Reviewer comment 1

General comments:

The manuscript by Merve Polat et al. describes the development and optimization of novel method for CH_4 removal from air via chlorine-initiated oxidation with the focus to minimize spectral interferences during N_2O isotope analysis by CRDS (Picarro G5131-i). The study includes the design and validation of a proof-of-concept device and the validation of a kinetic model to predict the dependence of the CH_4removal efficiency on methane concentration, chlorine photolysis rate, chlorine concentration, and residence time.

I find the manuscript timely as the strong CH_4 interference of the Picarro N_2O isotope analyzer was recently identified by Harris et al. (AMT, 2020). Therefore, a technique for specific CH_4 removal is of high interest for the users of these analyzers but complicated. An alternative concept would be removal of N_2O and release in a well-defined gas matrix as applied by IRMS and also laser spectroscopy.

REPLY. Thanks very much, we are glad you also find it interesting. It would also be possible in theory to do as you suggest, given a suitable separation method, and as long as complications due to the separation are not an issue. Many separation technologies fractionate isotopes.

I doubt whether addition of a toxic substance such as Cl_2 should be propagated for CH_4 removal. I therefore assume (hope) the study is more focusing on the feasibility of such a technique than suggesting its use.

REPLY. Toxicity is always a question of context. Any element or chemical compound is toxic in the wrong circumstances. Chlorine is very common in the natural environment without being toxic, the main concern is anthropogenic organochlorine compounds. We have done modeling which demonstrates this is not an issue. Chlorine can be and is handled safelty in laboratories around the world.

The wording of the manuscript should be strongly improved by careful proofreading! In addition the technical quality is not yet good enough, spaces are missing, brackets are not closed, superscripts are not used, etc., please carefully check for this.

REPLY. Thank you, the manuscript has been carefully proofread, also by a native speaker, and corrected as needed. The corrections can be seen in the track changes/latexdiff version.

In addition the structure of the experimental section should be streamlined to improve readability (see below).

REPLY. Thank you, we have done as suggested.

Further, I have a number of specific comments and technical corrections the authors should consider before publication is feasible.

Specific comments:

The abbreviations applied for setups, experiments and flasks in Table 1 +2 are confusing. Why not using one simplified setup (Figure 1), which guides the reader in a better way (see specific comments below).

REPLY. Done.

The experiments in the results section should be streamlined, only experiments required to tell the main story should be selected, ordered in a well-motivated manner, and main results provided in the main text of the manuscript. Currently all results are mentioned in the results section but removal efficiencies only given in the appendix (D1 – D3).

REPLY. We have extracted the relevant experiments from table D1-D3 and now present them in the main text in a summary Table 3 (Exp C, E-I.))

The modelling and experimental results should be combined to cross-validate each other. Why not displaying the modelled functions in e.g. Figure 4?

REPLY. The modelling and experiments are cross-validated in figure 6. The text now makes this more clear.

Technical corrections:

Page 1 Line 19: Possibly "High-resolution instruments targeting at specific rovibrational transitions …"

or similar.

REPLY. Thank you, we have written 'High-resolution instruments based on specific rovibrational transitions are becoming available to characterize the abundance of rare isotopocules within gases.'

Page 2 Line 27: Please change to $\delta^{15}N^{\alpha}, \delta^{15}N^{\beta}$ here and elsewhere in the text.

REPLY. We have changed this example and throughout the text.

Page 2 Lines 27 – 28: The term "biological activity in agricultural soils" is very unspecific; in addition the message of the sentence is unclear. Would the following sentence fit better? "These instruments are often used to measure isotopic signatures of N_2O emitted from soils (Ibraim et al. (2019a), Wolf et al. (2015)), which can help to differentiate different microbial and abiotic production pathways."

REPLY. Thanks very good, we have changed as suggested. ' These instruments are often used to measure isotopic signatures of N2O emitted froms oils, (Ibraim et al. (2019a), Wolf et al. (2015), Yu et al. (2020)), which can help to differentiate distinct microbial and abiotic production pathways. '

Page 2 Lines 29 – 30: The subsequent sentence might be changed to: "N_2O formation in soils is commonly accompanied by production / uptake of other trace gases such as CH_4, CO_2, and water vapor (Erler et al. (2019), Ibraim et al. (2019b))."

REPLY. Thanks we agree and have changed as suggested.

Page 2 Line 30 – 31: The message of the sentence "In some samples, changes in CH_4 and CO_2 can exceed 1.8 ppm and 200 ppm, respectively (M. Zimnoch and Rozanski (2010))." is unclear and the numbers seem arbitrary. Please provide a more profound statement on N_2O, CH_4, CO_2 concentrations above different soils. I would suggest to give a high and low emission scenario for both CH_4 and CO_2. This should give the reader a feeling on usual CH_4 and CO_2 changes along with targeted N_2O concentration (and isotope) changes.

REPLY. Thank you, we have modified to present the argument more clearly. 'These variations complicate measurements. An example of the relevant variation of CO_2 and CH_4 can be found in the work of (M. Zimnoch and Rozanski (2010)) where the background level of CH_4 and CO_2 at 1.8 ppm and 380 ppm, can change suddenly to levels above 3.6 ppm and 560 ppm.'

Page 2 Line 31 – 33: A number "5 ‰" is provided without a statement on whether the main interference is from CH_4 or CO_2 and which delta values are affected most. Please give the deviations for a specific delta value for the high and low CH_4, CO_2 emission scenario (statement above).

REPLY. We have added an explanation for 5 ‰ as part of our modification.

Page 2 Line 33: The statement "improve the accuracy by controlling these interferences" is questionable? Possibly "Improve the accuracy by either removing the interfering trace gases (i.e. CH_4, CO_2) or the target substance (N_2O) or the analysis of interferants and implementation of a correction algorithm."

REPLY. We have changed the wording to give the correct description which is 'accounting for' rather than 'controlling'. We have also added a descrition of trapping N_2O and releasing it into a well-defined matrix.

Page 2 Line 35: How should the "a careful determination of the calibration curve.(Kantnerová et al. (2020))" help? Please rephrase or delete this sub-sentence.

REPLY. Deleted.

Page 2 Line 38: Place replace "continued" by "on-line" or "monitoring applications" or similar.

REPLY. Changed to 'on-line'

Page 3 Table 1 and 2: The wording of setups should be simplified to support the readers, e.g. using "Xe lamp" instead of "XPXL", or "Photochemical Device" instead of "STH-MFC-PD", etc.? The different setups are quite similar, would it be possible to show one setup only and mention difference in the others?

REPLY: We have changed the setup illustration to be one that is exemplary for all the setups and added the difference in the figure text. The names for the setups have been changed to setup 1-4 and are summarized in Table 1.

The experiments are labelled (A-I) same than the flasks (A-D), please change one label.

REPLY: We have changed the gas flask numbers to roman numbers

Page 3 Line 64: The end of the sentence "… applying the method to measurements of N_2O." should be reformulated.

REPLY: Has been changed to: "With the method developed and refined, a final set of experiments is conducted using a Picarro CRDS model G5131-i, capable of measuring N2O mixing ratio and its isotopic abundance"

Page 3 Line 65 – 66: The last sentence of the introduction should be rephrased, e.g. "the measured isotopic data of isotopes", "compared to the stable values", etc.

REPLY: We have rephased it to: "The measured values of , $\delta^{15}N^{\alpha}, and\ \delta^{18}O$, subject to methane interference, are compared to data corrected for methane levels, as these corrected isotopologue levels remained stable across the experiment")

Page 3 Line 67: The structure of the method section should be rethought: 2.1.1 Methane experiments; 2.1.2 Post photolysis scrubbing. I assume Post photolysis scrubbing is part of the Methane removal experiments, so should be integrated in 2.1.1?

REPLY: "Post photolysis scrubbing" is a part of "methane experiments# and it is set as a subsection to that.

Page 3 Line 71: What is a "Flow-Controlled Chlorine Waste", please rephrase.

REPLY: The Chlorine waste line is either flow controlled or pressure controlled. It is made more clear in Table 1.

Page 3 Line 70 – 73: The section should be rephrased considering the final.

REPLY: We have included a table (table 1) providing an overview of the setups and the experiments. With this we have also rephased to "Four different variations of the setup seen in Figure 1 are used during our experiments, summarized in Table 1 together withwhich experiments they were used for."

Page 4 Figure 1: Please show one exemplary setup and mention differences for the others?

REPLY: Figure 1 have been edited to a general phtochamber and differences are described in the figure text.

Page 4 Line 74 – 82: First there are some sentences on gas cylinders flows and setup, thereafter a section "Manifold" dealing specifically with the setup? Please combine and rephrase both sections.

REPLY: We have delete the " manifold" headline and combined

Page 5 Line 98: The statement "they were found to likewise remove $HCl\ and\ Cl_2$" Is unspecific for such an important question. How was this determined and what happens with the Picarro analyzer if it is flushed with HCl or Cl_2?

REPLY: The Picarro can not handle corrosive materials. The flow after the trap is tested for Cl_2 with the Cl_2 monitor. None was observed. Additional samples were also collected for measurements with GC-MS, and here the introduction of the ascarite trap was shown to remove HCl as well.

Which chlorinated species pass the Ascarite trap and are scrubbed with the activated carbon trap, please specify? Is it advisable to purge these species through a Picarro CRDS analyzer?

REPLY: The flow is tested with the GCMS before and after the ACT and the Ascarite. It is shown that CCl_4, other Chlorinated VOCs, and HCl are removed.

Page 5 Section 2.1.3: The authors should mention how measurements were referenced to scales? Were the delta values of the applied N_2O gases known and deviations analyzed for the CH_4 addition experiments and the CH_4 removal experiments?

REPLY: Unfortunately no, as the calibration gasses we had intended to use for scaling the delta values had not arrived when we began our experiments. So the size of the delta values is indeed unbound. Fortunately, this is not an issue as what we present is the relative change. We have normalize our delta values to methane corrected delta values.

Page 7 section 3.1: The author show results of experiment H first, but do not indicate how this is motivated?
REPLY: Exp. H is a combination of change residence time and increased power input. We have included this statement as explanaton for our choice: "As an example of our data, we present the results formexperiment H, Figure 3, during which we achieved our highest level of removal."

In addition, main results (Table D1 – D3) are hidden in the appendix. I would suggest to streamline the structure of the results section, and provide important results in the main text in a wellmotivated order.

REPLY: We agree, and we made a summary table of this in the main text. See Table

Page 7 Line 151: "experiment 3 step 5" is this "experiment C step 5"?

REPLY: We agree, it has been changed to C.

Page 8 Figure 3: The authors mention in the legend that "the experimental step is indicated at the top" but the experiments are named Sx, while in the text the terms Hx are used, please change?

REPLY:We have changed all experimental figures to be named Ax, Bx, etc

Page 8 Line 160 - 162: The sentence should be reformulated, was it really a pressure drop in the cylinder?
REPLY: We are indeed wrong to say the cylinder, as the pressure drop occurred at the regulator on the cylinder, and we have changed it accordingly.

If a pressure reduction valve was used this seems unplausible? As a Cl_2 sensor was used this should have been noted during experiments

REPLY: While we agree that a pressure reduction valve should not lead to this, unfortunately, we failed in applying best practice when installing the regulator, as it had not been sufficiently flushed through with dry air before the experiment. It is therefore assumed that a small amount of humidity was present on the inside, which should have been avoided at all cost when working with Cl_2, as it allows for the initiation of corrosion. The pressure drop from the regulator is, therefore, explained as corrosion affecting the regulator. While this is a strong point against the use of Cl_2, we will argue that it can be done properly if the equipment is correctly prepared. And explanation of this has been included in the manuscript.

Page 10 section 3.1.1: Figure 5 provides the main finding of the manuscript with respect to consistency of delta values for CH_4 addition / correction and CH_4 removal / correction.

I have some concerns:

1.The authors did not achieve complete CH_4 removal, which would be needed to waive the need for CH_4 interference correction. What was the reason for this as experimental details for quantitative removal are known from the preceding section?

REPLY: The experimental conditions during the N_2O experiments did not allow for the same removal conditions as used when 99% removal was achieved We have included an explanantion of this: “In the N_2O experiments it was not possible to apply the same conditions that lead to the highest levels of removal presented in the earlierexperiments. The reason for this was the addition of the G5131-i increased the minimum flow through the photo-chemical-device, thus decreasing the maximum residence time. Additionally not having a high concentration N_2O source capped the dilution, as the N_2O needed to remain in the linear range of the G5131-i. The limit on the dilution therefore also limited the concentration of Cl_2 available. With a higher concentration Cl_2 source available and a properly prepared regulator, the setupwould have been able to deliver sufficient CH_4 removal for more than 24 hours, at which point the ascarite trap would needreplenishment”

2) The indicated $\delta^{18}O$ and $\delta^{15}N$ numbers are highlight unplausible, not normalized to scales? This might be ok for a feasibility study, but why are results not normalized to the N_2O isotopic composition without CH_4 addition?

REPLY: Certainly correct, and as stated in response to one of the previous comments, we have normalized it to the CH_4 corrected values.

3) Figure 5 shows mainly instrumental noise of the CRDS analyzer, with some plausible drops in the signal, when CH_4 was removed.

REPLY: Indeed the value of $\delta^{18}O$ seems dominated by instrumental noise. We have inserted the table (as Table 4) of the experimental results in the maintext to better convey the improvement.

4) Why did the authors observe variations in N_2O concentrations? This a very critical observation if N_2O was removed by a chemical process and would question the approach. Please comment on this?

REPLY: Variation in N_2O was indeed observed, but we are confident it can be explained by the drop in Cl_2 flow. Firstly because the observed change was an increase in concentration and therefore does not point to a removal. Secondly, because similar increases were observed in the methane concentration at the same time. Variation also took place during dark periods indicating it is not due to chemical reactions.

table from the appendix to the main text.