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Comment on acp-2021-146

Anonymous Referee #1

Referee comment on "Methane (CH_4) sources in Krakow, Poland: insights from isotope analysis" by Malika Menoud et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-146-RC1, 2021

Review of Menoud et al: Methane (CH4) sources in Krakow, Poland: insights from isotope analysis

General comments

This is a nice paper with detailed analysis of methane and d13C-CH4 and d2H-CH4 from a region with under-constrained methane sources. I think that there are many edits that could made to make the study easier to follow for the reader – it gets a bit confusing as to which measurements are from what kind of sampling, and in some places, what is modeled and what is measured.

I would have appreciated a lot more detail as to measurement uncertainty, and I am a bit troubled by the 70 ppm offset in the two instruments measuring methane. Also, Figure S2 was really confusing. It seems like some kind of quality control could have prevented a situation where you're not sure which instrument is making the accurate measurement and which one has the problem. Some other metrics of data quality (ie, accuracy and precison of a known unknown) would have been helpful for interpreting the other data presented here.

Furthermore, I found Tables 1 and 2 a bit confusing – it was hard to tell what was measured in this study versus others, how many measurements were included, how they correspond to figure 6A. When there were few measurements (ie, wetlands), maybe other studies should have been incorporated. Also, sources were measured with just a few samples when the mobile sampling was above ambient; but the isotopic signature still consists of a contribution from background. Some acknowledgment of this (or a better, Keeling-type strategy) seems necessary.

I also would have liked to see more use of the Miller-Tans plots – perhaps using wind direction or seasons as a method to separate source signatures.

Although Figure 7 is really nicely plotted, with a ton of information, I found that the text seemed to sound like a lot of hand-waving. Some editing will help with clarity (ie., it was not always clear when you were referring to Feb or to Nov). Also, the distribution of sources in the model doesn't seem to address uncertainty in the source attributions – some acknowledgment of this might have tempered the conclusions. However, I think that acknowledgment of the uncertainties doesn't take away the gist of the conclusions, ie local

vs USCB sources.

In sum, this is a really interesting, detailed look at methane sources in Krakow, which highlights both the utility of methane stable isotopes the limitations, and the need to make more measurements at regional scales. I think it's important not to overstate conclusions (note my word choice suggestions in the conclusions), and to acknowledge the difficulty in separating isotopically-overlapping sources (ie., coal and natural gas). And yet the isotopes clearly show where the inventories are wrong, as well as specific mis-attributions of sources, and this is very useful. I appreciated the comparison to the Netherlands studies, where different methane sources are dominant. Further discussion of how approaches like these could be used in mitigation efforts would be really interesting.

Thanks for the opportunity to dive in to this work.

Specific comments

-P1 L18: you don't name the second inventory in the abstract – so, Edgar is better than what?

P2L1: "Greenhouse gas" is somewhat colloquial – "climate forcing trace gas" is more meaningful. If you want to use GHG, perhaps define it better

P2 L25: "negative consequences" is a bit vague

P2L52: Can you summarize the previous studies from USCB?

P3L65: The USCB is pretty big – is the center 50 km west of Krakow, or the eastern edge? This could be more descriptive. Also, Figure 1 is not very high quality – I can't read the names of the towns, so maybe leave them off?

P3: There is no description here of Kasprowy Wierch, so when I saw the results I was confused

P3L83: One to three samples … clearly not enough for a Keeling plot, so were these assumed to be entirely source methane?

Figure S2: Is there a pump that pulls the sample through? Are the arrow shapes vents? Valves?

P4L99: I'm curious about the calibration of the IRMS mole fraction measurements (especially since it becomes an issue) – can you expand on this? Is it a one-point calibration? Can you point to the accuracy/precision of this method? Also, can you cite accuracy/precision on the Picarro? Which should I trust more?

Also, nothing about the accuracy/precision about the isotopic measurements?

Table 1: I see a reference 2 but no data pointing to it.

P6L52: Considering that you have different wind directions for different times of the year, is it appropriate to use M-T plots over the entire dataset?

P6L168: Yikes, this is a huge mismatch. What is the mismatch at other times? You corrected the IRMS data? Also, figure S2 is really confusing – I don't understand the x axis. Was there any qc through either instrument (a surveillance cylinder?) that would

have caught a problem in either instrument?

P7L200: Any signs of seasonality in the background? (maybe it was hard to see in 6 months, but seasonal cycles are quite evident that far north)

P8L216. This sentence implies that pollution events and diurnal cycle are related. Are they? Maybe you should show the lack of diurnal cycle in winter in figure S3?

P8L218: If you are referring to the slopes, maybe print the on the plots with the r2?

Figure 6A: Blue is the keeling plot derived source signatures, correct? Can you explain where the uncertainties came from? Why don't the red or black dots have uncertainties? Colored ovals: these are from the bags you collected on your mobile campaign? (But not a Keeling plot analysis, just the samples themselves?) The data from the ovals are in table 2? How did you decide on the shape of the wetlands oval, since you have just one point? Can you use another study?

Speaking of table 1, assigned $d^{13}C$ and $d\ ^{2}H$, it would be helpful if you listed the number of samples and associated error (or point the reader to table 2 …)

Table 2: Some of the data in table 2 are also in table 1… so this is confusing.

P8L238: Maybe refer to mobile sampling as you did in the methods

P8L247: Agreed to within 10 % or 10 permil. This is confusing.

P9L265: Would ethane or another measurement help to confirm this?

P9L266: I'm not sure where to find these data

P9L274: You sampled outside the shafts if the methane was 200 ppm above background … so your "signature" still contained a lot of background. I don't think you've reported how far above background these plumes were.

P10L294: How do you determine the percentage above background?

Figure S6: So each data point plotted here that is not an X (literature value) is one bag of collected sample?

P10L313: "In general" maybe should be "In November"? I'm confused

P10L316: "The modelled peaks C,D,E, and G". Also, why no discussion of H, it's a big one?

Figure 7: What is ENB?

P12L382: "the modelled isotopic signatures with CAMS are always more isotopically depleted in d13C"… but wait, waste emissions have a large influence? Or just in the CAMS inventory? It is unclear what is inventory/model and what is real.

P13L409: R2 describes the variance; to say that something is correlated you need to look at the slope of the line and whether it's statistically different than 0.

P13L416: It's interesting that you need hydrogen isotopes to separate fossil fuel from biogenic sources, yet you say that you are limited by what you can do with $d\ ^{2}H$.

P14L428: Well-understood … maybe. Your measurements from the USCB mines don't

agree very well with previous studies.

P14L436: I'm not sure about "rather" well. Maybe somewhat?

P14L450: Again, "precise identification" seems like a bit of a stretch.

P14L451: "help mitigation" seems a bit vague – can you expand on this? It seems like identifying leaks is an obvious way that your method could be useful

P15L453: $d\,^2H$ more powerful than $d^{13}C$ in this study? But then you say that $d\,^2H$ conclusions are limiting. So maybe you want to say that it was essential to have $d\,^2H$ measurements in this case, without saying that they are "better" than $d^{13}C$.

Technical corrections

In general: please be careful about the use of "depleted" and "enriched" without specifying which isotope you are referring to.

P2 L 29: "of the ones of CO2" is awkward

P2 L 30: "total CH4" not "the total CH4"

P2 L39: "scales" can go before the references

P2 L54: Can you merge the sentences "In this study we investigate …. " and "we attempted"; because they are the same effort, not two different goals, correct?

P3 L60: compare not compared

P5L20: methane mole fractions

P5L24: "enhancements" instead of elevations?

Figure S1 label: steel not steal

P7L191: "mainly from the west, with a small contribution (x %?) from the east/northeast"

P7L211: the fall of 2018 (or fall 2018)

Figure 2: your legend is 'IRMS' and 'Kasprowy Wierch'. A legend of 'IRMS, Krakow' and 'Picarro, Kasprowy Wierch' might be better.

Figure S3: no comma after "measurement period". "Bar lengths are percentages of records from that wind direction during the specified month"

Figure 3: I think I see a few differences in the CH4 mole fraction data between this plot and Figure 2 early in the record. Probably doesn't matter, but presumably you intend to show the same record?

P8L224: too-low (or insufficient)

P8L220: "When using CAMS in the model, …". This paragraph could be more clear in general.

P8L234: Don’t start a sentence with a number.

P9L251: Proportions vary or proportion varies

P9L252: too many commas – awkward

Figure S6 legend: “which peak isotopic signatures did not significantly differ”

P9L370: delete “found”

P9L280: in regard to (instead of “as regards”)

P10L306: add “at Lutjewad”

P10L312” extra spaces

P10L316: “The modelled peaks C,D,E, and G”

P11L346: “depleted of heavy isotopes

P13L390: There are 5 times

P13L405: don’t need a new paragraph.

P13L413: combustion-related

P13L414: findings from analyzing the emission peak signatures” =wordy and unclear

P14L424: fossil fuel-related

P14L430: coal-related

P15L457: were collected

P15L459 : are particularly helpful