Atmospheric
Measurement
Techniques

Supplement of

A high-accuracy dynamic dilution method for generating reference gas mixtures of carbonyl sulfide at sub-nanomole-per-mole levels for long-term atmospheric observation

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1 **Description**

2 We conducted three experiments described below to examine the factors that affect the dilution precision

3 of our dynamic dilution method with respect to carbonyl sulfide (COS). We present the key findings,

4 upon which we based our development of the dynamic dilution method described in the main text. Note

5 that the experiments presented here are referred to as the pilot study in the main text of this study.

6

7 **1 Experiment-S1**

8 We initiated the pilot study by constructing a simple dilution system that blended two gas flows of a

9 parent and a diluent gas; the gas flows were monitored by a Molbloc system and regulated by thermal-

10 based mass flow controllers (MFCs). The experimental system and gases were the same as those

11 described in Sect. 2 in the main manuscript, except that the experimental system did not include the

12 branch exhaust system. To condition the experimental system before starting the experiment, we purged

13 the system for 30 min with the parent and diluent gases at the flow rates that would be set in the dilution

14 experiment. Similarly, after the system purge, one preliminary measurement of the dynamically

15 generated gas mixture was conducted to minimise adsorption and desorption effects of COS on inner

16 surface of the gas chromatography–mass spectrometry (GC/MS)-based sample determination system

17 (hereafter referred as GC/MS measurement system) (described in Sect. 2.4 in the main manuscript)

18 before the target gas determination (COS and chlorodifluoromethane [HCFC-22]). In this experiment,

19 the flow rates for the diluent and parent gases were set at approximately 5000 and 2.5 mL/min by volume,

20 respectively, via MFCs A and B (see Fig. 1 in the main manuscript). The mole fractions of the target

21 gases in the generated gas mixture were determined by using the GC/MS measurement system.

22   Figure S1 shows example data from the Molbloc and the GC/MS measurements during the first

23 gas dilution experiment (EX-S1: Experiment-S1). We calculated mole fractions along with relative

24 standard deviations (RSDs) for the target gases in the dynamically generated gas mixture from each

25 Molbloc and GC/MS measurement. The mole fractions of the target gases from the Molbloc

26 measurements were directly calculated from the measured mass flow rates for the parent and diluent

27 gases; however, we only obtained a normalised ratio, which was calculated as a ratio of the GC/MS

response of COS in a sample gas mixture to that in a reference gas mixture from GC/MS measurements as expressed in Equation (3) in the main text because we had no reliable reference gas mixtures of COS with a known mole fraction at ambient level at that time. In order to compare the results from the GC/MS measurements with those from the Molbloc system, it was necessary to determine the mole fraction of COS in the reference gas mixture for the calculation of the COS mole fractions from the normalised ratios from the GC/MS measurements. Therefore, in this experiment, we estimated the mole fractions of the target gases in an ambient-air-based reference gas mixture (hereafter referred as GC/MS reference gas) based on the measurement results. The estimate was obtained to minimise the differences between the COS values determined by the Molbloc system and the GC/MS measurements obtained in each experiment by the linear least-squares method, as follows:

$$[\widehat{COS}]_{ref} = \text{Arg min} \left\{ \sum_{i=1}^{n} \left(\frac{R_{dyn,i}}{\hat{R}_{ref,i}} \times [COS]_{ref} - [COS]_{Molbloc,i} \right)^2 \right\}, \quad (S1)$$

where Arg min is a function that defines the decision variable minimising the objective function shown in the braces in Equation (S1). The bracketed COS-hat on the left-hand side is the estimated mole fraction of COS in the reference gas mixture. Similarly, on the right-hand, the variables R_{dyn} and $R\text{-hat}_{ref}$ denote the GC/MS responses of COS in the dynamically generated gas mixture and the estimated GC/MS response by linear interpolation of the GC/MS responses from the measurements of reference gas mixtures before and after the measurements of a sample gas mixture, respectively. The bracketed COS with subscripts *ref* and *Molbloc*, is the mole fraction of COS in the reference gas mixture as the decision variable and the calculated COS value from the Molbloc measurements, respectively. It should be noted that if the target gases were generated according to the dilution ratio, the consistent reference value should be obtained in each experiment, but if this is not the case, this would indicate the occurrence of a dilution bias. The estimated reference values can therefore be used as a diagnostic parameter for dilution precision.

From the Molbloc measurements, the average calculated mole fraction was 503.7 pmol mol^{-1} for

COS and 499.1 pmol mol^{-1} for HCFC-22, and the corresponding RSDs were both about 0.1%. These results showed that the mass flow rates for the parent and diluent gases remained highly stable during the experiments. In contrast, mole fractions of COS and HCFC-22 from the GC/MS measurements against the estimated GC/MS reference value showed a gradual increase in the mole fractions of the generated target gases in response to the increase in the number of measurements, resulting in a large variability. The observed RSDs for COS and HCFC-22 were 1.0% and 0.8%, respectively, which are greater than the typical analytical precision of the GC/MS (approximately 0.5%) determined from repeated measurement of a compressed cylinder gas (Fig. S1a, b). The ratio of the COS mole fraction to that of HCFC-22 was distributed around 1.01, which corresponds to the ratio for the nominal values for the target gases in the parent gravimetric gas mixture (Fig. S1c) and showed no clear systematic variation. This indicates that COS and HCFC-22 were increased at nearly the same rate, but the observed gradual increase suggested that there was systematic bias in the gas blending process that could not be directly explained from the measurement of the mass flow rate. This implied that the estimated GC/MS reference gas values of 564.0 pmol mol^{-1} for COS and 293.1 pmol mol^{-1} for HCFC-22 were probably both biased and included a large uncertainty.

Further inspection of the Molbloc measurements showed that the parent gas pressure linearly increased, whereas that for the diluent gas was nearly constant during the experiment (Fig. S1d). This might be due to a lack of stability arising from the pressure regulator's being used at very low flow rate. The parent gas pressure increased by 12% from the preliminary to the fifth measurement. Similarly, the mass flow rate of the parent gas showed a slight gradual increase from the preliminary measurement (Fig. S1e). The increase of the parent gas flow rate from the preliminary to fifth measurement was about 0.5%, whereas the increase for the diluent gas was only marginal. These results suggested that the increase of the parent gas pressure could be responsible for the observed increases of the target gases.
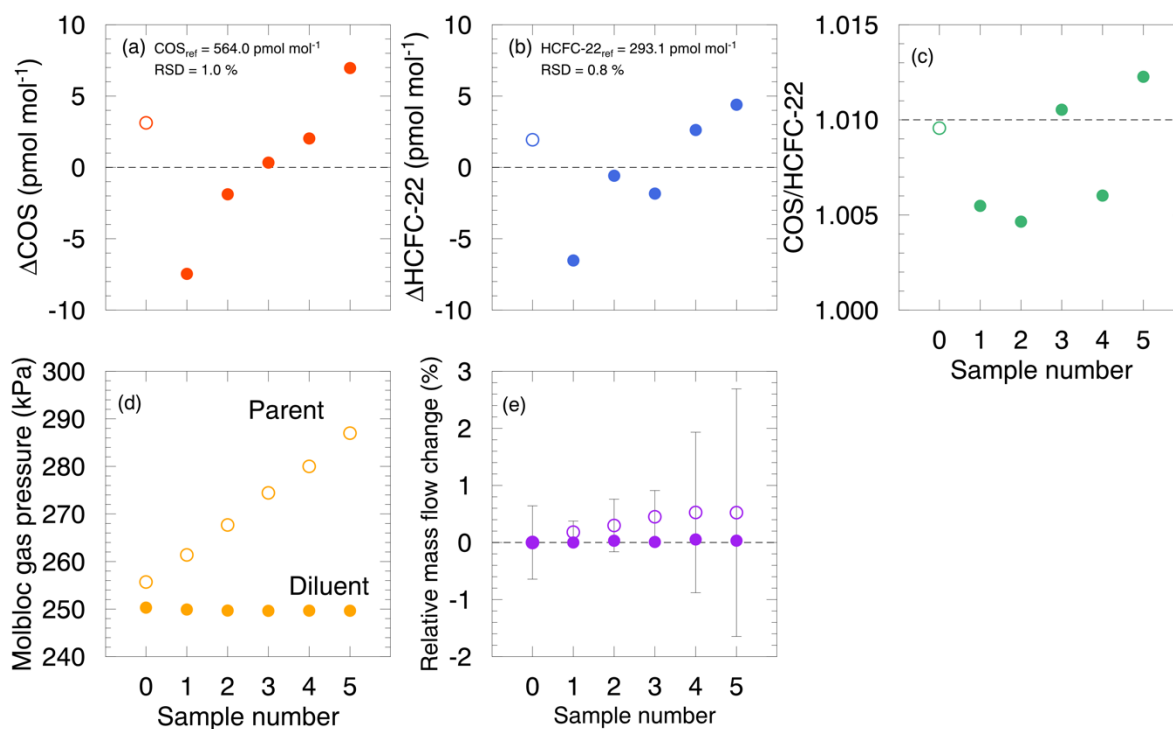
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2 **Figure S1: Example data from the gas dilution experiment S1 (EX-S1). The deviations of the mole**

3 **fractions of COS (a) and HCFC-22 (b) in dynamically generated gas mixtures, as determined by**

4 **the GC/MS-based sample determination system from those determined through the Molbloc**

5 **system that are plotted against the sample number. (c) The ratio of the determined mole fraction**

6 **of COS to that of HCFC-22. Open circles in (a–c) indicate data from the preliminary measurement**

7 **(sample number zero). The GC/MS measurements were calibrated with a GC/MS reference gas,**

8 **for which the mole fractions of COS and HCFC-22 were estimated as COS_{ref} (a) and HCFC-22$_{ref}$**

9 **(b), respectively. The estimate of these reference values was calculated from the data, excluding**

10 **the preliminary measurements according to Equation (S1). The variability of the mole fractions**

11 **of COS and HCFC-22 determined by the GC/MS measurements was also expressed as relative**

12 **standard deviation (RSD). The dashed line in (c) indicates the ratio of the mole fraction of COS**

13 **to that of HCFC-22 derived from the nominal values in the parent gas mixture. Gas pressures and**

14 **relative change in mass flow rates for the parent and diluent gases, respectively, as recorded by**

15 **the Molbloc system (d, e). The data for the parent and diluent gases are expressed as open and**

16 **filled circles, respectively. In (e), the error bars represent standard deviations calculated from the**

4

1   **Molbloc measurements.**

2

3   **2 Experiment-S2**

4   To investigate the possible influence of gas pressure on the gas mixing, we performed a gas dilution

5   experiment in which the gas pressures both for the parent and diluent gas were adjusted at every diluted

6   gas generation to keep the gas pressures constant during the experiment (EX-S2: Experiment S2). In

7   EX-S2, the diluted gas mixture was generated with the same flow rates as those used in EX-S1 (2.5

8   mL/min for the parent gas and 5000 mL/min for the diluent gas). Also, the estimate of the mole fractions

9   for the target gases in the reference gas mixture and the subsequent calibration were conducted in the

10   same manner as in EX-S1. The pressure was controlled manually by using the cylinder regulator and

11   the pressure regulating valve for the parent and diluent gas, respectively, and both pressures were

12   adjusted to match each other within ±1 kPa based on the Molbloc reading measured at the Molbloc

13   elements before the start of the analysis of the generated gas mixture. After allowing 10 min of

14   stabilization time at the adjusted condition, the generated gas mixture was introduced into the GC/MS

15   measurement system for analysis.

16   Figure S2 shows example data from EX-S2. Different behavior in the obtained target gas mole

17   fractions compared with EX-S1 was observed. First, focusing on HCFC-22, we found a marked

18   improvement in repeatability for the GC/MS values (Fig. S2b) with the pressure regulation; the RSD

19   value was decreased to 0.2% in EX-S2 in comparison to 0.8% in EX-S1. The obtained RSD was close

20   to that from the Molbloc measurements (0.14%), regardless of whether the analytical error of the GC/MS

21   was included. In addition, no gradual increase with pressure was observed in the generated HCFC-22

22   values. The estimated reference value was 288.4 pmol mol^{-1}, which was decreased by about 5 pmol

23   mol^{-1} from that determined in EX-S1 (293.1 pmol mol^{-1}). This difference suggested that the systematic

24   bias was a result of the gas pressure condition.

25   In contrast, no significant improvement was obtained for COS (Fig. S2a). The mole fraction of

26   COS showed a logarithmic increase larger than that observed in EX-S1, even though the experiment

27   was conducted with the same protocol as in EX-S1. A similar logarithmic increase was observed in the

1 ratio of COS to HCFC-22 (Fig. S2c), and the estimated COS reference value was 596.2 pmol mol^{-1},

2 which was substantially higher than the value from EX-S1 (564.0 pmol mol^{-1}). Considering the result

3 for HCFC-22, pressure regulation must be a key factor for obtaining high-precision dynamic dilution;

4 however, the result for COS implied that there were other factors influencing the dilution precision. The

5 observed logarithmic increase in the generated mole fraction of COS, as well as in the ratio of COS to

6 HCFC-22, suggested that the observed dilution bias was specific to COS, which might be related to

7 differences of the physical properties between COS and HCFC-22.

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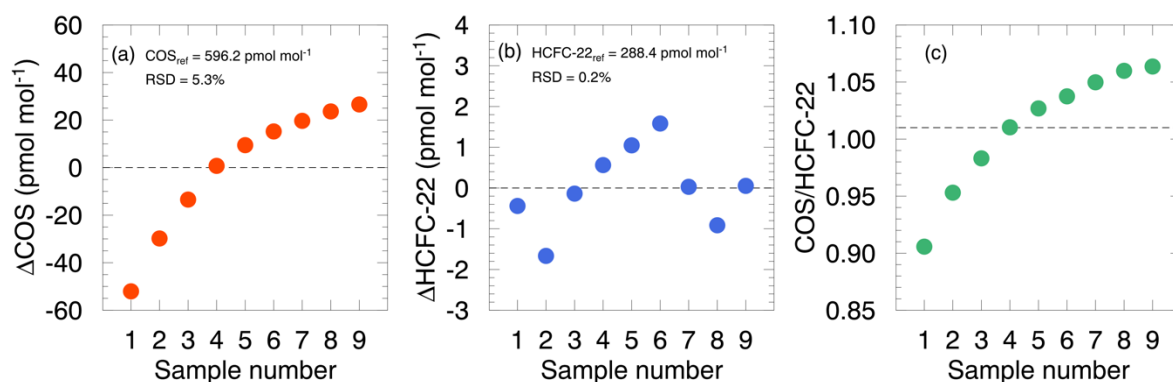
10 **Figure S2: Results from EX-S2. Panels are as described in the caption for Fig. S1a–c.**

11

12 **3 Experiment-S3**

13 To examine the potential dependence of dilution precision on flow rate, we conducted a dilution

14 experiment similar to that conducted in EX-S2 but with the parent flow rate set at 10 mL/min (EX-S3:

15 Experiment-S3). In this experiment, we obtained good repeatability for HCFC-22; the RSD value was

16 0.2%, which was comparable to that obtained in EX-S2 (0.2%) (Fig. S3). The estimated HCFC-22 value

17 for the reference gas mixture was 290.2 pmol mol^{-1}. A slightly higher value was obtained from EX-S3

18 compared to that from EX-S2 by about 1.7 pmol mol^{-1} (288.4 pmol mol^{-1} from EX-S2), but the value

19 was still lower than that from EX-S1. Among the pilot experiments, the EX-S1 value was the highest,

20 which we attribute to the systematic dilution bias observed in EX-S1. Therefore, the estimated values

21 from EX-S2 and S-3 without apparent dilution bias should be closer to the true value.

1   For COS, a gradual increase in the generated COS mole fraction, similar to the results obtained in

2   EX-S2, was subsequently observed in EX-S3, whereas the ratios of COS to HCFC-22 were randomly

3   distributed around the mole fraction ratio corresponding to that of the nominal value in the parent gas.

4   The obtained RSD value for COS was 0.3%, which was the smallest obtained from the pilot experiments.

5   Furthermore, the RSD value was comparable to that for HCFC-22 and was within the typical analytical

6   precision of approximately 0.5%. Therefore, the observed gradual increase may indicate the occurrence

7   of a COS-specific bias even at the increased flow rate, but the impact of the COS-specific bias was

8   considerably reduced. These results showed that the occurrence of the COS-specific bias was

9   independent of the flow rate of the parent gas and that the magnitude of this systematic pattern was not

10   proportional to the flow rate. Simultaneously, the obtained results implied that the estimated COS

11   reference value of 554.2 pmol mol^{-1} should be closer to the true value, similar to the results of HCFC-

12   22.

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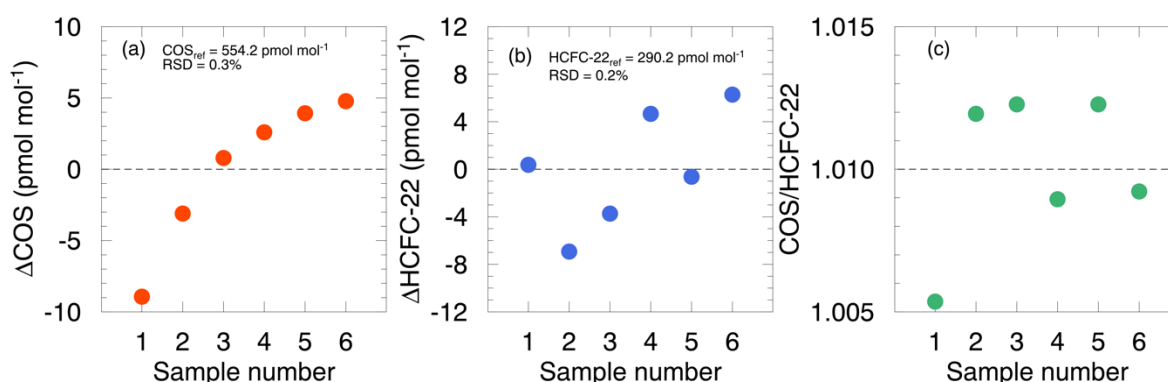
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15   **Figure S3: Results from EX-S3. Panels are as described in the caption for Fig. S1a–c.**

16

17   **Discussion for the development of a dynamic dilution system**

18   Our pilot studies showed that there was an undefined mechanism leading to a COS-specific bias.

19   Although no clear explanation can be given at this stage, we can suggest some possible factors

20   contributing to the bias. The most plausible factor is adsorption and desorption of COS onto the inner

21   surface of the flow path in the dilution system. Under non-equilibrium conditions for the adsorption and

desorption of COS, adsorption loss should be observed strongly in the early stage of the experiment. By repeating the dilution experiment, the condition of the dilution system moved closer to equilibrium, and consequently, the amount of COS lost decreased gradually, resulting in an apparent gradual increase of generated COS. Because the observed impact of the COS adsorption loss likely depends on the initial equilibrium condition in the dilution system, it is reasonable that the COS-specific bias was not consistently reproduced in the pilot experiments.

To examine the contribution of the COS adsorption loss, we tested whether preconditioning of the dilution system from the day before the dilution experiment could improve the dilution bias. This preconditioning involved keeping the dilution system under the same constant pressure as used for the gas generation by closing the related valves and preventing any pressure release. However, even after this overnight preconditioning, we observed a significant COS-specific bias in the next dilution experiment. This may suggest that there are additional factors that explain the dilution bias while we cannot completely remove the contribution of COS adsorption loss.

The remaining possible factors for the COS-specific bias might be the involvement of factors related to the cylinder and regulator causing fractionation of the outflowing target gases. As we observed in EX-S3, an increase in the parent gas flow rate resulted in reducing the impact of the COS-specific bias. If the flow rate of the parent gas is related to the COS-specific bias, it may be that the cylinder and regulator were involved in the occurrence of the COS-specific bias before the parent gas flowed into the dilution system. Based on these considerations, we next improved the dilution method by focusing on the possible dilution bias arising from both COS adsorption loss and also from factors related to the cylinder and regulator. To address the possible adsorption loss of COS, we increased the purge time of the dilution system before every diluted gas generation and controlled the system pressure more precisely to prevent any shift of the adsorption–desorption equilibrium. To address the possible dilution bias due to the cylinder and regulators, we tested the flow rate dependency by increasing the parent gas flow rate out from the cylinder via the regulator at over 10 sccm. To increase the parent gas flow rate without altering the mole fraction of COS in the generated gas mixture, an exhaust system was installed so that only the gas flow needed for the dilution was introduced into the mixing chamber and the excess

1 flow was exhausted out of the dilution system. In the main text, we evaluated the effectiveness of the

2 above strategy by conducting repeatability and reproducibility tests in which the impact of the COS-

3 specific bias was considered.