Review

Atmospheric Chemistry and Physics Manuscript #2021-661

Limitations of the Radon Tracer Method (RTM) to estimate regional Greenhouse Gases (GHG) emissions – a case study for methane in Heidelberg

(Levin, Karstens, Hammer, DellaColetta, Maier and Gachkivskyi)

23rd September 2021

Overall recommendation: Accept after minor changes

General comments

This is a very interesting and valuable study applying the Radon Tracer Method (RTM) to estimate trends in nocturnal methane emissions in a complex region around Heidelberg over the period 1996-2020 and comparing the results to EDGARv6.0 bottom-up inventories. Emphasis is placed on the shortcomings of the technique, particularly in the critical importance of having accurate and representative knowledge of radon emissions from soils in the flux footprint, including the influence of time-varying soil moisture, and the interference of significant point-source pollution in the calculations.

This paper contributes topical original research falling within the scope of *Atmospheric Chemistry and Physics*. The manuscript is methodical, clearly written and logically structured. The experimental design is appropriate, and the authors utilise a range of appropriate analysis techniques and visual presentation tools to illustrate the relevant information required to support their arguments and conclusions. The outcomes and implications of the study are well summarised in the Conclusions and Abstract.

I am very happy with the paper and recommend acceptance after attention has been paid to a few minor issues listed below.

Specific comments

(1) I believe this manuscript would benefit greatly by clearer elucidation of the role of the "nocturnal accumulation" RTM within the broader context of European top-down trace gas emission estimates using radon. This could be accomplished quite easily by adding short paragraphs in the Introduction, Methods and Discussion sections (suggested locations are provided below under "**Minor and technical comments /**

suggestions"), outlining the differences in scope and implementation between the "nocturnal accumulation" (this paper), "tall tower" and "baseline" (mountaintop and remote location) applications of RTM, and emphasizing their complementarity. The "nocturnal accumulation" RTM, applied in the current study, uses surface-based measurements for estimating local fluxes (say, up to 200km spatial scale), and should be contrasted with the RTM as applied to measurements from tall towers, which estimates fluxes up to the regional scale (200-1000km). In the latter case, trace gases are monitored in the deeper mixed / residual layer above the nocturnal inversion and are therefore integrative of the whole boundary layer, the entire diurnal cycle and much bigger fetch areas (regional to continental scale). For these reasons, they are not restricted to nocturnal-only measurements and do not suffer so much from the problem of representing local point sources within the footprint (the strong boundary layer regional mixing process tends to increase the comparability of the trace gas and radon signals). However, they require different assumptions about reference ("background") signals and exchanges with the free troposphere, and have their own special implementation difficulties (e.g., increased uncertainty in the definition of the footprint, losses/gains at the boundaries and the top of the box, non-stationarity due to synoptic weather influences etc.). Finally, RTM applications at baseline stations (mountaintops and remote locations) are similar in implementation to the tall tower case and can be used to estimate fluxes from regional to continental and even hemispheric scales.

(2) With regards to the discussions on the effects of point source emissions on the RTM results: If point source emissions are injected directly into the nocturnal inversion layer, or if they are injected above (i.e., from tall stacks) but are then fully or partially incorporated into the inversion layer by subsequent "fumigation" events, then they may be mixed in the footprint of the measurement site and influence the average trace gas levels experienced on a given night. If this is an uncommon occurrence, it will be dismissed as an outlier in the analysis. However, if it happens often, then it may end up being correlated with the radon observations because both scalars are mixed (or partially mixed!) within the same nocturnal volume. In other words, this could lead to a range of scatt in the correlation plots...

(3) Seasonal variations in the radon flux translate to seasonal variations in the measured atmospheric radon concentrations. The latter are only partially matched by corresponding variations in the measured CH_4 concentrations, resulting in a residual seasonality in the computed $CH_4/^{222}Rn$ ratios. This latter seasonality is initially removed from the ratios, so that a focus can be placed on the effects of the absolute flux errors. The intention appears to be (according to the first paragraph of Section 3.1) that the seasonality in the ratios would be returned to later for separate investigation; however, this is never done.

(4) There is no comment anywhere (unless I missed it?) on the bias introduced into the trace gas flux estimations by the fact that only nocturnal measurements are used in this flavour of the RTM. If there is a strong diurnal variation in the fluxes estimated by the nocturnal RTM method, then the results will not be an accurate representation of the diurnal average flux (e.g., CO_2 will only deliver respiration fluxes). This should perhaps be noted in the description of the method, along with a justification for why the problem "might not be too bad" for CH_4.

Minor and technical comments / suggestions

(1) [Abstract] p2, line 16: Here and elsewhere in the manuscript, the authors might consider changing “catchment area” to “flux footprint” or similar. In my experience, the word “catchment” is a hydrological term that refers specifically to an area defined by a watershed (topographical high-altitude line).
(2) [Abstract] p2, line 18: Change “total CH_4 emission” to “total nocturnal CH_4 emission”.
(3) [Abstract] p2, line 19: Change “exhalation rate from soils” to “exhalation rates estimated from soils”.
(4) [Abstract] p2, line 23: Change “RTM-based top-down with bottom-up” to “RTM-based top-down flux estimates with bottom-up”.
(5) [Abstract] p2, line 26: Change “as their emissions are not captured by the RTM method” to “as their emissions may not be fully captured by the RTM method, for example if stack emissions are injected above the top of the nocturnal inversion layer, or if point source emissions from the surface are not well mixed into the footprint of the measurement site”.
(6) [Introduction] p2, line 37: Change “(UNFCCC, 2015). But only the” to “(UNFCCC, 2015), but only the” OR “(UNFCCC, 2015). However, the”.
(7) [Introduction] p2, line 41: Change “A possibility to estimate continental” to “A possibility for estimating continental nocturnal”.
(8) [Introduction] p3, line 45: Change “lifetime of about 5.5 days” to “half-lifetime of about 3.8 days”.
(9) [Introduction] p3, line 48: After “Liu et al., 1984”, you might consider adding “Williams et al., 2011”. Reference: Williams AG, Zahorowski W, Chambers SD and Griffiths A, 2011: The vertical distribution of radon in clear and cloudy daytime terrestrial boundary layers. *J Atmos Sci.* **68**:155–174.
(10) [Introduction] p3, line 50: Change “correlated increases” to “correlated overnight increases”.
(11) [Introduction] p3, line 52: Change “recommended to use this tracer for transport model validation but also to apply the RTM” to “recommended for use in transport model validation and application of the RTM”.
(12) [Introduction] p3, end of line 53: This might be a good place to remind the reader that the "nocturnal accumulation" application of the RTM is significantly different from "tall tower" RTM applications. See “**Specific comments**” #1.
(13) [Introduction] p3, line 65: Change “when missing precipitation” to “when a lack of precipitation”.
(14) [Introduction] p3, end of line 68: It would be helpful here to have a short summary of the known effects of increasing near-surface soil moisture on the radon flux. For example, is it a linear / logarithmic relationship, or is it a negligible effect until the soil gets very close to saturation? This would help the reader to get a feel for the potential severity of the problem and prepare them for your discussion of radon fluxes around Heidelberg in later sections.
(15) [Introduction] p3, line 73: Remove “and CH_4”. Otherwise, it is a circular statement ("we use CH_4 flux variability to evaluate CH_4 emission estimates").
(16) [Methods 2.1] p4, lines 89-91: Consider enhancing the discussion of H(t) like this: H(t) is a length scale corresponding to the ‘effective’ depth that the stable layer would have if the trace gases of interest were uniformly mixed vertically within it. The layer is

assumed to be mixed 'well enough' that the measured near-surface concentrations can be considered as representative of the layer-averaged values (Williams et al., 2016). Reference: Williams AG, Chambers SD, Conen F, Reimann S, Hill M, Griffiths AD and Crawford J, 2016: Radon as a tracer of atmospheric influences on traffic-related air pollution in a small inland city. *Tellus B* **68**, 30967. http://dx.doi.org/10.3402/tellusb.v68.30967

(17) [Methods 2.1] p5, lines 107-108: "… residual layer air that has a $CH_4/^{222}Rn$ ratio similar to that at the start of the night-time observation period". I assume this is the value you use to define the reference point for ΔC in the equations above? If so, then maybe mention that here. The encroachment of residual layer air into the growing nocturnal boundary layer is also discussed by Williams et al. (2016): see ref above.

(18) [Methods 2.1] p5, line 113: After "and the trace gas", consider adding ", or at least that surface source functions can be considered to be essentially random and uncorrelated with atmospheric processes operating on short temporal and small spatial scales".

(19) [Methods 2.1] p5, lines 113-120: With regards to the discussions on the effects of point source emissions on the RTM results, you could discuss this further as per "**Specific comments**" #2.

(20) [Methods 2.1] p5, line 116: Change "relevant" to "present".

(21) [Methods 2.2] p6, line 168: "… this method is only applicable for area sources that are similarly homogeneously distributed as those of ^{222}Rn (Eq. 4)". This is true, but see "**Specific comments**" #2.

(22) [Methods 2.2] p7, line 169: Maybe change "be missing" to "be wholly or partially missing". See "**Specific comments**" #2.

(23) [Methods 2.2] p7, lines 174-176: "In the inventories these fluxes are associated with much larger uncertainties than those from point sources and are thus a rewarding target for the RTM". This is an excellent point! See "**Specific comments**" #1.

(24) [Methods 2.3] p7, line 179: "The most important pre-requisite to apply the Radon Tracer Method for quantitative GHGs flux estimates are representative ^{222}Rn soil exhalation rates in the catchment area". Maybe you should remind the reader here that Eqn (4) implies that errors in the derived GHG fluxes will be directly proportional to errors in the radon fluxes used.

(25) [Methods 2.3] p7, line 198: Change "from the sandy soils of M1 and M3" to "from sandy soils (denoted M1 and M3)".

(26) [Methods 2.3] p8, line 206: Change "from M2, M4 and M5" to "from soil types denoted M2, M4 and M5".

(27) [Methods 2.3] p8, lines 216-218: Change "This seasonality… lower right panel of Fig. 4" to "This seasonality in the radon fluxes leads to a seasonal variation in atmospheric radon concentrations which then transfers to the computed $CH_4/^{222}Rn$ ratios because the corresponding CH_4 seasonality is relatively small in amplitude. In order to investigate this seasonality separately from the overall effects of the absolute flux errors, the measured and modelled seasonality of ^{222}Rn fluxes in the two pixels south of Heidelberg were first normalised to the respective annual means and are shown in the lower right panel of Fig. 4. This will be discussed further in the Results section".

(28) [Results 3.1] p10, line 291: After "during all nights", maybe add a description of typical conditions during excluded nights. For example: "Nights excluded by this restriction tended to have higher wind speeds, be cloudy or were disturbed by passing synoptic weather patterns (e.g., fronts)".

(29) [Results 3.1] p10, line 295: Change "the ^{222}Rn exhalation rate from soils has a pronounced seasonality" to "as discussed in Section 2.3, the measured and modelled ^{222}Rn exhalation rates from soils both exhibit a pronounced seasonality".

(30) [Results 3.1] p10, lines 297-298: Change "This seasonality of the ^{222}Rn flux imposes a seasonality on the CH_4/^{222}Rn ratios. We therefore normalised…" to "This seasonality of the ^{222}Rn flux results in a seasonality in atmospheric radon concentrations and consequently also the computed CH_4/^{222}Rn ratios (as the corresponding CH_4 seasonality is relatively small in amplitude). In the analysis to follow, we first normalised...".

(31) [Results 3.1] p11, lines 297-299: Change "to the annual mean ^{222}Rn flux" to "that adjusts the ^{222}Rn flux to its annual mean value".

(32) [Results 3.1] p11, lines 300-301: Change "This intermediate step was taken because of the large uncertainty of the *absolute* ^{222}Rn flux in contrast to its much better defined seasonality" to "This intermediate step was taken in order to separately study both the large uncertainty of the *absolute* ^{222}Rn flux and its much better defined seasonality". See "**Specific comments**" #3.

(33) [Results 3.1] p11, lines 325-328: "As mentioned … afternoon before". It would be really nice to see an illustration of this by showing examples of ^{222}Rn and CH_4 hourly time series for two contrasting nights characterized by strong positive and strong negative correlations. In the latter case, is the computed equivalent mixing layer depth H close to 30m?

(34) [Results 3.2] p12, lines 334-336: Change "The CH_4/^{222}Rn slopes displayed … in the footprint of Heidelberg" to "The CH_4/^{222}Rn slopes displayed in Fig. 5 show large variability. It is of interest to explore if this variability can be explained by spatial variations in the CH_4 emissions, and if so, the extent to which we can associate the high-slope cases with hot spot emission areas in the footprint of Heidelberg".

(35) [Results 3.2] p12, line 336: Change "air mass influence" to "air mass footprint".

(36) [Results 3.2] p12, line 338: Change "origin is from" to "has passed over".

(37) [Results 3.2] p12, line 358: Change "will not be captured" to "may not be fully captured". See my previous comments.

(38) [Results 3.2] p12, line 360: Change "can we" to "we can".

(39) [Results 3.4] p13, line 384: Change "M2, M4 and M5 to" to "M2, M4 and M5 to be".

(40) [Results 3.4] p13, line 385: Change "The corresponding CH_4 flux it is plotted as" to "The corresponding calculated CH_4 flux is plotted as the".

(41) [Discussion 4.1] p16, line 483: Change "captured" to "fully captured".

(42) [Discussion 4.2] p18, line 543-544: Change "could show" to "have shown".

(43) [Discussion 4.2] p18, line 545: Change "ask for" to "dictate a need for".

(44) [Discussion 4.2] p18, lines 546-550: "A second problem … less well-defined ^{222}Rn fluxes". I think a slightly more detailed discussion is needed here. See my suggestions in "**Specific comments**" #1.

(45) [Conclusions 5] p19, line 583: Change "quantitative flux estimation relies on the accuracy" to "quantitative flux estimation relies critically on the accuracy".

(46) [Conclusions 5] p19, line 583: Change "catchment" to "footprint".

(47) [Conclusions 5] p19, line 585: Change "catchment" to "footprint".