1   *Supplemental information*

3   **A high-accuracy dynamic dilution method for generating reference gas**

4   **mixtures of carbonyl sulfide at sub-nanomole-per-mole levels for long-term**

5   **atmospheric observation**

7   Hideki Nara, Takuya Saito, Taku Umezawa, Yasunori Tohjima

9   National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

10

11   *Correspondence to*: Hideki Nara (nara.hideki@nies.go.jp)

12

13   **Description**

14   We conducted three experiments described below to examine the factors that affect the dilution accuracy

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

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

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

18

19   **1 Experiment-S1**

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

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

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

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

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

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

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

1 generated gas mixture was conducted to eliminate blank COS accumulated in the gas chromatography–

2 mass spectrometry (GCMS)-based sample determination system (described in Sect. 2.4 in the main

3 manuscript). In this experiment, the flow rates for the diluent and parent gases were set at approximately

4 5000 and 2.5 mL/min by volume, respectively, via MFCs A and B (see Fig. 1 in the main manuscript).

5 The mole fractions of the target gases (COS and chlorodifluoromethane [HCFC-22]) in the generated

6 gas mixture were determined by using the sample determination system.

7   Figure S1 shows example data from the GCMS and the Molbloc measurements during the first gas

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

9 deviations (RSDs) for the target gases in the dynamically generated gas mixture from each GCMS and

10 Molbloc measurement. The COS values from the Molbloc measurements were directly calculated from

11 the measured mass flow rates for the parent and diluent gases, whereas those from the GCMS

12 measurements were calculated by assigning the COS value in the reference gas mixture used for the

13 GCMS calibration based on the Molbloc COS values. Assignments were made to minimize the

14 difference between the calculated and calibrated COS values from the Molbloc and the GCMS,

15 respectively, as below:

16

17 $[COS]_{reference} = Arg \min\{\sum([COS]_{GCMS} - [COS]_{Molbloc})^2\}$,   (S1)

18

19 where the bracketed COS is the mole fraction of COS corresponding to the subscripted variables

20 *reference*, *GCMS*, and *Molbloc.* These three variables indicate the assigned COS value for the reference

21 gas mixture, the COS value from the GCMS measurements calibrated against the assigned reference

22 value, and the calculated COS value from the Molbloc measurements, respectively.

23   The average calculated mole fraction from the Molbloc measurements was 503.7 pmol mol^{-1} for

24 COS and 499.1 pmol mol^{-1} for HCFC-22, and the corresponding RSDs were both about 0.1%. These

25 results showed that the mass flow rates for the parent and diluent gases remained highly stable during

26 the experiments. In contrast, the GCMS measurements showed a gradual increase in the mole fractions

1   of the generated target gases in response to the increase in the number of measurements, resulting in a

2   large variability. The observed RSDs for COS and HCFC-22 were 0.97% and 0.77%, respectively,

3   which are greater than the typical analytical precision of GCMS (0.5%) (Fig. S1a, b). The ratio of the

4   COS mole fraction to that of HCFC-22 was distributed around 1.01, which corresponds to the ratio for

5   the nominal values for the target gases in the parent gravimetric gas mixture (Fig. S1c) and showed no

6   clear systematic variation. This indicates that COS and HCFC-22 were increased at nearly the same rate.

7   The discrepancy between the results from the measurements by the Molbloc and the GCMS suggested

8   that there was systematic bias in the gas blending process that could not be directly explained from the

9   measurement of the mass flow rate. This implied that the assigned values of 564.0 pmol mol^{-1} for COS

10   and 293.1 pmol mol^{-1} for HCFC-22 were probably both biased and included a large uncertainty.

11   Further inspection of the Molbloc measurements showed that the flow pressure for the parent gas

12   linearly increased, whereas that for the diluent gas was nearly constant during the experiment (Fig. S1d).

13   This might be due to a lack of stability arising from the pressure regulator's being used at very low flow

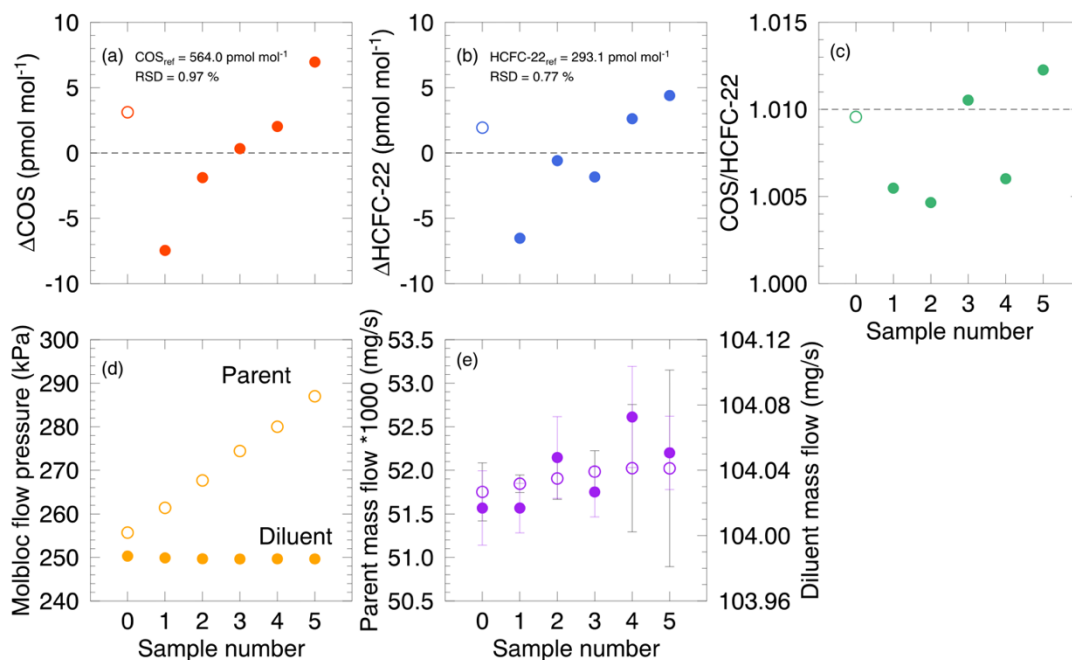
14   rate. The flow pressure increased by 12% from the preliminary to the fifth measurement. Similarly, the

15   mass flow rate of the parent gas showed a slight gradual increase from the preliminary measurement

16   (Fig. S1e). The increase of the parent gas flow rate from the preliminary to fifth measurement was about

17   0.5%, whereas the increase for the diluent gas was only marginal. These results suggested that the

18   increase of the parent flow pressure could be responsible for the observed increases of the target gases.

19

2 **Figure S1: Example data from the gas dilution experiment S1 (EX-S1). Deviations of the mole**

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

4 **the GCMS-based sample determination system from those determined with the Molbloc system**

5 **were plotted against the sample number. (c) Ratio of the determined mole fraction of COS to that**

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

7 **number zero). The GCMS measurements were calibrated with a reference gas mixture for which**

8 **the mole fractions of COS and HCFC-22 were assigned as COS_{ref} and $HCFC-22_{ref}$, respectively,**

9 **based on the Molbloc measurements. Then, reference values and relative standard deviations were**

10 **calculated from the data excluding the preliminary measurements. The dashed line in (c) indicates**

11 **the ratio of the mole fraction of COS to HCFC-22 derived from the nominal values in the parent**

12 **gas mixture. (d, e) Flow pressures and mass flow rates for the parent and diluent gas, respectively,**

13 **as recorded by the Molbloc. The data for the parent and diluent gases are expressed as open and**

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

15 **the Molbloc measurements.**

16

17 **2 Experiment-S2**

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

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

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

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

5   mL/min for the parent gas and 5000 mL/min for the diluent gas). Also, the assignment of the mole

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

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

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

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

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

11 stabilization time at the adjusted condition, the generated gas mixture was introduced into the sample

12 determination system for analysis.

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

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

15 improvement in repeatability for the GCMS values (Fig. S2b) with the pressure regulation; the RSD

16 value was decreased to 0.19% in EX-S2 in comparison to 0.77% in EX-S1. The obtained RSD was close

17 to that from the Molbloc measurements (0.14%), regardless of whether the analytical error of the GCMS

18 was included. In addition, no gradual increase was observed in the generated HCFC-22 values. The

19 assigned reference value was 288.4 pmol mol^{-1}, which was decreased by about 5 pmol mol^{-1} from that

20 determined in EX-S1 (293.1 pmol mol^{-1}). This difference suggested that the systematic bias was a result

21 of the flow pressure condition.

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

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

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

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

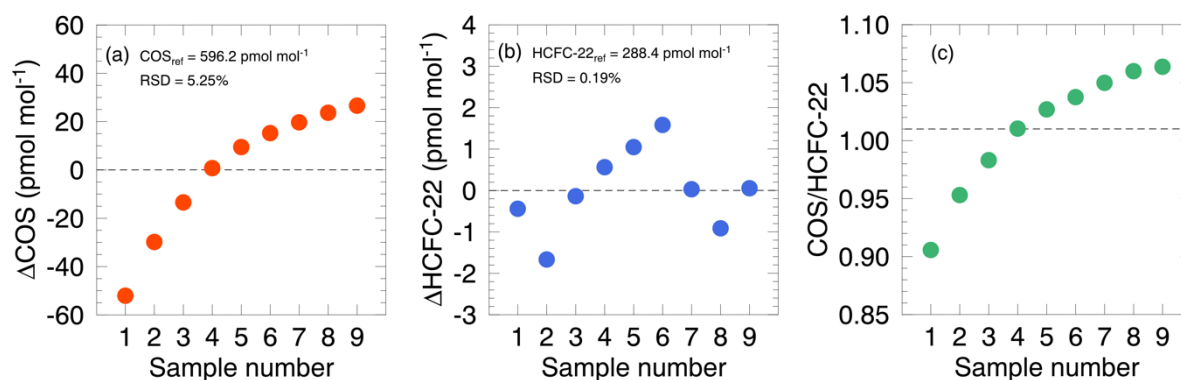
26 which was substantially higher than the value from EX-S1 (564.0 pmol mol^{-1}). Considering the result

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

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

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

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

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

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

9 **3 Experiment-S3**

10 To examine the potential dependence of dilution accuracy on flow rate, we conducted a dilution

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

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

13 0.22%, which was comparable to that obtained in EX-S2 (0.19%) (Fig. S3). The assigned HCFC-22

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

15 EX-S3 compared to that from EX-S2 by 1.8 pmol mol^{-1} (288.4 pmol mol^{-1} from EX-S2), but the value

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

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

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

19   For COS, a gradual increase in the generated COS mole fraction was again observed as in EX-S2,

20 whereas the ratios of COS to HCFC-22 were randomly distributed around the mole fraction ratio

21 corresponding to that of the nominal value in the parent gas. The obtained RSD value for COS was

0.29%, which was the smallest obtained from the pilot experiments. Furthermore, the RSD value was comparable to that for HCFC-22 and was within the typical analytical precision of ±0.5%. Therefore, the observed gradual increase may indicate the occurrence of a COS-specific bias even at the increased flow rate, but the impact of the COS-specific bias was considerably reduced. These results showed that the COS-specific bias was not proportional to the flow rate of the parent gas.

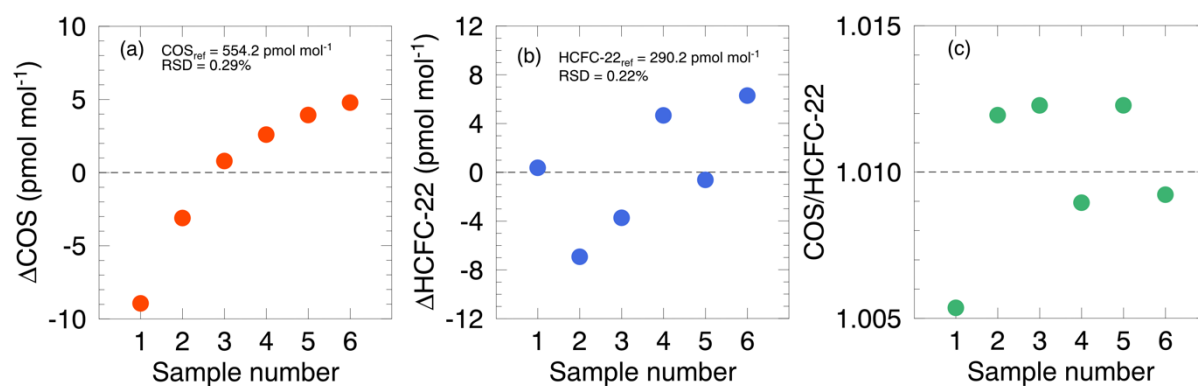



Figure S3: Results from EX-S3. Panels are as described in the caption for Fig. S1a–c.

Discussion for the development of a dynamic dilution system

Our pilot studies showed that there was an undefined mechanism leading to a COS-specific bias. Although no clear explanation can be given at this stage, we can suggest some possible factors contributing to the bias. The most plausible factor is adsorption and desorption of COS onto the inner 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 suggests 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 flow was exhausted out of the dilution system. In the main text, we evaluated the effectiveness of the above strategy by conducting repeatability and reproducibility tests in which the impact of the COS-specific bias was considered.