

Reviewer comment 2

Comments on “Photochemical method for removing methane interference for improved gas analysis” by Merve Polat et al.

General comments:

This manuscript describes a photochemical scrubbing method, using Cl_2 , for the removal of CH_4 in whole air samples. This described method is intended to enable accurate determination of the isotopic composition of N_2O ($\delta^{15}N^\alpha$, $\delta^{15}N^\beta$, and $\delta^{18}O$) by minimizing the spectroscopic interference arising from CH_4 (among several others), which poses immense challenge. This method indeed shows potential as the removal of CH_4 through this photochemical scrubbing does not alter the matrix composition dramatically. In addition to the experimental work, the authors have also complemented their experimental results with predictions using a kinetic model studying all the dependencies. This method in general can be used for any application requiring removal of CH_4 (and other hydrocarbons/VOCs), and is not just limited to the measurements involving N_2O . And hence is an important development that the scientific community could benefit from.

Although the content of the manuscript is very interesting, consisting of appropriate method-development related experiments and complementing model prediction, the manuscript itself is difficult to follow at times due to: the use of too many abbreviations, and having to go back-and-forth between the main section of the manuscript and the supplementary section where part of the information is.

REPLY: We agree that the current structure of the manuscript forces readers to go back and forth between the supplementary section and the main text, and we have corrected for this issue. With regards to the use of abbreviations, we have attempted to limit our use of them.

Additionally, there are sections where the texts require rephrasing to make the content more understandable. Please see details in the specific comments section.

REPLY: We are happy to apply your suggestions to make the text more easily readable

While this proof-of-concept method is aimed towards reducing the interferences of CH_4 during the measurements of the singly-substituted isotopologues of N_2O , the experiments and results shown to demonstrate the applicability is very limited. Since the removal efficiency of CH_4 achieved is never ~100%, discussion on its implication was not evaluated thoroughly.

REPLY: It is unfortunate that the parameters available to us when doing the measurements of N_2O , did not allow for the removal of >98% we achieved during the parameters testing. Regardless of this, we now agree that the acquired results should be discussed in more detail and be related clearly to our declared goal. So we want the variation in methane reaching the Picarro G5131-i to be less than 0.2 ppm as the size of this variation will then be below the detection limit of the instrument.

This is particularly concerning because one has to then always co-measure methane, which is partially scrubbed, in order to incorporate any possible CH_4 -dependent correction. So does the method provide any benefit over performing a careful CH_4 -dependent interference correction?

REPLY: With the presented removal during the N_2O experiment, indeed, it would still necessitate co-measurements of CH_4 . But we will argue that by improving upon the photochamber, it would be possible to continuously remove more than 98% of CH_4 . We have added the arguments for this in the manuscript, in combination with the explanation for why we did not achieve >98% removal as seen in the earlier experiments. (see reply to first concern from Reviewer one)

Additional experiments showing the repeatability expected from this method using isotopically-calibrated N_2O samples was also missing.

REPLY: Fair point, that we do not have data to describe.

The manuscript in its current form requires considerable rework and I would recommend publication after all concerns have been addressed.

Specific comments:

Line 74 and Table 2: How is tank A calibrated for $[Cl_2]$? Is this a commercial product?

REPLY: Yes, it is a commercial product.

Line 82: The chlorine detector is rated for 0-20 ppm, so how were chlorine concentrations determined in experiments done above 20 ppm, shown later in the manuscript?

REPLY: The Cl concentration is theoretically determined

Line 85: LED already stands for Light emitting diodes, so should be mentioned “LED” only and not “LED diodes”. Please correct this throughout the manuscript.

REPLY: We have changed this throughout the manuscript.

Line 93: Please provide supplier details/ part number for Krytox™.

REPLY: We have added (DuPont GPL 205 Krytox Performance Grease)

Line 96: Magnesium perchlorate is $Mg(ClO_4)_2$

REPLY: We agree, we have changed it.

Line 100: Please provide supplier details, part number, specification for the activated carbon trap used.

REPLY: We have added (Bead-Shaped Activated Carbon, KUREHA Corporation)

Line 103: “A final set of experiments is conducted using a Picarro CRDS model G5131-i, capable of measuring N_2O mixing ratio and its isotopic abundance.”

REPLY: We have changed it to the line as suggested “A final set of experiments is conducted using a Picarro CRDS model G5131-i, capable of measuring N_2O mixing ratio and isotopic abundance”

Lines 150-152: Throughout the manuscript, the steps are referred to as S1, S2.... and not as in your example C5 (line 152), please check and revise accordingly to be consistent. Line 155: “H5”: please see my previous comment.

REPLY: We have edited the steps to be referred to as their experimental name.

Lines 159-162: This paragraph somehow feels very unlinked with the previous paragraph. Please explain the “issue” by pointing the reader to the graph, what exactly to look at? How does the build-up of H_2O happen? Why is the Cl_2 raw data not shown along with?

REPLY: We have added the call to attention “...as can be seen from the slope in step H1.” To the explanation. The build-up of moisture arose from leaving most of the setup system open over night, which allowed lab air to enter. With regards to the lack of raw Cl_2 data, the sensors used for Cl_2 were a “cheap” monitor intended for safety and did not come with logging. This is also the reason it, unfortunately, was not able to measure Cl_2 concentration as high as we would have liked. Our Cl_2 measurements were therefore used to confirm that the concentration of Cl_2 had not changed compared to the onset. Unfortunately, as we described in the paragraph in question, we did observe a drop in Cl_2 , but we, unfortunately, do not have the Cl_2 data to show for it..

Figure 4: Typically, when you have units shown on the axis label, you don't have to show them on the tick labels, so the % signs on the ticks can be removed. And the abbreviation RE has not been introduced anywhere in the text, so please include this.

REPLY: We have changed the figure axis as suggested and introduced RE in the figure text.

Line 187: What is d here? Please define your notation. Is it delta that you are referring to? If so, please describe how often you measure your reference/ calibration etc. Please check and change this throughout the manuscript.

REPLY: That is indeed intended to be delta. It will be corrected throughout the article. For explanation we have written; "The delta values are self-referenced to the gas without the addition of CH₄." As for the measurements of reference/calibration gas, we certainly desired to do it, to follow the recommendations by the paper of Harris. Unfortunately, our calibration gasses first arrived after the completion of these experiments. We argue that while calibration of the isotopologues would be preferable, it is in the end unnecessary as we are only determining the relative change of the acquired delta values.

Line 187-188: "The results are from experiment L, where a softocat trap had been installed to remove the CO formed by the CH₄ oxidation."

REPLY: We have changed it to "The results are from experiment L, where a softocat trap had been installed to remove the CO formed by the CH₄ oxidation"

Line 189: "...it was found that the isotopic enrichments ..." Please introduce this to the reader why they should expect isotopic enrichment and not depletion in $\delta^{15}\text{N}\alpha$ and $\delta^{18}\text{O}$.

REPLY :We see the error we invite by our phrasing, as we are not talking about an enrichment but rather the actual isotopologue level. We have rephrased to "it was found that the isotopologue levels remained stable through the oxidation (grey line)."

Line 190: How stable is the oxidation process in a prolonged time period, e.g. during a continuous 10 hr measurement period, and in practice you would really turn it ON all the time during a measurement. How much of the variability in $[Cl_2]$ translates into your final measurement uncertainty?

REPLY: The ideal is to turn it on and leave it running, but we have not left it running for multiple hours. The longest continuous running was for roughly 100 minutes (as shown in fig 3), where the performance was stable. We expect that this performance could be maintained for several hours but we have not done the experiment to show it. This does touch on another problem that would arise from long-continued measurement, which is the Ascarite trap will be used up and in need of a replacement after roughly 22.5L had passed it. (corresponding roughly to one day's worth of measurements at 15ml/min). In our description of the N₂O results we have written "With a higher concentration Cl₂ source available and a properly prepared regulator, the setup would have been able to deliver sufficient CH₄ removal for more than 24 hours, at which point the ascarite trap would need replenishment."

And for the final subquestion, how does the variability in Cl_2 affect the overall uncertainty? While it will depend on the concentration and the amount of Cl_2 introduced, in our experiment we have estimated the uncertainty of the Cl_2 flow to be 8.3%, which is the greatest source of uncertainty in our work. The uncertainty of the concentration of Cl_2 comes to be around 10%.

The solution to this would be to make a better and more stable supply of Cl_2 , and/or have a high enough concentration source so that the variation in Cl_2 will not result in any relevant variation in methane removal potential.

Line 193-194: How is the variation in $[N_2O]$ due to variation in $[Cl_2]$, is it not due to dilution? And correct the spelling of variation in Line 194.

REPLY: Correct that would be a more accurate description, as the variation in Cl_2 is also due to changes in the dilution. We have rephrased to avoid confusion as “Variations of roughly 5% were observed in $[N_2O]$ but are accounted for by variations in the flow of $[Cl_2]$, thus changing the dilution, rather than transformation of N_2O due to the photochemistry.”

Section 3.1.1 (in general): Why was the method with the highest removal efficiency not used here?

REPLY: We have answer the same question from the first reviewer, and included an explanation in the text.

Line 229: “... that an increase in Cl_2 concentrations increases the $[CCl_4]$ production (see Figures 7a, 7b and 7d.)”

REPLY: Yes, we have changed as suggested to “Figure 7a showsthat an increase in Cl_2 concentrations increases the $[CCl_4]$ production.”

Figure 7 (caption): “The Removal efficiency of methane depletion (Black), ...” should be “The removal efficiency of methane (Black), ...”

REPLY: Yes, we have changed it as suggested to “The removal efficiency of methane (Black), $[CCl_4]$ (Red) and $[Cl]$ (Grey) is shown in the Figures a-d.”

Line 233-234: If you use NaOH to remove CO_2 from a sample, the matrix changes significantly. To what level of matrix alteration not a problem?

REPLY: The removal of CO_2 has an effect, but as CO_2 is only (in the high emission situation) 560ppm, removing it results in a 0.056% increase in the concentration of the remaining gasses, which can be worth considering, though we do not agree with it being significant. H_2O removal however does pose a significant alteration to the matrix, and we should include a recommendation of measurement of H_2O , so this matrix alteration can be accounted for.

Lines 234-235: “The NO_x concentration in our experiments is insignificant and hence these reactions have not been included in the model.”

REPLY: Yes, we have changed it as suggested to “The NO_x concentration in our experiments is insignificant and hence these reactions have not been included in the model.”

APPENDIX

Line 252: What is the typical concentration range of Cl_2 produced by this method? Please elaborate this and describe the calibration and monitoring/ data recording method for Cl_2 .

REPLY: We can expand further on this proof-of-concept experiment, but the assessment of the Cl_2 production is made difficult by high variation and an upper limit of detection for the Cl_2 monitor at 20ppm. We have elaborated by writing: “The ambient air standard was enriched in Cl_2 by in-situ production of Cl_2 , ranging from 1ppm to <20ppm, through electrolysis of a saltwater mixture.”

Line 285-286: Please rephrase.

REPLY: We have rephrased to “28 LED (385 nm), UV LED LAMP-VAOL-5EUV8T4, diodes was installed in the chamber, directed at a quartz tube, OD: 4mm L: 20cm, placed through the chamber.”

Lines 331-336: Please avoid repeating texts already used in the main body of the manuscript (lines 89-93). REPLY: Well spotted. We will corrected for this.

Figure B1: Abbreviations are typically introduced once, the first time they come up in the document. So please don't expand your abbreviations every time you describe a figure.

REPLY: Noted. We have simplified the figures and removed the multiple sets of abbreviations.

Line 354: How does CO interfere with N_2O , please elaborate this and remind the reader which isotopologues are specifically affected.

REPLY: Certainly, we have included the following explanation "The trap was installed to prevent effects on the N_2O isotope signal from CO, as presented in (Harris et al. (2020)) the presence of CO 1 ppm gives rise to an erroneous offset in the observed isotopologue values of 1.2, 2.4 and 0.4 ‰ for $\delta^{15}N\alpha$, $\delta^{15}N\beta$, and $\delta^{18}O$ respectively."

Figure C1: Why repeat a figure when you can refer to Figure 2?

REPLY: We agree, and this repeat has been removed.

Lines 407-410: Please rephrase this paragraph and elaborate on "This effect...". The explanation is not clear.

REPLY: Our attempts to calculate the photolysis rate based on the parameters, did not scale linearly with power input. This offset is what we refer to as the "effect", and upon rereading we agree that the section is not clear, especially as the function presented is linear. We have rephrased it to "Where W is the power supplied to the diodes, and values for the constants a and b are fitted in the model to match the experiment. The function C10 accounts for additional variations such as effects due to temperature, the cross-section area of the quartz tube, the conductance of the photochamber and the quality of the distribution fit. This is reflected in the constants a and b varying in response to changes in these parameters. As this is used as a simple empirical stand-in function we do not intend to speculate further on how these changes change the constants."

Table D4 (Caption): "... refer to the three isotypes of N_2O ." should be something like "... in ‰ refers to the three isotopologue measurements of N_2O ."

REPLY: We have adopted the suggested change and moved the