Response to Reviewers of Manuscript

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
by H. Nara et al.

We are grateful to the referee for their time and comments on our manuscript. We considered all the comments to have them incorporated into our manuscript, which we acknowledge has led to substantial improvement. Below we detail our responses in blue plain text along with the original comments from the referees in *italic*.

Reviwer#1

◎*General comments*
This study developed a dynamic dilution method for generating COS reference gas mixtures at ambient level, which would avoid issues related to poor stability of COS stored in high-pressure cylinders. Good performance in terms of repeatability, repeatability, linearity, and accuracy was obtained, demonstrating this method can be used for accurate long-term COS observations and applied to the preparation of other reference gases containing unstable species. Overall, the manuscript is well-written. Therefore, I suggest accepting this manuscript for publication after addressing my comments below.

Thank you for this positive comment.

◎Specific comments

Comment 1
It is better to mention the WMO goal for COS measurement (such as inter-laboratory compatibility or other requirements) somewhere if available.

To our knowledge, there has been no WMO goal established for COS measurement. Regarding this, however, intercomparison experiments of COS measurements showed presence of large differences among laboratories (Hall et al., 2014). Since then, atmospheric COS observations have gained increasing attention and measurement techniques have been advanced. Our present work will contribute to discussion about a compatibility goal in the international research community such as via WMO.

Comment 2

Page 11: Please check the two formulas carefully. The comma at top right of the parentheses in Formula (1) should be removed, as well as the superscript "2" at far right of Formula (2).

For Formula (1), we have confirmed that a comma has been inserted after the description of the equation. This visibility problem can be caused by Microsoft Word software. We have also changed Formula (2), accordingly.

Comment 3

Page 11, line 26: According to Figure 2, the uncertainty "increased" rather than "decreased" with a decreasing flow rate.

We have changed the text accordingly.

Comment 4

Page 23, line 3: Generally, uncertainty of reference gas is combined by a series of components which include but not limited to measurement error. So is it appropriate to define the uncertainty as standard error here? Or if there are some literatures to support this?

Thank you for your valuable comments. Indeed, the number of experimental data may not be sufficient to determine whether the combined uncertainty associated with the analysis follows a normal distribution. We have decided to follow your suggestion and use standard deviation instead standard errors. Please see Table 3, line 4 on page 24.

Comment 5

According to Figure 4 and Table 3, the measurement of COS seemed to be more stable than that of HCFC-22, although the latter is identified as the one with greater stability. Are there some potential reasons related to this discrepancy?

We thank the referee for this important question. Our current consideration is as follows.

We believe that the measurement result could be influenced by differences in the physical properties of COS and HCFC-22. As we described in the discussion section, COS has stronger adsorption property than HCFC-22. If COS was physically adsorbed on wetted surfaces of the dilution system, then COS can also be desorbed reversibly depending on COS mole fractions in the sample gas mixture at the surface. Although, in our linearity test for the dilution system, no significant memory effects were observed on COS against large increment/decrement change of 50 pmol mol-1 present in Figure 5, the absorption/desorption of COS could buffer against slight fluctuations of COS mole fractions in the generated gas mixture once after COS has reached absorption/desorption equilibrium with the internal surface of the dilution system. We do not include these speculative considerations in our text, but we need to understand above consideration for more high accuracy measurements of COS.

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Reviwer#2

◎*General comments*

This paper describes a method to produce a reproducible, traceable gas stream containing carbonyl sulfide at the parts-per-trillion level for calibration purposes. While dynamic dilution systems have been described previously, this paper introduces some additional controls to stabilize pressure, which they show are important for large dilution ratios and a small (10 cc/min) flow of parent gas that interacts via adsorption/desorption with surfaces, such as carbonyl sulfide. The scientific methods are sound and the conclusions are reasonable. Some of the terminology used could be improved (see comments below).

Thank you for this positive comment. The referee's comments below are accurate and helpful feedback and were very helpful in revising the manuscript. Our responses are listed below.

◎Specific comments

Comment 1
Pg 3. Line 11: Need a space before "Wehr"

We have made the correction accordingly.

P3, line 11
Original: …Maseyk et al., 2014;Wehr et al., 2016; Yang et al., 2018…
Corrected: …Maseyk et al., 2014; Wehr et al., 2016; Yang et al., 2018…

Comment 2
Pg 3, line 20: Are you sure you have the correct citation? COS is known to be unstable in some

cylinders, but I don't recall that being demonstrated in the Hall et al. (2014) paper, and certainly not to the point we would say that stability is the most important factor limiting our understanding its global distribution and budget. The seasonal cycle of COS is several 10s of ppt in the northern hemisphere, and while smaller in magnitude, is clearly detectable in the southern hemisphere. Spatial gradients in COS are observable, despite issues related to stability in cylinders.

Thank you for your thorough criticism. We agree to the referee in that seasonality and spatial gradients are observable against reference COS values if the COS drift can be detected and corrected reasonably. However, if not the case, observation data from different laboratories could be suffered from systematic biases due to individual COS calibration scales. We have made the following change.

Original: The fundamental reason for this is the difficulty in establishing reliable reference gas mixtures containing ambient levels of COS (ca. 500 pmol mol^{-1}) due to the instability of COS stored in high-pressure cylinders (Hall et al., 2014).

Corrected: One fundamental reason for this is the difficulty in establishing reliable reference gas mixtures containing ambient levels of COS (ca. 500 pmol mol^{-1}). Hall et al. (2014) reported significant differences of the COS measurements from the laboratories from the inter-comparison experiment. This might be attributed to the instability of COS stored in high-pressure cylinders as well as difficulties in accurate COS measurements.

<u>Comment 3</u>

Pg 4, line 5: Consider changing the sentence to "In addition, gravimetric dilution into cylinders may introduce uncertainties related to surface effects that can vary by cylinder type."

We have made the following corrections.

Page 4, lines 6 – 8

Original: This multistep procedure results in the accumulation of preparation uncertainty. In addition, the prepared gas mixtures were filled in a gas cylinder, in which storage stability was not guaranteed for gases such as COS.

Corrected: This multistep procedure results in the accumulation of preparation uncertainty from weighing, and in addition, gravimetric dilution into cylinders may introduce uncertainties related to surface effects that can vary by cylinder type.

Comment 4

Pg 6, line 19: How much is a small amount of COS in the dilution gas? Can you be more specific? < 1 ppt?, 5 ppt?

At the time of the experiment, approximately 8 pmol mol^{-1} of COS was detected from measurements of the COS-free gas from alternate injection of an ambient-air-based reference gas mixture and the COS-free gases (purified air, high purity nitrogen and helium). However, repeated measurements of the high purity nitrogen as diluent gas without injection of the ambient-air-based reference gas mixture showed that the GC/MS response of COS progressively decreased and eventually fell below the detection limit. This indicates that the presence of COS was not significant in the GC/MS measurement system and in the gas cylinders used in our experiments. Also the repeated measurements indicates that the detected 8 pmol mol^{-1} of COS was memory effect due to desorption of COS which was absorbed in the GC/MS measurement system during measurements of the ambient-air-based reference gas mixture before injection of the COS-free gases. From the test for dilution linearity in Section 4.2, we observed excellent linearity for COS. This linearity test supports that the memory effect was not at a significant level within the mole fraction range studied in the experiment, contrasting to the measurements of COS-free gases. In light of these considerations, we have carefully revised the following

Page 6, line 18 – 25

Original: The presence of COS as a contaminant in the diluent gas was verified···, which may have biased the determination of COS and HCFC-22 in our experiments.

Corrected: The presence of COS as a contaminant in the diluent gas was verified before each experiment using a GC/MS measurement system (see Section 2.4). Repeated measurements of the diluent gas showed that small amounts of COS (but not HCFC-22) were detected initially, but the amounts decreased with the number of measurements and were finally below the detection limit. This COS decrease was most likely ascribed to adsorption/desorption in the GC/MS system, rather than the contamination from the dilution gas as well as helium gas used as the carrier gas for the GC/MS system. These repeated measurements of the diluent gas ensured that there was no COS contamination from the diluent or carrier gases, which may have biased the determination of COS and HCFC-22 in our experiment.

Comment 5

Pg 8, line 13: The term "flow pressure" is used several times, while "pressure" is also used. For "flow pressure" do you mean the pressure applied to the MFC? I can see how you *would want to keep the pressures on the mass flow controllers constant, but the term "flow pressure" may not be a well-known term.*

According to your suggestion, we have made the following corrections at several relevant places.

Page 6, line 13
Original: The outflow pressures from the parent and diluent gas cylinders…
Corrected: The pressures of the parent and diluent gases supplied from respective cylinders…

Page 8, line 18
Original: for dynamic buffering of the parent flow pressure…
Corrected: for dynamic buffering of the parent gas pressure…

Page 9, line 18
Original: …the flow pressures of the two gas flows were adjusted to…
Corrected: …the pressures of the two gases downstream respective Molbloc elements were adjusted to…

Page 9, line 26
Original: The flow pressure of the diluent gas…
Corrected: The pressure of the diluent gas…

Page 10, line 4
Original: …with the outflow pressure set by the cylinder regulator…
Corrected: …with the pressure set by the cylinder regulator…

Page 10, line 12
Original: …to facilitate the stabilisation of the parent flow pressure…
Corrected: …to facilitate the stabilisation of the parent gas pressure…

Page 27, line 21
Original: …and stabilise the flow pressure of the gravimetric parent gas…
Corrected: …and stabilise the pressure of the gravimetric parent gas…

Comment 6

Pg 10, line 23: Were internal surfaces of the static mixer also coated with Sulfinert?

As described in lines 26 – 27 on page 8, the static mixer was electrically polished but not coated with Sulfinert. The description has been amended as follows:

Original: To prevent the possible loss of COS by adsorption, a Sulfinert coating (Restek Corporation, PA) was applied to all tubes, fittings, and valves that were exposed to the parent gas and generated gas mixtures.

Corrected: To prevent the possible loss of COS by adsorption, a Sulfinert coating (Restek Corporation, PA) was applied to all tubes, fittings, and valves that were exposed to the parent gas and generated gas mixtures, except the static mixer.

Comment 7

Pg 14, line 9: You say that ambient air reference standards prepared in aluminum cylinders are unstable. Please clarify if these were dry air, or humidified air. In the previous section you discussed a reference standard that was humidified to 500 ppm H2O to enhance COS stability.

We have added the description whether cylinder condition was dry or humid throughout the manuscript. We note here that only dry reference gas mixtures of COS were available from the Japanese gas manufacturer due to their quality assurance policy. The availability was the main reason why our tests for COS stability in high-pressure aluminium cylinders were examined with dry reference gas mixtures of COS at ambient levels.

Page 14, line 19 –

Original: In the past, we have prepared several COS reference gas mixtures at ambient levels filled in high-pressure aluminium cylinders by the gravimetric method…

Corrected: In the past, we have prepared several dry reference gas mixtures of COS at ambient levels filled in high-pressure aluminium cylinders by the gravimetric method…

Related amendments:

Page 2, line 7 – 8

Original: …measurement system and a gravimetrically prepared gas mixture containing…

Corrected: …measurement system and a dry reference gas mixture prepared gravimetrically as parent gas mixture containing…

Page 4, line 26 – 27

Original: …long-term stability of COS stored in…

Corrected: …long-term stability of a dry reference gas mixture of COS stored in…

Page 5, line 26

Original: …A gas mixture of COS and chlorodifluoromethane…

Corrected: …A dry gas mixture of COS and chlorodifluoromethane…

Page 14, line 19

Original: …we have prepared several COS reference gas mixtures at ambient levels…

Corrected: …we have prepared several dry reference gas mixtures of COS at ambient levels…

Page 15, line 2: Figure caption

Original: Time-series variation of the COS mole fraction in a reference gas mixture during long-term storage in a high-pressure aluminium cylinder.

Corrected: Time-series of COS mole fraction in a non-passivated high-pressure aluminium cylinder. The standard gas was prepared gravimetrically to contain approximately 500 pmol mol^{-1} COS in dry nitrogen.

Page 25, line 23

Original: …investigating the stability of ambient levels of COS…

Corrected: …investigating the stability of a dry reference gas mixture containing ambient levels of COS…

Page 27, line 7

Original: …the stability of ambient levels of COS stored…

Corrected: …the stability of a dry reference gas mixture containing ambient levels of COS stored…

Page 27, line 9

Original: …at higher mole fractions (approximately 5 µmol mol^{-1}), COS gravimetric gas mixtures were…

Corrected: …at higher mole fractions (approximately 5 µmol mol^{-1}), COS dry gas mixtures were…

<u>Comment 8</u>

Pg 14, line 24: It seems strange why you chose to perform value-assignments to compressed air in a manganese (steel) cylinder as opposed to humidified ambient air in aluminum cylinders discussed on page 13. I am not questioning the results, only that the discussion includes dry air in aluminum cylinder, humidified air in aluminum cylinders, and "compressed" air in manganese (steel) cylinders. This leads to some confusion. I recommend being more specific *with respect to dry air and humidified air.*

Please see our reply to the next referee's comments 9.

<u>Comment 9</u>

Pg 15. line 5: You mention that you determined the linearity of the GC/MS using a totally separate dilutions system. Why? You created what appears to be a very good dilution system as the subject of this paper. And then later in the document you show that the dynamic dilution appears to be very linear on the GC/MS (figure 5). I don't really understand the need for the commercial system, unless you are trying to compare a commercial system to the one you built.

Before starting this study, we established automated measurement system combining the commercial dilutor and the GC/MS measurement system. If COS drift occurs in the high-pressure aluminium cylinders, a significant change in the mole fraction of COS should be observed depending on the storage time. Since the dynamic dilution system using the Molbloc system developed in this study required manual operation for dynamic gas dilution and subsequent GC/MS measurements, it was convenient to use the automated measurement system to detect such COS drift, even though the automated measurement system has a lower dilution accuracy than that of the dilution system using the Molbloc system.

We have amended the text in Section 3 taking into above contents.

<u>Comment 10</u>

Pg 15, figure 3: (i) Please provide more details about the aluminum cylinder (dry air, no passivation treatment?, etc?). Although Aculife-treated aluminum cylinders from Airgas can drift, they tend to perform much better than this. This picture gives the impression that aluminum cylinders are almost useless for COS. (ii) Also, I would argue that would be difficult to conclude that this is exponential decay based on only the 3 data points shown.

(i) We have carefully modified the figure caption as follows. We are aware that humidification greatly improves the stability of COS in aluminium cylinders. However, we prepared primary standards in dry nitrogen to avoid possible contamination caused by the humidification (due to gas manufacturer's quality assurance policy). Unfortunately, the Aculife-treated aluminium cylinders are not available in Japan.

Page 15, line 2 – 4

Original: Figure 3: Time-series variation of the COS mole fraction in a reference gas mixture during long-term storage in a high-pressure aluminium cylinder.

Corrected: Figure 3: Time-series of COS mole fraction in a non-passivated high-pressure aluminium cylinder. The standard gas was prepared gravimetrically to contain approximately 500 pmol mol^{-1} COS in dry nitrogen.

(ii) We agree with the argument about "exponential decrease" on Page 14, line12. We have amended the related sentences as below.

Page 14, line 22
Original: in which we observed an exponential decrease in the mole fraction of COS.
Corrected: in which we observed a substantial decrease in the mole fraction of COS.

Page 27, line 8
Original: Although an exponential decrease in the mole fraction of COS…
Corrected: Although a substantial decrease in the mole fraction of COS…

Comment 11
Pg 16, line 6: This is confusing. How can the commercial dynamic dilution system be both stable and unstable?

As shown in Supplemental information using Molbloc dilution system, we were also often plagued by the same problem in the dilution of reference gas mixtures containing micromole-per-mole level of COS using the commercial dilutor; determined COS values showed gradual increase/decrease with increase the number of measurements. If the measured COS values converge (stable), we can easily determine the COS mole fraction, but if this is not the case (unstable), we need to scrutinise these experimental data for COS determination. We have amended the text in Section 3 without using the term "stable" and "unstable".

Comment 12
Pg 20, line 21: I suggest referring to the traceability path here because the GCMS measurements are used in two ways:
consider: "There was a slight difference between the two average values; HCFC-22 measurements traceable to the gravimetrically-prepared mixture were approximately 2 pmol/mol lower than those traceable to the Molbloc dilution".

We agree to the comments. We have made the following amendments.

Page 21, line 25 – Page 22, line 15

Original: There was a slight difference between the two average values; the GC/MS measurements were approximately 2 pmol mol^{-1} lower than the Molbloc measurements…

Corrected: There was a slight difference between the two average values…we concluded that dynamic dilution method could accurately generate COS reference gas mixtures at ambient levels from those at micromolar-per-mole levels.

Comment 13

Pg 24, line 19: change "On the other hands" to "On the other hand"

We amended the typo accordingly.

Comment 14

Pg 28, line 8: WMO compatibility goal for CO

Thank you for suggestion. We added "for CO" into the sentence as:

Page 26 line 25 – 26

Original: …to fulfilling the WMO compatibility goal, even without gravimetric preparation…

Corrected: …to fulfilling the WMO compatibility goal for CO, even without gravimetric preparation…

Comment 15

Table 2: I think I understand this table, but the labels could lead to some confusion. This appears to be a comparison of GCMS results based on two traceability paths: dilution of a 1 ppm parent mixture to 500 ppt using the Molbloc system and a gravimetric dilution of the same 1 ppm parent mixture to 500 ppt in a cylinder (from figure 6)? In the text you say that there was a 2 ppt difference between the gravimetric standard and the dilution system. But as written, both rows in the table 2 refer to dynamic dilution. What exactly is meant by "sample determination system"? It might be easier for the reader to understand if you refer to traceability instead since evaluation requires GC/MS analysis. You have two traceability paths to make value-assignments based on GC/MS analysis a) dynamic dilution of a 1 ppm gravimetric mixture, and b) static gravimetric dilution of the same 1 ppm gravimetric mixture.

Thank you for very helpful comments. We have revised Figure 6 to make the traceability pathway easier to understand and also Table 2 to make it simpler. Also, we have amended the text in Section 4.3 with adding estimation of preparation uncertainty. These revision does not change our discussion, but we believe it improved readability.

<u>Comment 16</u>

Table 3 caption: I also find this caption confusion. Would it be correct to say:
"Table 3: Mole fraction assignments of ambient air reference gas mixture based on GC/MS analysis, calibrated using a Molbloc dilution system and a 1.01 ppm COS (1.00 ppm HCFC-22) reference standard."

Thank you for your suggestion. We have made the following changes according to your suggestions.

Original: **Table 3: Mole fraction assignment for the target gases in an ambient air-based reference gas mixture based on the measurements by the Molbloc and sample determination systems.**

Corrected: **Table 3: Mole fraction assignments of COS and HCFC-22 contained in an ambient air-based reference gas mixture based on GC/MS analysis, calibrated with a Molbloc dynamic dilution system using a parent gas mixture containing 1.01 and 1.00 µmol mol^{-1} of COS and HCFC-22.**

○Supplemental information

<u>Comment 17</u>

Pg. 2, line 10: I am still having a hard time understanding the value assignments. Since both are based on the Molbloc dilution, shouldn't they be the same? Would is suffice to say in this section, that mixing ratios based on the Molbloc (flow) were expected to have been stable, but the GC/MS measurements showed changes over time (figure S1).

This is a good suggestion to avoid complexity, but in this case a comparison between Molbloc and GC/MS would not be possible without determination of target gas mole fractions. We believe that the determination is necessary to explicitly understand the dilution precision in response to the method improvement from the experimental results described in the dilution experiments in S-1, S-2, and S-3. Nevertheless, by taking into account the comments received, we have tried to revise the text to make it more readable.

<u>Comment 18</u>

Pg 7, line 11: You mention a COS-specific bias. The COS problem looks like it is related to stability (e.g. surfaces not fully equilibrated), rather than bias. It's not like you get a stable

COS result that differs from what is expected (=bias). You saw a time-dependent change for COS. I fully agree that the problem was probably related to adsorption/desorption of COS, and that your efforts improve the system by adding exhaust flow paths are significant.

Thank you for your opinion regarding the adsorption/desorption of COS. We too consider adsorption/desorption to be the main factor for the observed COS bias, but we could not exclude the possibility that other factors contribute to the dilution uncertainty. In most dilution experiments, we observed a logarithmic change of COS in response to increase the number of sample measurements. If the bias is fully ascribed to the adsorption/desorption, a stabilized measured value of COS would imply that the system approached to equilibrium in terms of adsorption/desorption, and the value would be consistent with that calculated from the Molbloc system. However, we often observed both values differed from each other. Such differences are seldom observed in the dilution experiments after development of the present method, but the cause has not yet been identified. One possibility is COS removal on SUS316L, as suggested by Referee#3. More experiments are needed to better understand processes influencing COS mole fraction in the dynamic dilution of COS.

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Reviwer#3

◎General comments

The authors present a very valuable technical solution to a long-standing problem of calibrating analytical instruments to measure carbonyl sulfide (COS) mole fractions at the parts per trillion (ppt) level in the atmosphere. Most analytical instruments to measure trace gas mole fractions are calibrated by means of a suite of reference gases in compressed air cylinders that span a range of target gas mole fractions including the range measured in the atmosphere. Such reference gases are typically designed to last several years or even decades of continuous analysis and represent an integral component of the achievable analytical continuity. Atmospheric COS mole fractions range between 400-600 ppt. At such low COS mole fractions, compressed gas mixtures including COS show that COS mole fractions are not stable with time, thereby breaking a fundamental requirement to a suitable calibration system. The authors present a technique that circumvents the problem of low mole fractions within compressed air cylinders by using a cylinder with COS mole fractions orders of magnitude higher than atmospheric levels, followed by consecutive dilution to atmospheric levels prior to analysis. This is a technically very challenging analysis. I congratulate the authors and would like to state that this work deserves a lot of credit for the achieved instrumental performance. Even though this general idea has been applied to other gases before, it is new to COS to my best knowledge and has great scientific merit. In my view, this will be a very valuable addition to the scientific literature that is well within the scope of AMT.

However, I'd suggest that the manuscript needs some major revisions. In my view, some clarification on major analytical aspects would be very helpful or even required. Also, the manuscript lacks a comparison with other atmospheric laboratories measuring COS or available scale gases to provide a linkage to the global observations as outlined in the introduction. This may be out of scope for this publication, but it should be discussed.

We sincerely appreciate the referee's evaluation of the present study and constructive comments to improve our manuscript. Our best responses are detailed below.

General comment 1

As a person without personal experience with GC/MS but great interest in all things COS, I suggest adding a paragraph in the main text on how the GC/MS system is setup, how it is calibrated, and how it performs. It isn't clear to me how the GC/MS system is calibrated for COS and HCFC. At some place the manuscript talks about a system blank. This is hard to understand without a clear description. The figures show delta values between Molebloc and GC/MS, but how GC/MS raw values are calibrated and then used for comparison isn't clear to me. At several places, the main text talks about normalising data. If that is related to this, please explain in detail what is done, how it's against what gas. Please explain in detail how you calibrate your GC/MS system, what are the COS/HCFC-22 ranges in your calibration gases and how stable is your system with time. Somewhere in the supplements you talk about the uncertainty of the analytical system on its own, please include that in the main text as well and expand on this.

For a response to these general comments, we refer to Saito et al. (2010) cited in the text (e.g. on the basic performance and configuration of the GC/MS measurement system). Below are the main points to the comments.

(i)how the GC/MS system is setup, how it is calibrated, and how it performs

We added description of the basic configuration of the GC/MS measurement system in Section 2.4. For more details, please see our paper by Saito et al. (2010).

(ii) *At some place the manuscript talks about a system blank.*

We have changed the description of system blanks in the text. Please see last paragraph of Section 2.1.1 and our reply to the comment 4 received from the referee 2.

(iii)how GC/MS raw values are calibrated and then used for comparison

Please see Section 2.4. The normalised ratio was defined as the ratio of a GC/MS response (raw value) of a target gas measured in the sample gas mixture relative to that in a reference gas mixture according to equation (3). By multiplying the known mole fraction of COS in the reference gas mixture to the normalised ratio, then we obtain the COS mole fraction in the sample gas. Thus, the normalised ratio is not a value converted into mole fractions, but a value with respect to a reference gas mixture.

(iv) *At several places, the main text talks about normalising data. If that is related to this, please explain in detail what is done, how it's against what gas.*

See our response in (iii) above.

(v)*what are the COS/HCFC-22 ranges in your calibration gases and how stable is your system with time.*

Please see Section 2.4 and equation (3). In general, sensitivity of a mass spectrometer decreases with time but for most compounds remains constant within a few % for a measurement period of several months. To correct the gradual change of GC/MS responses, mole fractions are determined relative to that for a reference gas mixture. The normalised ratio described in the text was as such defined. The reference gas mixture used as our working standard has nominal mole fraction values of approximately 554.5 pmol mol^{-1} and 289.1 pmol mol^{-1} for COS and HCFC-22, respectively. These were determined values in Section 4.4.

(vi)*Somewhere in the supplements you talk about the uncertainty of the analytical system on its own, please include that in the main text as well and expand on this.*

We have added the brief explanation of how the repeatability of the GC/MS measurement system was determined.

Page 14, line 5 –

Original: The typical analytical precision for COS and HCFC-22 was a relative standard deviation (RSD) was RSD of less than 0.5% during the study period.

Corrected: The typical repeatability for COS and HCFC-22 determined from repeated measurement of a compressed cylinder gas was RSD of approximately 0.5% during the study period.

<u>General comment 2</u>

Maybe related to the previous point, please explain in more detail what the "reference gas mixture" in Figure 1 is used for.

We have rephrased "Reference gas mixture" in Figure 1 to "ambient air-base reference gas mixture" and added a brief explanation in the figure caption.

General comment 3

Commercial providers of gas mixtures do often not meet the strict requirements of the atmospheric community. Therefore, the atmospheric community developed an approach of Central Calibration Laboratories (CCLs). If I understand the manuscript and the described technique correctly, the scale realisation for COS and HCFC-22 enabled by this instrument is a propagation of the gravimetric scale provided by the gas provider. Mixing ratio calculations in the diluted gas depend on the values in the parental mixture. Given that there are other laboratories making such measurements since a long time and that provide reference gases to the atmospheric community, I wonder if the authors have thought about a comparison of their measurements with those within the atmospheric community? It is my understanding of the manuscript that the authors tested for accuracy by comparing their results with gravimetric dilutions of the very same parental tank used by the gas provider. I wonder if this comparison is showing whether or not the presented system and the gravimetric system of the gas provider achieve different results using the same gases. To some degree, this is a great local verification as the same gases are used, but it isn't a global verification where laboratories have to use materials from different providers. The authors state that "absolute determination of the target gases in the parent gas mixture is required…" (P22-L23+24) and that "COS-specific bias is not clearly understood" (P24-L5). I would expect that those effects are a limitation on what can be stated on the achievable accuracy of this method. However, this is in strong contrast to the title statement this as "high accuracy… method". Do the authors think this system is fit for purpose as it is, or is absolute calibration still required to fully assess the accuracy performance of this method? This is not clear to me, but I'd consider this a major point in need of clarification.

This study presents an accurate method for dynamic dilution of COS from micromole-per-mole to the ambient levels (several hundred picomole-per-mole), and accuracy of absolute mole fraction of COS in dynamically generated gas mixtures are not discussed because it depends on the accuracy of the gravimetric preparation of the parent gas mixture as described in above comments. Therefore, establishing a calibration scale for COS is our next work although atmospheric COS can be observed on the temporal calibration scale of a gravimetrically prepared parent gas mixture from the gas manufacturer (Japan Fine Products).

The gas manufacturer that prepared the COS reference gas mixtures in this study is the manufacturer that we have provided technical assistance in the establishment of NIES (National Institute for Environmental Studies, Japan) calibration scales for CO_2, CH_4, N_2O, and so on. These calibration scales have been evaluated in intercomparison experiments such as BIPM key-comparison, WMO round robin and Cucumbers programme. Thus the gas manufacturers are reliable and highly skilled. However, we consider that there are factors potentially affecting the preparation accuracy that are not yet known other than the strong adsorption and desorption properties of COS, and that verification as described above is necessary.

We are currently planning to develop an absolute determination method and system and to carry out intercomparison experiments. Our work is already underway on the former plan. In this study, we have used a micromole-per-mole level of COS filled in a high-pressure aluminium cylinder for the dynamic dilution system and, as long as this parent gas mixture is stable, the developed dynamic dilution method has a great advantage that the observed COS values can be recalculated on the updated scale after scale establishment and even on the scale from other laboratories through an intercomparison experiment.

We have added discussion underlined above in section 4.4.

General comment 4

Also, can the authors comment on the potential accuracy of the gravimetric standards, and the purity of the applied gases? The authors provide purity levels of the gases used, i.e., 99.99995% etc. Theoretically, this allows for 0.00005% of contaminating gases. Even if a very small fraction of the contaminating gases was COS, this method would have a severe bias. Can you elaborate on the composition of the contaminating gases, is there a certificate?

For the gravimetric dilution of the parent gas mixture, we made rough estimation of the uncertainty in the gas preparation based on typical measurement uncertainty of a weighing scale (± 25 mg, 2σ). Please see Section 4.3 Validation of dilution accuracy. Although we have no information on the COS purity used to prepare the parent gas mixture with a COS mole fraction of about 1 μmol mol^{-1}, but the purity (it was perhaps 99.9%) was considered to calculate the nominal mole fractions. For the N_2 and He gases used in this study, the gas purity was guaranteed to be greater than 99.99995%, as determined by the manufacturer using FTIR. Further contamination check in these cylinders was conducted as described in section 2.1.1.

General comment 5

Pressure regulators and cylinders are known to have huge effect on cylinders. Please provide exact details on those components, i.e., pressure regulator manufacturer, model, materials used in wetted surfaces, materials avoided in wetted surfaces. Same for cylinders, Molebloc and all other components. Really important for people attempting to implement your work.

Details of the experimental components are given in the revised manuscript. Please see our response to the comment# 11, 15, 23, 24.

General comment 6

Generally, the wording could be shortened or simplified throughout the manuscript without reducing the level of information. As an example, the authors talk about the GC/MS system and the "sample determination system". Is this not referring to the same system? If it was, can you consider referring to it as the "GC/MS system" consistently?

The sample determination system is the combined system of sample concentration system and GC/MS. In the revised manuscript, we consistently use "GC/MS measurement system" instead "the sample determination system" after defining the term in the lead paragraph of Section 2. Materials and method.

◎Specific comments

Comment 1

P2-L9: you mention that the system is validated for 10 years. Can you show quality control data over 10 years of how the system is performing? What variability do you see in COS on that time period? I know this is the abstract, but showing this in the main text would be great.

We experimentally validated the stability of a micromole-per-mole level of COS during the storage by evaluating whether the nominal COS values for three gravimetrically prepared dry reference gas mixtures were kept at the time of this study in 2023. Until this experiment, no experiments had been conducted to evaluate the COS stability and therefore there are no data to show the time-series variation of the COS mole fraction after preparation. However, our validation experiment suggested that relationship between these three nominal values was at least kept at this experiment. This would be sufficient to validate the COS stability.

To clear the original text, we have changed as follows.

Page 2, lines 6 – 10

Original: Our method combined a dynamic dilution system employing a high-accuracy mass flow measurement system and a gravimetrically prepared parent gas mixture containing a micromole-per-mole level of COS filled in a high-pressure aluminium cylinder, the COS stability of which we experimentally validated for at least 10 years.

Corrected: Our method combined a dynamic dilution system employing a high-accuracy mass flow measurement system and a dry reference gas mixture prepared gravimetrically as parent gas mixture containing a micromole-per-mole level of COS filled in a high-pressure aluminium cylinder. The storage stability of COS at this level was experimentally validated for three gravimetrically prepared dry reference gas mixtures over the period of more than a decade.

Comment 2

P2-L12+L13+20 and elsewhere in the text: you use statistical concepts of repeatability, reproducibility, standard error. Please explain how you calculate each (in the main text, not the abstract).

We will refer to ISO documents that describe the definition of repeatability and reproducibility, but we avoid using "standard error" in Table 3 in response to the comments from referee#1. For repeatability and reproducibility, please see our response to the comment 34.

Comment 3

P2-L16: GC/MS in the main text and GCMS in the supplements. It would be easier if this was consistent.

We will use GC/MS uniformly in the text.

Comment 4

P3-L3 delete the work "on".

We deleted "on" from the sentence.

Comment 5

P3-L17: "that allow precise determination of atmospheric COS levels". I understand that the goal of this manuscript is more about accuracy than precision. Maybe "that allow precise and accurate determination…"?

Thanks for your suggestion. In this study, we define that accuracy consists of trueness and precision according to the ISO's definition (also, precision consists of repeatability and reproducibility). We have therefore amended the text as below.

P3, line 17
Original: …that allow precise determination of atmospheric COS levels…
Corrected: …that allow accurate determination of atmospheric COS levels…

Comment 6

P3-L19+20: I am not sure if the statement of both sentences is warranted, and if the technique presented in this manuscript would provide a breakthrough to better understand COS globally. I'd suggest starting P3-L20 with "One fundamental…".

Thanks for your suggestion. We have changed the text according to the suggestion.

P3, line 20
Original: The fundamental reason for this is…
Corrected: One fundamental reason for this is…

Comment 7

P4-L14: "eliminates need for storage". Your system still requires long term storage of the 1 ppm COS gas and this seems to be assumed here. Is there any proof or demonstration that a 1 ppm COS gas is stable in a cylinder over long time periods, i.e., the 10 years mentioned in the abstract? Can you elaborate on what is known and your thinking here?

Here we described general advantages of dynamic dilution methods as were mentioned in previous studies, not specific to our dilution method. So we think it is OK to keep the text as it is. Regarding the stability of the 1 μmol mol^{-1} of COS, it has not been established whether the stability of COS demonstrated at 5 μmol mol^{-1} is also obtained at 1 μmol mol^{-1}. However, the same mechanism that leads to a COS decrease at ambient level mole fractions in a high-pressure aluminium cylinder is expected to occur at 1 μmol mol^{-1} as well as 5 μmol mol^{-1}. In this case, no significant changes in COS mole fraction would be observed for at least several years, but intercomparison experiments and absolute determination of COS would be necessary to confirm this.

Comment 8

P4-L22: "which we expect"… this sounds as if you are not fully convinced that the method is fit for purpose? Otherwise, could you say "which has the demonstrated capability to support…."?

We have decided to follow the suggestion and have amended the text accordingly.

Comment 9

P5-L9: "COS-free diluent gas", can you provide an estimate of the COS blank? Have you tried to reduce the COS blank? (Nickel very effectively removes COS, a piece of 1/16" Ni tubing in the supply line might effectively remove any remaining COS?

Thank you for your valuable information about COS removal by Nickel. Can you publish it as a technical note elsewhere?

At page 6 in lines 17 – 24, we changed the text describing COS contaminants in the COS-free diluent gas. Briefly, at the time of the experiment, approximately 8 pmol mol^{-1} of COS was detected from alternate injection of an ambient-air-based reference gas mixture and the COS-free gas according to the method described in Section 2.4. However, repeated measurements of a single COS-free diluent gas showed no significant presence of COS but at the same time suggested that memory effect can be significant due to adsorption/desorption in the GC/MS measurement system when the gas mixtures with substantially different COS mole fractions were injected alternately.

Comment 10

P5-L20: change "consisted" to "consists"

We have amended it accordingly.

Comment 11

P5-L25 and following lines: Provide all details possible on gases, purity levels, contaminants and their certified levels, cylinder manufacturers, cylinder valve type, wetted materials of cylinder, valve body, valve spindle, valve seat, burst disc, same for pressure regulators, Molebloc, static mixer, and all other components. Could be as table or text.

In order to provide as much detail as possible, the text in the following sections has been amended.

2.1.1 Parent and diluent gases (Cylinder, cylinder valve, and regulator)
2.1.2 High-precision flow measurement system (Molbloc element)
2.1.3 Thermal-based mass flow controllers
2.1.4 Static mixer
2.1.5 Automatic back-pressure regulator
2.4 Determination of COS in a diluted gas mixture
3 Long-term stability of COS in high-pressure aluminium cylinders

Comment 12

P6-L8: It seems that you and the gas provider use pure COS and pure HCFC-22 in pure N2. Is *there any evidence that COS in an N2 matrix behaves the same as COS in air matrix as is the case for samples?*

In GC/MS analysis, COS in a sample gas can be enriched without any problems at cryogenic traps in the GC/MS measurement system, irrespective of gas matrix and COS was further purified by GC separation. Therefore, we can consider that the difference between N_2 and air matrix has no effect on the GC/MS measurements. Next, Molbloc system can measure mass flow rates of sample gases in response to their gas types (e.g., N_2 or air), the difference has no effect on the measurement accuracy. Finally, stability of COS in high-pressure gas cylinders is generally considered to be more stable in nitrogen matrix than in a matrix containing oxygen, rather the stability would depend on the presence of water and cylinder materials.

Comment 13

P6-L10-11: Why do you use single and dual stage regulators? Could the use of single stage pressure regulator cause the pressure variability and therefore COS variability? We found severe differences in levels of COS contamination between different pressure regulators, despite all being high-quality. Because this is so critical for the success of the method, I strongly suggest to provide further information.

Thank you for your valuable feedback. The cylinder regulators we examined are manufactured to be used basically at flow rates of several litres per minute or more. In contrast, the flow rate of the parent gas in this study was around 10 sccm, which was substantially lower than the recommended flow rate. Under such flow conditions, we considered that a two-stage regulating mechanism could lead to pressure instability compared to a single-stage regulator. As for COS contamination, we also briefly investigated whether different regulators affect cylinder gas measurements using GC/MS, but no significant differences were found, at least for the regulators we investigated. We are still not sure about impact of the contamination from pressure regulators, but we have confirmed that there is no significant influence on COS measurements, at least for the regulator used in this study. The above description was given in lines from 26 on page 9.

Comment 14

P6-L19: "small amounts of COS…" because this is fundamental for the method, this needs a quantitative estimate. As asked above, what has been done to remove the blank, i.e., with Ni tubing?

As answered above in comment 9.

Comment 15

P7-L10: provide details on wetted materials of Molebloc

We added below explanation in the text.

Page 8, lines 5 – 6

Original: …at flow rates above and below 10% of the full-scale flow rate.

Corrected: …at flow rates above and below 10% of the full-scale flow rate. The gas contact area along the entire flow path of the Molbloc elements was SUS316L.

Comment 16

P8-L4: spell out abbreviations in headers

We have amended it accordingly.

Comment 17

P8-L8: "as the controller…" which one?

MFC-C is the same model for MFC-A and -B (both are model SEC-Z712MGX) while MFC-A, B, and C have different mass flow rates. We have amended the sentence as follows:

Original: MFC-C was the same model as the controller but with a…

Corrected: MFC-C was the same model as the controllers A and B but with a…

Comment 18

P8-L23: change "prevent" to "minimise"

We have amended it accordingly.

Comment 19

P8-L25 (and everywhere else): spell out abbreviations in headers

We have amended section headers of 2.1.3 and 2.1.5 as:

2.1.3

Original: 2.1.3 Thermal-based MFCs

Corrected: 2.1.3 Thermal-based mass flow controllers

2.1.5

Original: 2.1.5 ABPR

Corrected: 2.1.5 Automatic back-pressure regulator

Comment 20

P11-L15: Explain the use of all symbols, i.e., "δ"

We added the explanation of u_{diluted} and δ notation used in Eq (2) into the text as:

Page11, line 14: the uncertainty (u_{diluted}) in the mole fraction of the diluted gas x can be estimated from the uncertainty…

Page 11, line 21: where each δ symbol represents the uncertainty of corresponding variables $[x]_{\mathrm{parent}}$, f_{parent} and f_{diluent}.

Comment 21

P11-L19: Is the assumption of δ[x]parent = 0 valid? It seems critical for this method, please discuss the accuracy and consequence of this assumption.

Although it is not realistic to assume that there is no uncertainty in the preparation of the parent gas mixture, we here make that assumption in order to quantitatively estimate only the dilution uncertainty. Moreover, this study will not discuss the absolute mole fraction of the generated target gases using the developed dilution system. Overall uncertainty including preparation uncertainty of the parent gas mixture has to be investigated in our next study through an intercomparison of COS measurement scale, absolute determination of target gases contained in parent gas mixtures, and so on.

Comment 22

P12-L5: RSD is mentioned in the figure for the first time and continuously throughout the main text (I believe the abbreviation is explained in the supplements but needs to be stated in main text). Please explain how you use the terminology and how it is calculated.

The term RSD is defined as relative standard deviation in next section 2.4, (in line 24 on page 13 of original manuscript). So, we added the explanation of RSD in Section 2.3 as:

Page 11, line 23 – 25

Original: The mole fraction distributions of gas x and relevant dilution uncertainties are shown in Figure 2.

Corrected: The mole fraction distributions of gas x and relevant dilution uncertainties expressed as a relative standard deviation (RSD) are shown in Figure 2.

Comment 23

P13-L7: Please provide specs and precise details on mirror polished aluminium cylinders, manufacturer, valve, wetted materials, etc.

We have amended the text as below:

Page 13, line 14 –

Original: …filled into a 48-L high-pressure aluminium cylinder with an inner surface that had been mirror polished and anodised.

Corrected: …filled into a 48-L high-pressure aluminium cylinder (Luxfer) fitted with a brass-bodied cylinder valve (G55-L; Hamai Industries Limited, Tokyo, Japan). The inner surface of the cylinder had been polished and anodized using a proprietary method

(Japan Fine Products, Co.).

Comment 24

P14-L7: Please provide cylinder details, valve details etc…

We have amended the text as below:

Page 14, line 16 –

Original: However, in this study, we opted to use an aluminium cylinder…

Corrected: However, in this study, we opted to use Luxfer 9.4L aluminium cylinder with brass-bodied SUS316 metal diaphragm valves (G55-L; Hamai Industries Limited, Tokyo, Japan) …

Comment 25

P14-L15-17: Is this due to the amount of COS, i.e., passifying the cylinder, or is it due to the rate of COS change, that it can be neglected at ppm COS levels?

At present, the mechanisms of COS change in high-pressure cylinders are still not clearly understood and therefore we cannot give the reason for the apparent COS stability at a micromole-per-mole level. As you see, the most likely interpretation is described as below. We showed a significant decrease of COS at the ambient level in a non-passivated high-pressure aluminium cylinder during the storage in our experiments in Figure 3. At a micromole-per-mole level, the mole fraction of COS may similarly change by the same mechanisms as observed for ambient levels of COS, but the amount of COS change may be only marginal relative to the amount of COS filled, resulting in no apparent change.

Comment 26

P15-L2: It would be interesting to plot the pressure within the cylinder over this time.

Thank you for your interesting suggestion. The cylinder pressure has been kept at almost constant at initial filling pressure because the investigated cylinder shown in Figure 3 was not used except this stability check experiments. Conversely, as our findings, this result demonstrates that COS is reduced even under constant pressure in a non-passivated high-pressure aluminium cylinder.

Comment 27

P15-L9: you use "dilutor" and "diluter". Are these referring to different components or typo?

We have decided to use the term "dilutor" throughout this study.

Comment 28

P15-L14: "until the measured values stabilised", can you elaborate on this? How long does this take, how large is the effect with time, how many measurements does it need, is this constant?

In the experiments using the commercial dilutor, we observed gradual change in COS mole fraction determined using GC/MS in response to increase number of the measurement as was shown for the Molbloc dilution experiments described in Supplemental Information. The behaviour of the gradual change differed from experiment to experiment and thus needed number of measurement (or time) also depended on experiments until measured values converged asymptotically as observed in Figure S1-3. As limited case for this experiment, we performed COS determination by up to 8 times using the GC/MS. The determination needs to normalise the GC/MS response of COS from sample measurements based on that from measurements of reference gas mixture before and after the sample measurement. Therefore, a total of 17 injections of the sample and reference gas mixture has to be performed alternately (Reference→Sample→Reference…), corresponding to 17 hours, since the measurement time for a sample is 1 hour. Please note that the dynamic generation of the diluted gas mixture is stopped except during sample gas concentration and system purging time, so the conditions required for accurate COS determination are not simply determined by the number of measurements or hours of operation.

Comment 29

P15-L16: you could change "The measurements of COS in the compressed air showed high repeatability, of which standard deviations (1σ) were within 0.5 pmol mol−1." to "COS *measurements in the compressed air showed high repeatability with standard deviations (1σ) of 0.5 pmol mol−1."*

Thank you for the suggestion, but we have changed Section 3 significantly in this revision. Please see the revised Section 3.

Comment 30

P15-L17: I am not sure I understand this sentence: "The assigned COS values fell outside the 2-sigma range but were within 2%." Can this be clarified, assigned by what method, outside 2 sigma from what?

We have amended the text as follows:

Original: The assigned COS values fell outside the 2-sigma range but were within 2%.
Corrected: While the individual average COS values did not agree within each other within the 2-σ envelope of their corresponding measurement data, they were within 2% of the average values.

Comment 31

P15-L20: I am not sure I understand the underlying experiment leading to this statement, also Table 1. What exactly has been measured, why is nominal COS at 5 ppm and assigned value around 270 ppt? I understand the parent gas has 1 ppm COS, where does the 5 ppm originate from, what is 270 ppt when the system is used to dilute to 500 ppt?

We have carefully revised Section 3 to make it clearer. Briefly, in Section 3, we showed results from stability check experiments using a commercial dilutor, independent of the development of the dynamic dilution system using Molbloc. We prepared three reference gas mixtures in different years containing approximately 5 µmol mol^{-1} COS to check long-term storage stability. However, we did not establish a method for the determination of COS at the micromole-per-mole level using GC/MS. Therefore, we evaluated their storage stability by measuring compressed natural air against each of three reference gas mixtures. To obtain a linear response in the GC/MS measurement, the reference gas mixture was needed to be dynamically diluted to the ambient level using the commercial dilutor. The GC/MS measurements showed that the mole fractions of COS in the compressed natural air determined against each of the three reference gas mixtures were all around 270 pmol mol^{-1}, suggesting long-term storage stability of COS at the micromole-per-mole level in a high-pressure aluminium cylinder.

For the reason for using the commercial dilutor, please see our response to the comment 9 from Referee #2.

Comment 32

P16-L1: Change the sentence "These results imply that the impact of drift during storage is practically negligible when using a gas mixture containing COS at a micromole-per-mole level" to "These results imply that the impact of drift during storage is practically negligible when using a gas mixture containing COS at a micromole-per-mole level in this specific setup." or similar.

Thanks for your suggestion. We will change the sentence as:

Original: These results imply that the impact of drift during storage is practically negligible when using a gas mixture containing COS at a micromole-per-mole level.

Corrected: These results imply that in our experiments the impact of drift during storage is practically negligible when using a gas mixture containing COS at a micromole-per-mole level.

Comment 33

P16-L4: "Periodic absolute determination…" I wonder how you do this to meet the compatibility levels required for atmospheric research. It would be great to provide a perspective or guidance, including on the frequency required to achieve this over a range of COS mole fractions.

At this stage, we would prefer not to respond to this comment here because we are developing a method for the periodic absolute determination because the strategy will change depending on the method. Also, needed calibration frequency and acceptable uncertainty for the determination of COS should be considered based on actual observed data. These would be highly dependent on the COS storage stability in a high-pressure cylinder used for GC/MS calibration. At least, we need to develop the absolute determination methods of micromole-per-mole level COS.

Comment 34

P16-L7+8: Please explain how you calculate repeatability and reproducibility and what you learn from both parameters in your study.

For repeatability and reproducibility, we decided to avoid their use in Section 3 to simplify the descriptions and use these terms in Section 4 with adding the description of their definition and explanation according to the definition of ISO. See Section 4.1 and 4.3. Please check the revised Section 4.1. Based on the repeatability and reproducibility, we evaluated random and systematic errors from the GC/MS measurements and the dynamic dilutions.

Comment 35

P16-L11: Does this table suggest that you used your dilution system to produce dilutions with ~5 ppm COS and you measured air from different cylinders with different air fillings made in 2006, 2011 and 2015 and that you kept for COS measurements in 2023 and in those COS measurements you found COS values ranging from 270 to 275 ppt? Were the gases in cylinders stable over that period of time? Is the standard deviation in column 4 referring to the averages in column 3? What is n? What does the comment mean that COS was determined in 2023 if not what above? I am not sure I understand what the nominal mole fraction refers to, and even what this table exactly shows. Please clarify.

Firstly, please see our response to comments 1 and 31. Although we did not investigate the time-series variation of COS contained in the reference gas mixtures at a mole fraction of 5 μmol mol^{-1} of COS after preparation, the COS values from three measurements of compressed natural air by GC/MS against diluted parent gas mixtures from the respective parent gas mixtures performed in this study were almost similar. Such relationship suggests that the nominal COS values given by the gas manufacturer at the time of the reference gas preparation were validated over the period of more than a decade for all three cylinders.

Comment 36

P17-L13: Spell out RSD

We defined "RSD" as relative standard deviation in Page 11, line 24. Also, please see our response to the referee's comments 22.

Comment 37

P17-L15: Here and everywhere else: are the 2nd digits significant and needed, or is 0.3 %, 0.6 %, 0.2 % and 0.4 % a sufficient approximation? I wonder because you refer to a typical GC/MS repeatability of 0.5 % in L18.

You are right. We have amended description of analytical uncertainties throughout this manuscript.

Comment 38

P17-L18-22: I don't understand the discussion of the values, what we should learn from them and what the drawn conclusions are. Please clarify this paragraph.

We have added a detailed explanation of the analysis of the repeatability and reproducibility in Section 4.1 as described below.

In this study, the repeatability was defined as the standard deviation of the normalised responses obtained from repeated measurements in each experiment. From the experiments, we can evaluate the combined uncertainty consisting of the uncertainty from the GC/MS measurements and from the dynamic dilution. The obtained combined uncertainty was comparable to that of the GC/MS measurements estimated from repeat measurements of cylinder gas. These results suggest that the uncertainty from the dynamic dilution was not a dominant factor in the obtained combined uncertainty, which was dominated by the uncertainty from the GC/MS measurements. On the other hand, reproducibility was defined as the standard deviation of the average normalised responses obtained from each experiment performed in different days. The average normalised responses for both COS and HCFC-22 from the five experiments were in good agreement, showing RSD values 0.1% for COS and 0.3% for HCFC-22. These results suggest that the uncertainty in the target gas measurements was dominated by random error and that there was no significant measurement bias caused by systematic error between the experiments. Based on the evaluation of the repeatability and reproducibility, we concluded that the dilution system can generate dynamically diluted gas mixture, precision of which can be represented by the repeatability of the GC/MS measurements.

Comment 39

P18-L4: Here and everywhere else: What does “normalize” mean in your system/data processing? Please clarify.

In this study, signal responses for target gases from GC/MS measurements are reported as normalised values as described in Section 2.4 in lines 22 – 24 on page 13 and equation (3) because we did not have a reference gas mixture with a known mole fraction of COS. In section 4, GC/MS measurements were reported in the normalised values as described in lines 11-13 on Page 17.

Comment 40

P20-L10: Can you provide a time over which the COS decrease of 1/13th occurred? If you use this as an argument to not base your accuracy test on COS but solely on HCFC-22, then this should be clearly stated after this sentence (see comment on P20-L26+27).

Although we have no way of knowing the exact time from the gas preparation to the GC/MS measurements, it is probably within a month after the preparation. By taking this into account, we have amended the sentence as follows:

Page 21, line 13 –

Original: We expected a significant COS loss in the gravimetric reference gas mixtures, and a marked decrease in COS was observed (reduced to approximately 1/13 of the nominal value). However, we could analyse the dilution accuracy based on HCFC-22 determination because our experiments demonstrated comparable dilution performances between HCFC-22 and COS.

Corrected: We expected a significant loss of COS in this gravimetric gas preparation process, and a marked decrease in COS was observed: nominal value reduced to approximately 1/13 after preparation of the reference gas mixture, probably within one month. However, we could analyse the dilution accuracy based on the determination of HCFC-22 as our experiments demonstrated comparable dilution performances between HCFC-22 and COS, with no significant systematic dilution bias observed for COS, as presented in the Supplemental Information.

Comment 41

P20-L17: ", which measures the mass flow rates of the parent and diluent gases" has been mentioned before and can be deleted.

We have amended the text as suggested.

Comment 42

P20-L23: What points to the gravimetric dilution as the source for the offset? If a cause for the offset is decided upon, it should be explained. What is the uncertainty of the gravimetric system? What is typical and what uncertainties have been reported in the literature for other gravimetric systems?

We consider that there is no significant difference in the mole fractions of HCFC-22 based on the dynamic dilution and gravimetric dilution methods. As you know, the preparation uncertainty of the gravimetric dilution method can depend on ambient conditions such as temperature and humidity but can be estimated mainly by the weighing error. In contrast, for dynamic dilution methods, where all sources of uncertainty are not known, it is not clear whether the dilution uncertainty can be estimated solely based on flow measurement errors. For this reason, the accuracy of the dynamic dilution method is assessed by how much it differs from the method by gravimetry as a reference. For details of gravimetric methods, please see ISO (2015).

As we described in the text, we have not all weighing data from the gas manufacturer. However, the gravimetric preparation uncertainty of the reference gas mixture used for the GC/MS calibration can be roughly estimated to be ± 1.15 pmol $\mathrm{mol^{-1}}$ for HCFC-22. This uncertainty will propagate to the uncertainty of the GC/MS measurement. Based on the uncertainty estimate, the observed difference of about 2 pmol $\mathrm{mol^{-1}}$ is acceptable within the expanded uncertainty of 2.78 pmol mol^{-1} (k=2) calculated from the uncertainty of the GC/MS measurement and of the gravimetric preparation and is not fully significant even when considering only the preparation uncertainty of the gravimetric method.

Considering the above description, we have amended the sentence as follows:

Page 21, line 27 – Page 22, line 15

Original: The average values fell outside the 2-sigma range of one another, but the observed difference was likely due to preparation uncertainty from the gravimetric dilution. Although no estimated uncertainty was provided by the manufacturer, the observed difference corresponded to 0.4% of the nominal mole fraction of HCFC-22, which was acceptable as the gravimetric preparation uncertainty.

Corrected: The average values fell outside the 2-σ range of one another, indicating a potential difference in their trueness…we concluded that dynamic dilution method could accurately generate COS reference gas mixtures at ambient levels from those at micromolar-per-mole levels.

Comment 43

P20-L26+27: Do I understand correctly that the argument here is that the dynamic dilution system is considered accurate for COS, because it works for HCFC-22? If that's the case, please spell this out very clearly (see comment P20-L10). Is that a valid assumption? It sounds like there is a systematic bias as an offset in 2 ppt, but this is acceptable within the uncertainty of the gravimetric system (which needs to be demonstrated/referenced).

As the stable reference gas mixture containing COS at mole fraction of ambient level was not prepared in this study, we cannot make a direct comparison between the dynamic and gravimetric methods. However, the ratio of COS to HCFC-22 shown in Figure 4 indicates that there was no gradual change in the COS mole fractions as shown in the Supplemental Information. This strongly supports no systematic dilution bias occurred during the dynamic dilution. Therefore, it was rational that the dilution accuracy between COS and HCFC-22 could be considered comparable using the developed dilution method. Also, please see our response to the comment 42 describing that the observed difference of about 2 pmol mol^{-1} was not significant.

Comment 44

P21-L1: Are all gases really made from the very same parent gas mixture, or are all mixtures made using the same gravimetric system? Please ensure that the figure represents this accurately. If COS is not used in the accuracy test, maybe remove COS values from this figure to avoid confusion?

For clarity, some changes have been made to Figure 6. In the Figure, "Diluted parent gas mixture" (HCFC-22: 500 pmol mol^{-1}) was prepared from the parent gas mixture (HCFC-22: 1.00 µmol mol^{-1}) by gravimetry. By this preparation, the HCFC-22 mole fractions determined by the dynamic and gravimetric dilution can be compared on the same scale. In this experiment, COS was not discussed as pointed out, but identical parent gas mixture was used in all the experiments described in Section 2 and 4. By considering this, we decided to keep the COS description as it is although the suggestion has a point that it would be less confusing to remove the COS information. We are concerned that the removal of COS information leads to other confusion that the used parent gas mixture was different with that used in Section 2 and 4.

Comment 45

P21-L5: Does this table really need column 1 and 2, or could GC/MS, Molebloc and GC/MS – Molebloc be sufficient? How many digits are significant?

Thank you for suggestion. For clarity, we have simplified Table 2 as suggested and revised Figure 6 accordingly.

Comment 46

P22-L12: Explain all parameters and symbols in equation, what is Ř?

$\hat{R}$ (R-hat) is already defined in equation (3), in line 4 on page 14 as:

"…and $R_{x,sample}$ and $\hat{R}_{x,ref}$ are the signal responses for gas x in the sample gas mixture and the interpolated response for the reference gas mixture, respectively."

Comment 47

P22-L17-19: This sentence sounds like a conclusion before the values are presented and discussed.

As we already know from Figure 4 that the COS and HCFC-22 measurements showed high repeatability and reproducibility, the following sentences have been deleted to avoid duplication here.

Delete: The mole fractions of COS and HCFC-22 were precisely determined because of the high repeatability and reproducibility of the developed dynamic dilution method (see Section 4.1).

Comment 48

P22-L21: What does "sufficiently accurate" mean? You determine 554.51 ppt, but what is the target value that this gas has and that you assess the accuracy with? How is that target value determined, gravimetrically?

In this study, our target dilution uncertainty is to be accurate enough to understand the spatio-temporal variability of COS, in particular to detect the interannual variability, which was estimated to be a few to several pmol mol^{-1} as described in Introduction. We have amended the text as follows:

Page 24, lines 3-6

Original: These results were sufficiently accurate for the determination of COS and HCFC-22 in gas mixtures.

Corrected: These results suggest that the determination of COS and HCFC-22 contained in an ambient-air-based reference gas mixture used to calibrate the GC/MS system was performed with an accuracy that enables analysis of the spatio-temporal variability of the target gases, in particular, the interannual variability of COS.

Comment 49

P23-L1: Is the purpose is of table 3 to show results of 5 measurements and the average of those? If that's the case, the table structure seems overly complicated to me.

We have changed Table 3 to make it easier to understand.

Comment 50

P23-L3: Describe how you define/calculate the standard error.

According to the comment 4 from referee#1, we have decided not to use standard error and instead to use standard deviations.

Comment 51

P23-L15: "a greater bias was observed for COS than for HCFC-22."

We have amended the text as suggested.

Comment 52

P23-L15-17: Isn't the systematic COS increase referred to here (Fig S1-d, S2-a, S3-a) showing that significant absorption problems are apparent in this system that are not balancing and achieving equilibrium state, and therefore preclude from achieving high accuracy? And isn't this just as likely a cause for the accuracy offset of 2 ppt, that has been assigned to the gravimetric dilution method in section "4.3 Validation of dilution accuracy"? Please discuss this in the text.

Our dilution method was developed to minimise the effects of adsorption/desorption of COS according to the strategy described in Supplemental information. For the result shown in Table 2, the difference was not significant even when considering only the uncertainty for the gravimetric dilution as described in Section 4.3. It is therefore difficult to determine whether the difference was due to the adsorption/desorption or not.

Comment 53

P24-L21+22: You state that "the precision of the dynamic dilution method is inferior to that of gravimetry", yet the latter is suspected to have caused accuracy problems in "4.3 Validation of dilution accuracy". Is this contradictory? What is the typical precision/accuracy or *gravimetric methods, can you provide examples from literature?*

Please see revised text in Section 4.3.

First, please see references ISO 2015 and 2018 for the gravimetric preparation and dynamic dilution method, respectively, as described in the Introduction. In principle, current instrumental precision for flow measurements is generally lower than that of gravimetric measurements, resulting in more accurate dilution by gravimetric than dynamic methods. Therefore, gravimetric preparation is a standard and reliable method to be compared with other methods. In Section 4.3, considering the preparation uncertainty of the gravimetric dilution, the observed difference was not significant, showing that dynamic dilution method well agreed within an acceptable range of the preparation uncertainty by gravimetry.

Comment 54

P24-L25: What is automated and what is not in the presented system? Are you manually setting mass flow rates?

We have added detailed description into the sentence as below.

Page 26, lines 13-17

Original: …allow us to establish a fully automated dynamic dilution system.

Corrected: …enable us to establish an automatic dynamic dilution system that can generate a diluted reference gas mixture with precise pressure control of the parent and diluent gases, linked to the GC/MS system.

Comment 55

P24-L25: "This will expand the application of the dilution system to other analytical systems for different target gases and reduce labour and time required to conduct experiments."

Thank you for the suggestion. We amended it as such.

Comment 56

P26-L5: Excellent repeatability and reproducibility do not warrant accuracy.

Description of dilution accuracy was given in Page 27, line 27 – Page 28, line 5.

Comment 57

PS2-L1-2: "…to eliminate blank COS accumulated in the GC/MS based sample determination system and was excluded from further analysis (described in…"

Thank you for your suggestion. As described in our response to the general comment 1 and comment 9, we confirmed that there was no significant COS blank but was memory effect depending on the COS mole fraction in a sample gas mixture. We have amended the text to take this into account.

Page 1, line 26 – Page 2, line 4.

Original: Similarly, after the system purge, one preliminary measurement of the dynamically generated gas mixture was conducted to eliminate blank COS accumulated in the gas chromatography–mass spectrometry (GCMS)-based sample determination system (described in Sect. 2.4 in the main manuscript).

Corrected: Similarly, after the system purge, one preliminary measurement of the dynamically generated gas mixture was conducted to minimise adsorption and desorption effects of COS on inner surface of the gas chromatography–mass spectrometry (GC/MS)-based sample determination system (hereafter referred as GC/MS measurement system) (described in Sect. 2.4 in the main manuscript) before the target gas determination (COS and chlorodifluoromethane [HCFC-22]).

Comment 58

PS2-L11-13: Is this a circular argument?

The original text has been corrected as follows.

Page 2, line 11 – Page 3, line 12 in Supplemental Information

Original: The COS values from the Molbloc measurements were directly calculated from the measured mass flow rates for the parent and diluent gases, whereas those from the GCMS measurements were calculated by assigning the COS value in the reference gas mixture used for the GCMS calibration based on the Molbloc COS values.

Corrected: The mole fractions of the target gases from the Molbloc measurements were directly calculated from the measured mass flow rates for the parent and diluent gases; however…The estimated reference values can therefore be used as a diagnostic parameter for dilution precision.

<u>Comment 59</u>

PS2-L17: Clarify what "Arg min" stands for

We have amended the text by adding an explanation of the mathematical function Arg min. The amended points are the same as in the response to the above comment 58.

<u>Comment 60</u>

PS3-L9+10: Where do the values 564 ppt and 293 ppt come from? Uncertainties important?

These mole fraction values (564.0 pmol mol^{-1} for COS and 293.1 pmol mol^{-1} for HCFC-22) were estimated mole fraction of COS and HCFC-22 in the reference gas mixture used for calibrating the GC/MS by a linear-least square method expressed in Equation (S1). The RSD values for COS and HCFC-22 represents the variability of the mole fractions of COS and HCFC-22 determined by the GC/MS measurements. These RSD values can be a useful diagnostic parameter indicating the dilution repeatability; the values lower than typical GC/MS repeatability for COS and HCFC-22 (about 0.5%) suggest possible occurrence of dilution bias.

<u>Comment 61</u>

PS3-L14: Here and at other places, I am not familiar with the concept/terminology of "flow pressure", but either flow or pressure. What does it mean here?

This was also noted in Referee#2. We have replaced "flow pressure" with "gas pressure" in the Supplement text.

Comment 62

PS3-L17: These values are great, can the y-axes in Figure S1-e be changed to show relative flow changes?

Please check the updated Figure S1 according to the comment.

Comment 63

PS4-L14: You could use "error bars" instead of "vertical bars", as there are no horizontal error bars in this figure?

We amended it as such.

Comment 64

PS5-L18: "…no gradual increase with pressure was observed…"

We amended it as such.

Comment 65

PS-6-L19: Is this supposed to be "EX-S3" instead of "EX-S2"?

We have amended the text as follows:

Page 7, lines 11 – 12
Original: …a gradual increase in the generated COS mole fraction was again observed as in EX-S2,…
Corrected: …a gradual increase in the generated COS mole fraction, similar to the results obtained in EX-S2, was subsequently observed in EX-S3,…

Comment 66

PS7-L4+5: "These results showed that the occurrence of the COS-specific bias was not proportional to the flow rate of the parent gas, but the magnitude of this systematic pattern was."

Thank you for the suggestion. We amended the sentence as below.

Original: These results showed that the COS-specific bias was not proportional to the flow rate of the parent gas.

Corrected: These results showed that the occurrence of the COS-specific biases was independent of the flow rate of the parent gas and also that the magnitude of this systematic pattern was not proportional to the flow rate.