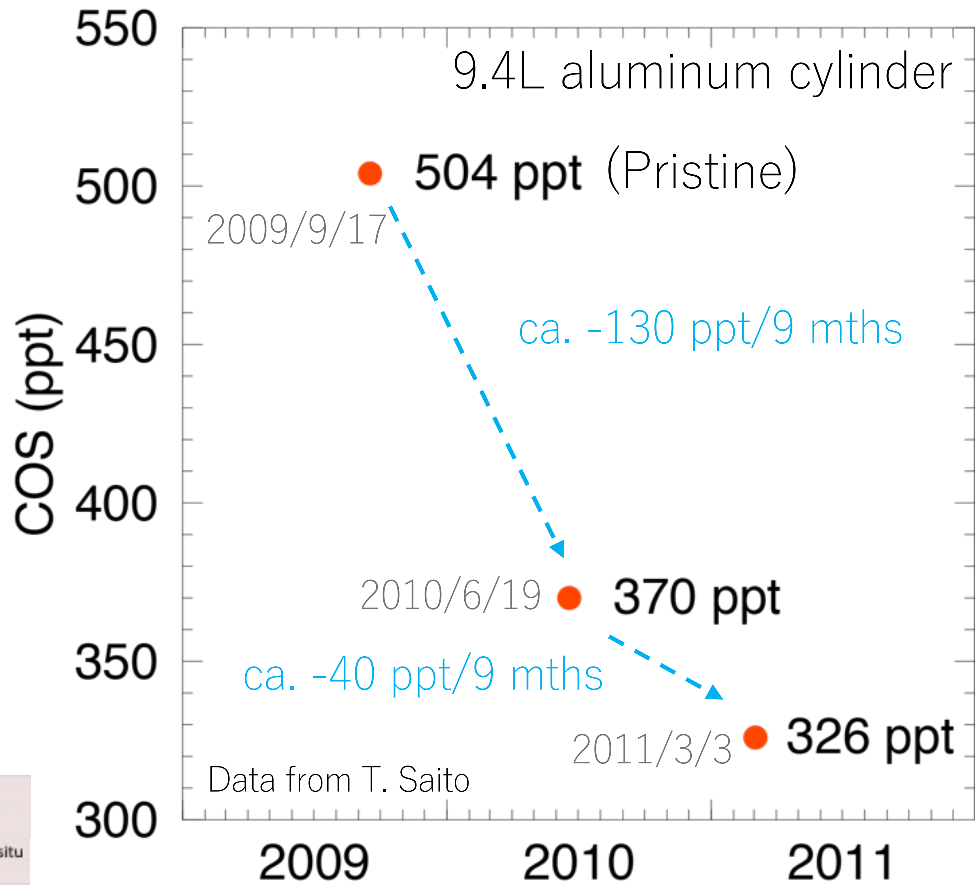
- Preindustrial era
  Analysis of Antarctic ice core : 300 – 350 ppt
- Current
  Global mean : 500 ppt



Mole Fraction				Annual Change in Mole Fraction		
2005	2006	2007	2008	2005/06	2006/07	2007/08
488	491	494	491	2.2	2.9	−2.1

Annual Mean Mole Fraction (ppt)			Change (2011–2012)	
2008	2011	2012	ppt yr^{-1}	% yr^{-1}
491	491	493	2	0.4

Chemical Formula	Common or Industrial Name	Annual Mean Mole Fraction (ppt)			Change (2015–2016)		Network, Method
		2012	2015	2016	ppt yr^{-1}	% yr^{-1}	
COS (ppt)	carbonyl sulfide	501	499	505	6	1.2	NOAA, flask and in situ (Global)



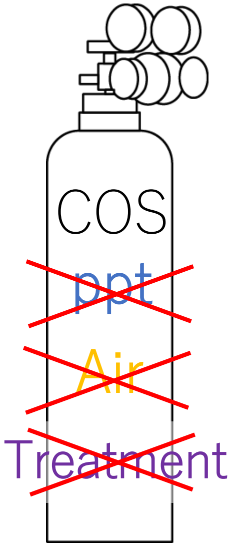
COS monitoring in the STD gas

- COS drift in a cylinder > Atmospheric COS variability

➢ Limited knowledge of global distribution, seasonal and annual variability

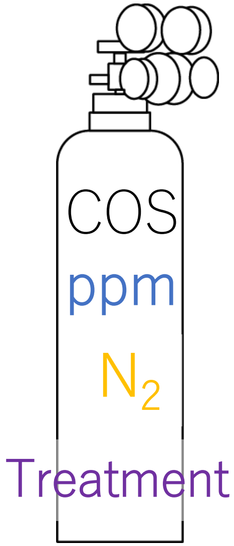
Our approach to the STD gas problem

Empirical



Degrade in high-pressure Al cylinder

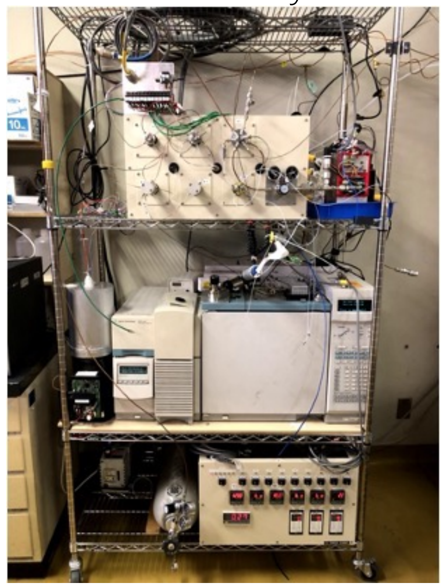
This study



High dry mole fraction (ppm) STD gas

N_2 dilution before analysis

GC/MS measurement system

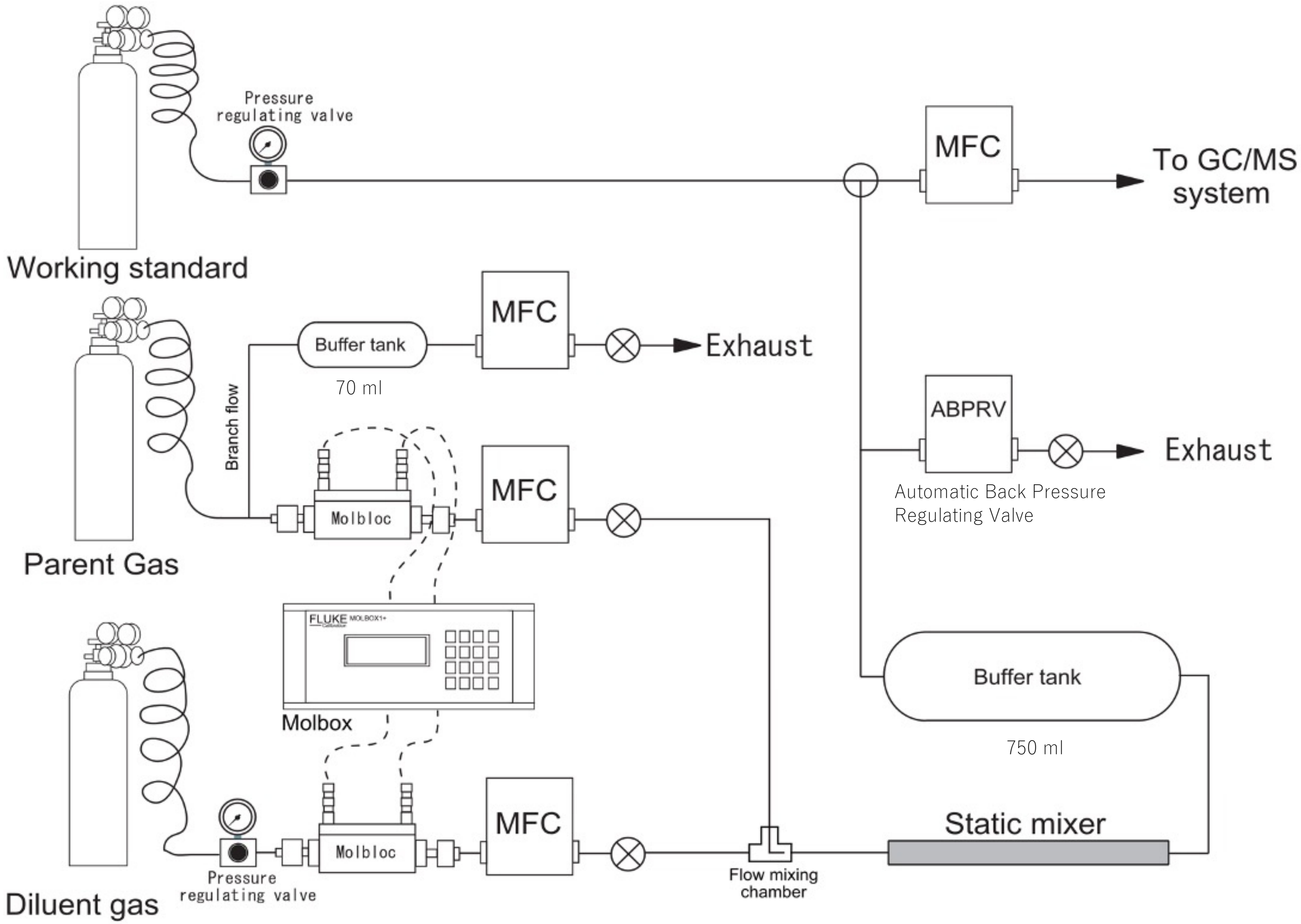


COS quantification

- ➢ Require ~ 10000-fold dilution system

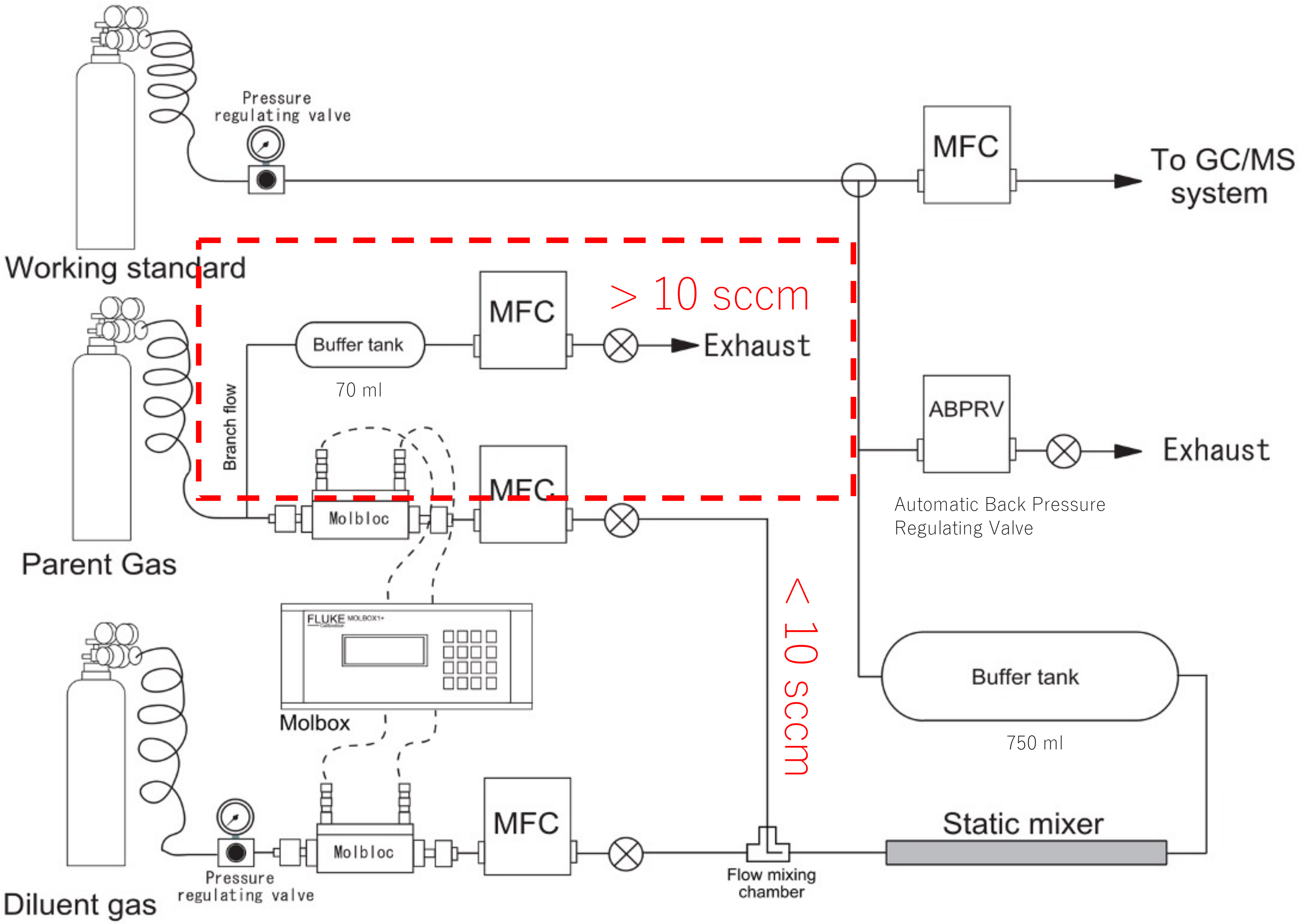
- ➢ We developed a high accuracy dynamic dilution system for long-term monitoring of atmospheric COS

Schematic view of the dynamic dilution system



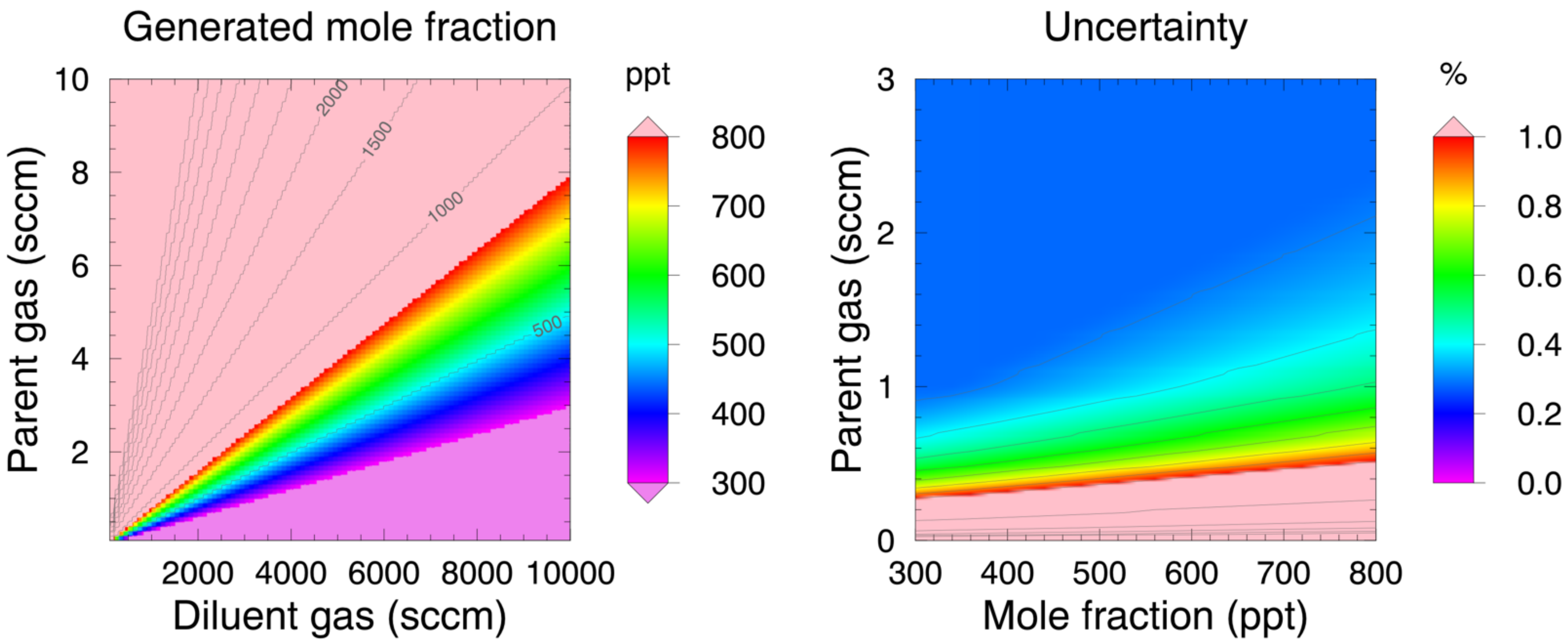
- Parent gas (gravimetric): 1.01 ppm COS + 1.00 ppm HCFC-22
- Diluent gas : high purity nitrogen > 99.99995 vol.%

Branch exhaust system



- The branch exhaust system was installed to minimize the pressure fluctuation of the parent gas flow and COS-specific dilution bias by increasing the discharge amount of the parent gas from the cylinder

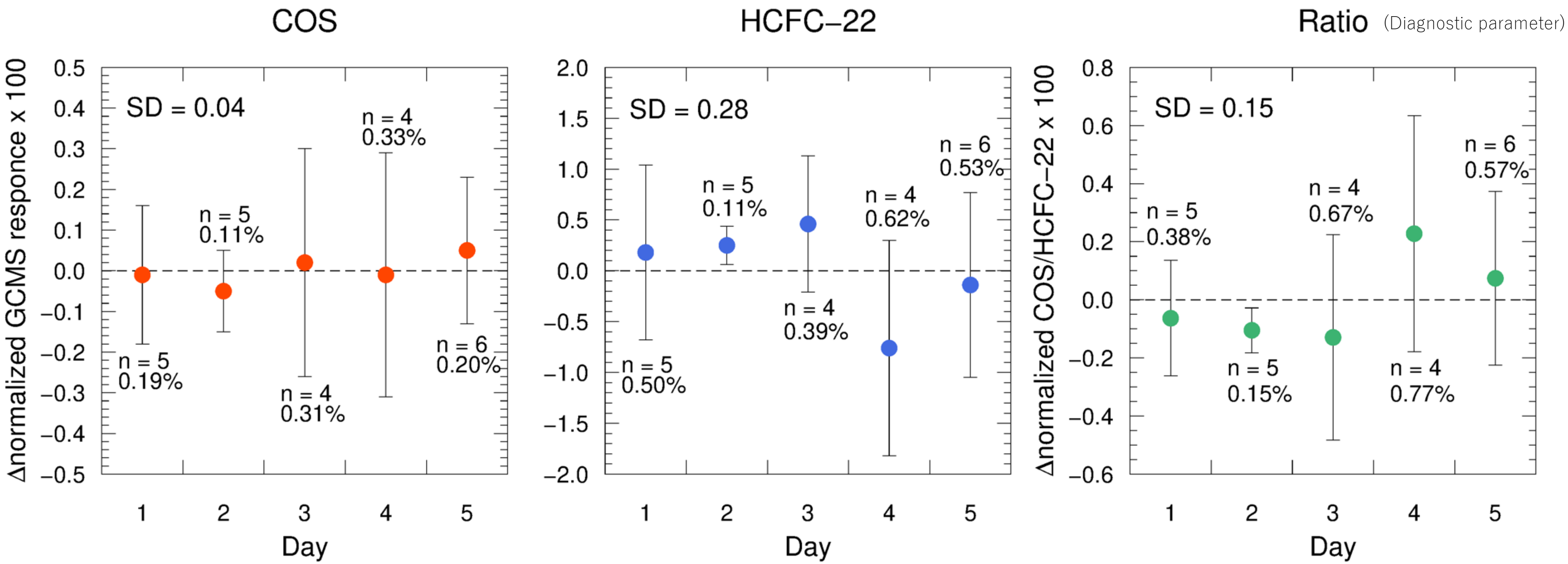
Dilution performance of the system



- The dilution system can generate a wide-range of COS mole fraction observed in the atmosphere from 1 ppm gravimetric standard
- The combined uncertainty for the gas dilution without uncertainty from gravimetric preparation shows sharp decrease below the flow rate of 1 sccm for the parent gas

➢ COS dilution uncertainty should be less than 0.3%

Repeatability and Reproducibility

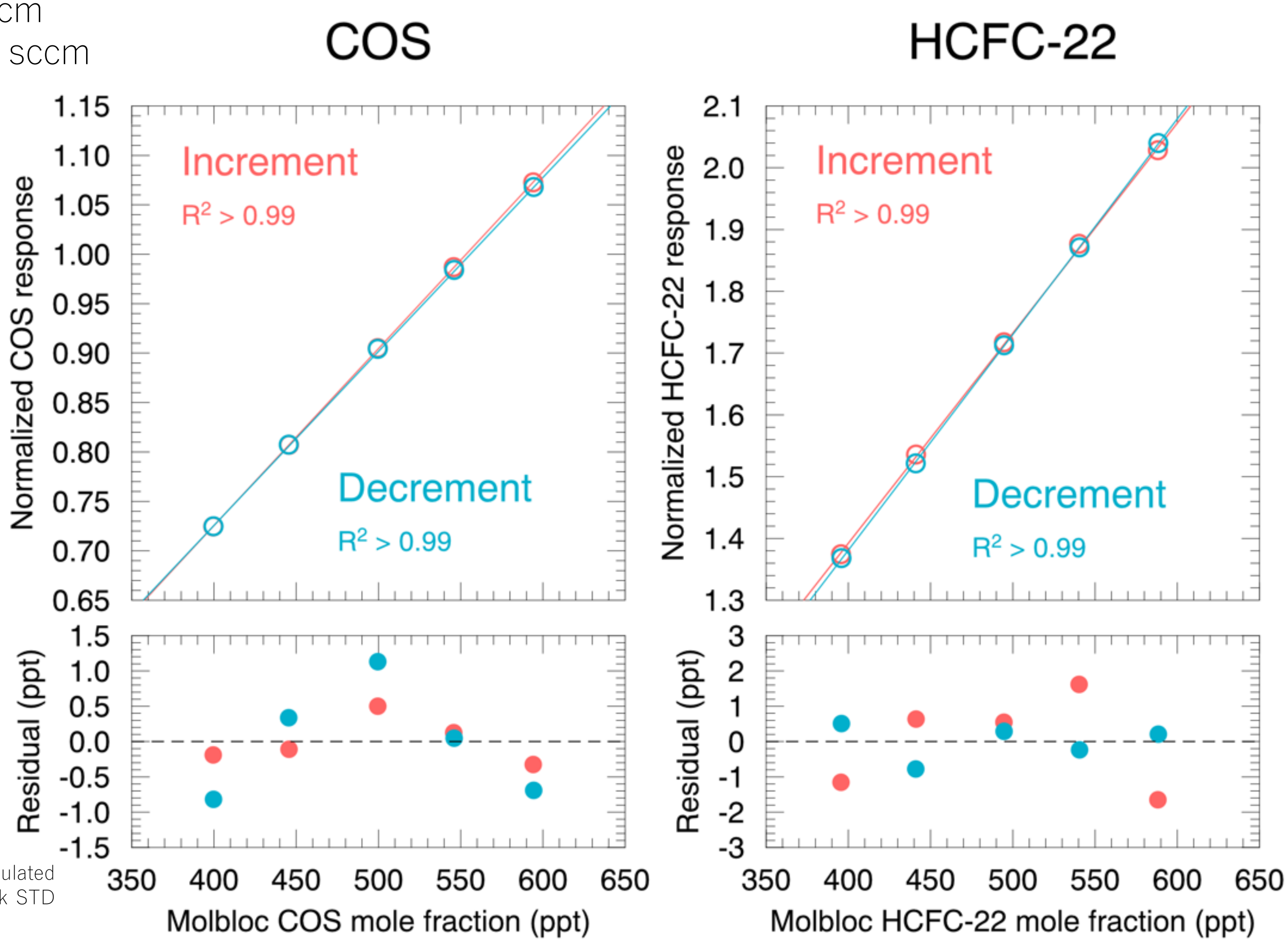


- Evaluation at constant dilution ratio 2000: diluent 5000 and parent 2.5 sccm, expected COS and HCFC-22: 500 and 495 ppt
  - Repeatability : COS < 0.4% RSD, HCFC-22 < 0.7% RSD
  - Reproducibility : COS = 0.02% RSE, HCFC-22 = 0.28% RSE
  - The ratio suggests no significant bias for COS (e.g., adsorption)

➢ Excellent repeatability and reproducibility was obtained

Dilution linearity

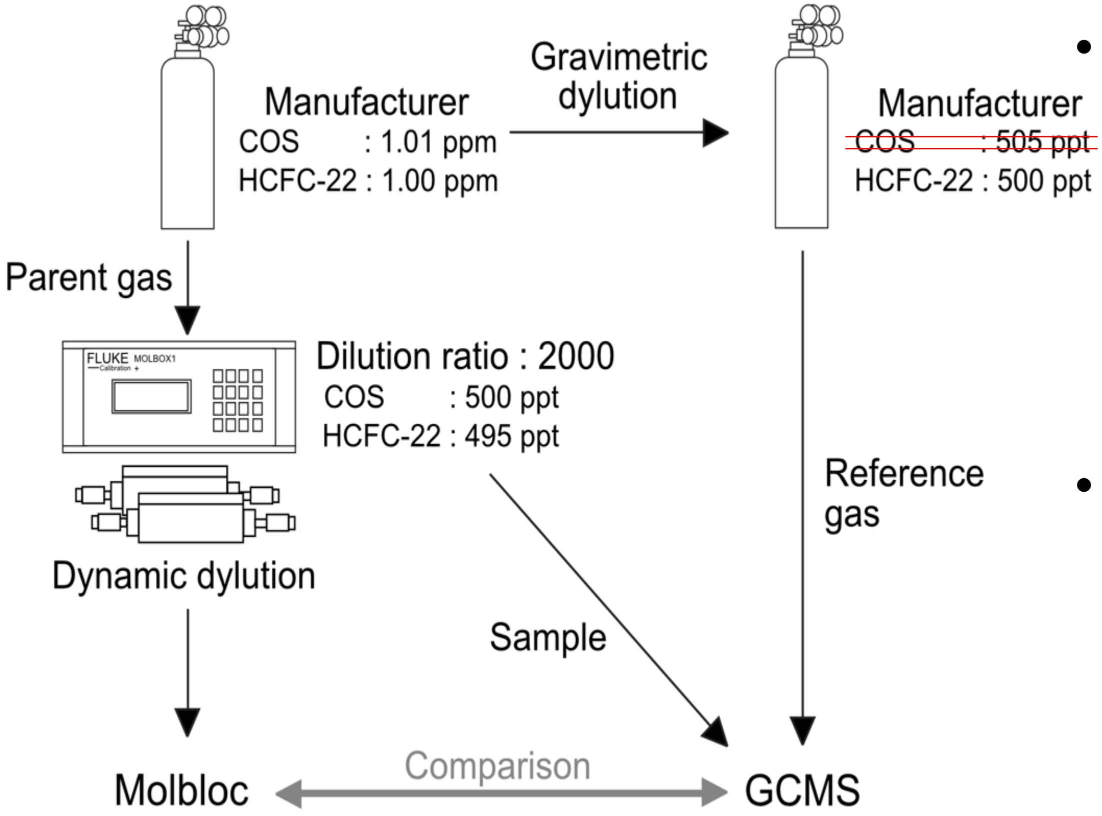
Diluent: 5000 sccm
Parent: 2.0 – 3.0 sccm



※Residuals were calculated based on the calibrated Wrk STD value later

- Excellent linearities were obtained for COS and HCFC-22 ($R^2 > 0.99$)
- Residuals distributed within ±1.5 ppt for COS, ±2.0 ppt for HCFC-22
- No significant memory effect from the previous dilution

Accuracy : Comparison with gravimetry



- Dilution accuracy was validated by comparing the methods between the dynamic dilution and gravimetry followed by the GCMS measurements

- The mole fraction of HCFC-22 generated by the dynamic dilution method agreed well with that from gravimetry on the GCMS measurements

Method	Calibration gas scale	HCFC-22 (ppt)
Dynamic dilution	Parent gas : Gravimetric preparation Molbloc : dilution ratio 2000	495.77 ± 0.12
GCMS	Gravimetrically diluted parent gas	493.71 ± 0.77
Difference against gravimetric	-	−2.06 ± 0.78

➢ Good agreement between the dynamic and gravimetric method

Dynamic calibration of COS and HCFC-22

Day	COS (ppt)		HCFC-22 (ppt)		Assigned value (ppt)	
	Mole fraction	Standard deviation	Mole fraction	Standard deviation	COS	HCFC-22
Day 1	554.68	1.20	288.85	1.53	554.51 ±0.13	289.11 ±0.34
Day 2	554.65	1.03	288.61	0.53		
Day 3	554.72	2.01	288.51	1.02		
Day 4	554.52	1.87	290.37	1.81		
Day 5	554.00	1.23	289.25	1.48		

- The compressed air sample filled in 48L aluminum cylinder used as Wrk STD in this study was calibrated

Repeatability (typically n=5)
- COS : 1.5 ppt (RSD:0.27%)
- HCFC-22 : 1.1 ppt (RSD:0.44%)

Reproducibility (N=5)
- COS : 0.1 ppt (RSE:0.02%)
- HCFC-22 : 0.3 ppt (RSE:0.12%)

- COS and HCFC-22 was calibrated accurately by the dynamic method on the temporal absolute scale

Discussion

- Our pilot study revealed key factors for the accurate dilution
  - ✓ Stabilizing the flow pressure of the parent gas
  - ✓ Rigorous pressure matching (within ±0.3 kPa)
  - ✓ Increase the parent gas flow rate: > 10 sccm
  - ➢ Install the branch exhaust system
- Detection of inter-annual variability of COS
  - ✓ COS shows a few ppt of inter-annual variability
  - ✓ The dilution performance for 500 ppt COS generation
    - ■ Repeatability : about 1.5 ppt (n=5)
    - ■ Reproducibility : about 0.1 ppt (N=5)
  - ➢ Frequent calibration allow to investigate the inter-annual variability
- Application of the dynamic calibration system to other gases
  - ✓ Advantage : dilution ratio can be easily changed
  - ✓ Unstable gases like COS (e.g., NOx, SOx, VOCs…)
  - ➢ The system can contribute to maintain CO scale

Conclusion and future study

Conclusion

- We developed high accuracy dynamic dilution system for the long-term monitoring of atmospheric COS
- The system showed excellent performance including repeatability, reproducibility and linearity, and the dilution accuracy was well validated
- We demonstrated that the dilution system was sufficiently capable of providing COS scale to reveal atmospheric COS distribution, seasonality and long-term trends.

Future study

✓ We are going to develop absolute calibration method to determine ppm-order COS standard precisely to establish our COS gas scale

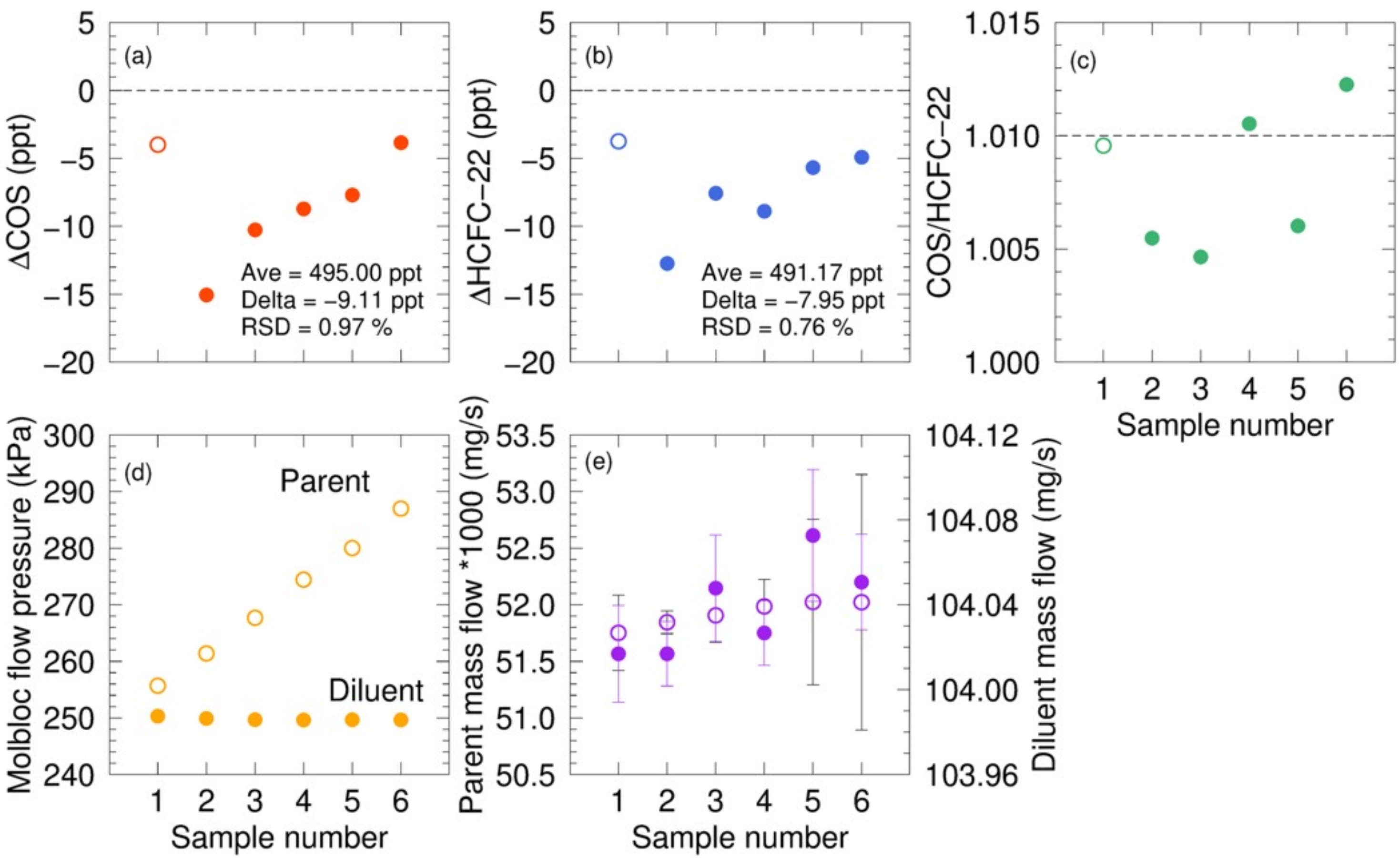
✓ We will improve the dilution system to automate all dilution process

- ➢ Reduce the amount of STD gas consumption
- ➢ Check the impact of automated pressure regulation using piezo valve

Supplemental information

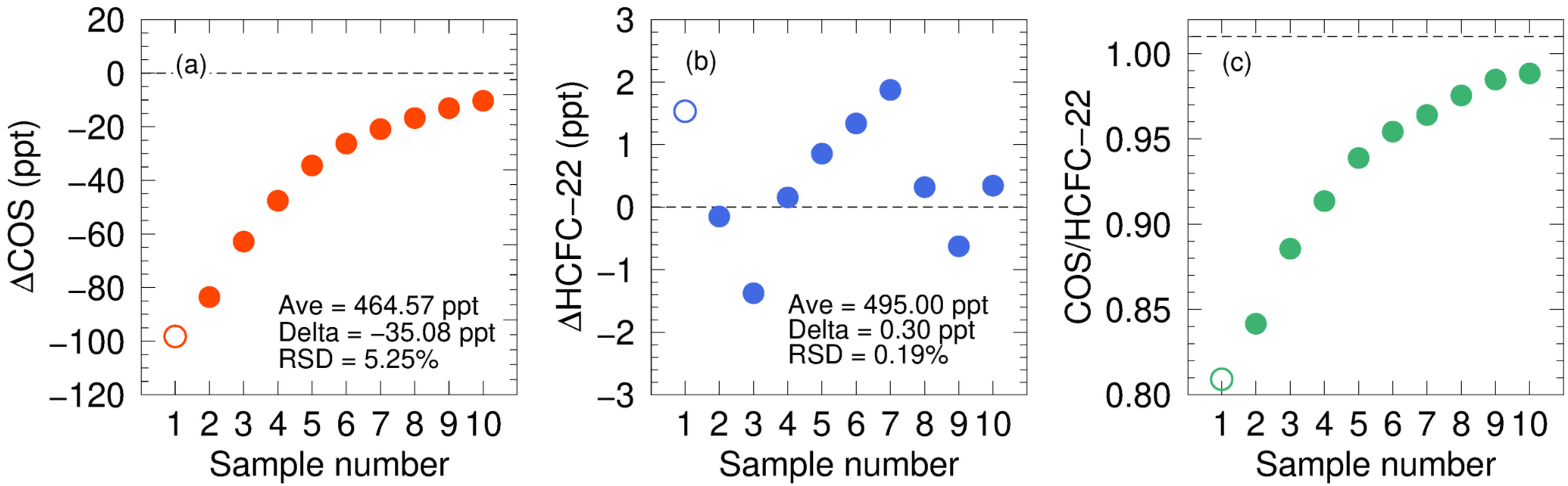
-Results from pilot study-

EX-S1: Only mass flow control



- Logarithmic increase was observed for COS and HCFC-22 while the ratio distributes around the Molbloc value
- The parent flow pressure showed linear increase in response to increase the sample number, implying the pressure influence

EX-S2: Pressure regulation and matching

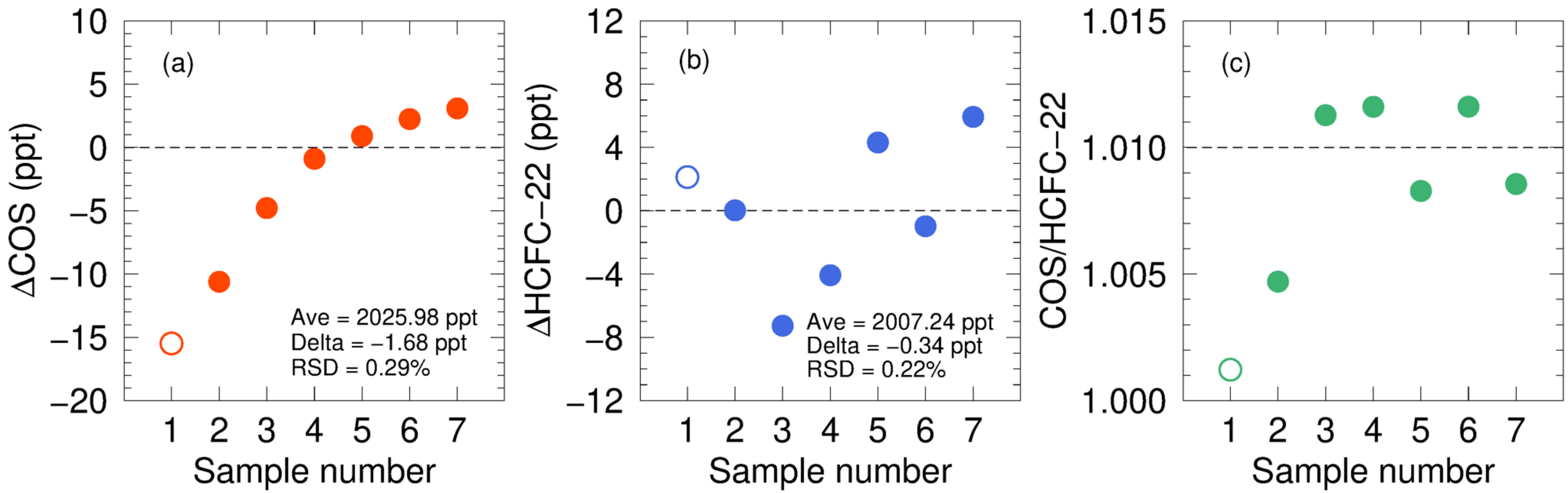


- Pressure regulation(stabilization) and matching between the parent and diluent within 1kPa at least resulted in improvement of HCFC-22 dilution, but not for COS

- The ratio showed similar logarithmic increase with that for COS due to the COS increase, suggested COS-specific dilution bias

EX-S3: increase the parent gas flow rate

S3



- Brewer et al. (2014) reported the flow-dependent dilution bias for SO_2 and CO dilution: diluted mole fraction was inversely proportional to the parent gas flow rate using the similar dynamic dilution system
- By increasing the parent gas flow rate from 2.5 to 10 sccm, dilution accuracy was improved significantly although amount of the logarithmic increase was not proportional to the parent gas flow rate
- The ratio distributed along the nominal ratio after 3th sample, suggesting negligible impact of the COS-specific dilution bias, which might be caused by COS absorption

Summary from the pilot study

- The pilot experiments suggested:
  - ✓ The pressure regulation and the matching is needed for the accurate dilution at least
  - ✓ Increase the parent gas flow rate can improve the dilution accuracy as well as minimizing the COS-specific dilution bias

➢ We improved the dynamic calibration system as:

- ✓ The flow pressures should be regulated rigorously within the difference ±0.3kPa based on Molbloc reading
- ✓ The branch exhaust system was installed to stabilize the flow pressure of the parent gas and increase the discharge amount of the parent gas from the cylinder
- ✓ Sufficient line rinsing should be made to minimize the impact of COS absorption/adsorption