

General comments:

The manuscript by Merve Polat et al. describes the development and optimization of novel method for CH₄ removal from air via chlorine-initiated oxidation with the focus to minimize spectral interferences during N₂O 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 CH₄ removal efficiency on methane concentration, chlorine photolysis rate, chlorine concentration, and residence time.

I find the manuscript timely as the strong CH₄ interference of the Picarro N₂O isotope analyzer was recently identified by Harris et al. (AMT, 2020). Therefore, a technique for specific CH₄ removal is of high interest for the users of these analyzers but complicated. An alternative concept would be removal of N₂O and release in a well-defined gas matrix as applied by IRMS and also laser spectroscopy.

I doubt whether addition of a toxic substance such as Cl₂ should be propagated for CH₄ removal. I therefore assume (hope) the study is more focusing on the feasibility of such a technique than suggesting its use.

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.

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

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).

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).

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

Technical corrections:

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

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

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))."

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.

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).

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."

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.

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

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?

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

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

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.

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?

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

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

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

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.

Page 5 Line 98: The statement "they were found to likewise remove HCl and Cl₂" 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 Cl₂?

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?

Page 5 Section 2.1.3: The authors should mention how measurements were referenced to scales? Were the delta values of the applied N₂O gases known and deviations analyzed for the CH₄ addition experiments and the CH₄ removal experiments?

Page 7 section 3.1: The author show results of experiment H first, but do not indicate how this is motivated? 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 well-motivated order.

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

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

Page 8 Line 160 - 162: The sentence should be reformulated, was it really a pressure drop in the cylinder? If a pressure reduction valve was used this seems unfeasible? As a Cl₂ sensor was used this should have been noted during experiments

Page 10 section 3.1.1: Figure 5 provides the main finding of the manuscript with respect to consistency of delta values for CH₄ addition / correction and CH₄ removal / correction.

I have some concerns:

- 1) The authors did not achieve complete CH₄ removal, which would be needed to waive the need for CH₄ interference correction. What was the reason for this as experimental details for quantitative removal are known from the preceding section?
- 2) The indicated $\delta^{18}\text{O}$ and $\delta^{15}\text{N}^{\alpha}$ numbers are highlight unfeasible, not normalized to scales? This might be ok for a feasibility study, but why are results not normalized to the N₂O isotopic composition without CH₄ addition?
- 3) Figure 5 shows mainly instrumental noise of the CRDS analyzer, with some plausible drops in the signal, when CH₄ was removed.
- 4) Why did the authors observe variations in N₂O concentrations? This a very critical observation if N₂O was removed by a chemical process and would question the approach. Please comment on this?