Review

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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)

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Overall recommendation: Accept after minor revisions

General comments

In this study the authors apply the Radon Tracer Method (RTM) using a 24-year dataset of atmospheric methane (CH_4) and radon (^{222}Rn) concentrations, measured at the Heidelberg city, to estimate the trend of methane emissions over the city surrounding area. Then they compare the RTM based CH_4 emissions with results obtained using the EDGARv6.0 bottom-up inventory. Authors, who were the first to introduce the RTM in Levin et al., 1999, also analyze the strength and weakness of the RTM application mainly in regards to the radon flux value used in it and the representability of the catchment area of the atmospheric station depending on the heterogeneity of the GHGs sources.

The aim of this paper follows completely within the scope of this journal. The study is well designed and the English of the manuscript has been already reviewed by the other reviewer, who is a native speaker. The work behind the achievement of the 24-year dataset is impressive and it gives a really robust statistics to the results obtained in this study.

On the other hand, some aspects of the manuscript could be improved for the fluency of the reading and to clearly identify what has been done so far in the field of the RTM application. The state of the art and the discussion of the results of this study are not updated and they did not consider past outcomes from others researchers.

The paper deserves to be published in the ACP journal after that some changes will be made as explained in details in the following sections.

Specific comments

Section: 1. Introduction

- In Lines 55-56 authors declare that RTM has been applied assuming a spatially homogenous radon flux (bibliography here stops to 2009 and they could also add Vogel et al., 2012 Wada et al., 2013 and Grossi et al., 2014). Furthermore, this sentence is not fully correct because Grossi et al., 2018 applied the RTM calculating the effective radon flux. This was calculated by coupling radon flux data, obtained using the output for the 40-year climatology obtained with the model developed by López-Coto et al. (2013), with the footprints calculated by the ECMWF-FLEXPART model (version 9.02) (Stohl, 1998) (For more info please look at the Figure 8 of Grossi et al., 2018 and equation n. 3). In addition, in Grossi et al., 2018 the CH_4 fluxes, obtained by RTM, were also compared for the first time with CH_4 fluxes obtained coupling the EDGAR inventory with ECMWF-FLEXPART footprints for the same period.

- In Lines 66-67 authors say that the basic assumption for the classical RTM application is of having a more or less constant radon flux. I do not personally agree with this and I think it already stays in the past. Nowadays it is known that for correctly applying the RTM we need high quality and reliable atmospheric GHGs and radon concentration data and validated radon flux models with as high as possible spatial and temporal resolution. These are actually between the main goals of the project EMPIR traceRadon (presented in Röttger et al., 2021) which wants to offer also a metrology for radon flux measurements and sensitivity studies for the RTM applications.

I think it will be nice to have all this previous information in the state of the art.

Section: 2. Methods

Radon flux estimation for the RTM application: The structure of this section does not help the reader to understand the methodology applied for the calculation of the radon flux used within the RTM. I had the impression that authors finally used a constant value of 18.3 ± 4.7 mBq m^{-2} s^{-1}. Is it correct? Did you not estimated the effective flux seen by the station coupling radon flux climatology output from Karstens et al., 2015 with STILT footprints? It may help to have this info in a dedicated paragraph where the estimation of the radon flux used for the RTM is clearly explained.

STILT footprints: It will help to have a dedicated section where the calculation of the STILT footprint is described. How long were the back trajectories used for it? Which was the height of the boundary layer used in the STILT simulations for it? I was not able to find this info in the manuscript and it could be useful, as explained in Grossi et al., 2018, when effective radon flux is estimated using also model footprints and for future RTM applications protocols.

CH_4 and ^{222}Rn measurements: I agree with the authors on the importance of correctly estimating the radon flux values used in the RTM but equation 3 gives the same weight to methane and radon concentration measurements too. I think it will be nice to have a paragraph dedicated to experimental measurements (CH_4, ^{222}Rn and meteorology). Here, a 24-year dataset of radon progeny (^{214}Po) concentration measured using a static filter method (Levin et al., 2002), and a

constant disequilibrium correction factor between ^{222}Rn and ^{214}Po of 1.11 (F_e), has been used as explained in lines 275-282. However, results from inter-comparison studies between radon and radon progeny monitors based on different measurements techniques (Grossi et al., 2016; Schmithüsen et al., 2017; Grossi et al. 2020) show that under saturated atmospheric water conditions and low atmospheric aerosol concentration this disequilibrium factor F_e could change inducing an underestimation of atmospheric radon activity concentration by static filter methods. In addition, Levin et al., 2017 estimated a correction factor to take into account the ^{222}Rn progeny loss in long tubing based on static filter measurements in the laboratory and in the field. Taking into account all these previous outcomes, I wonder if authors have filtered they data for rain/low aerosol episodes and/or applied these corrections factors before using the dataset for RTM calculation. It should be clearly stated in the manuscript. Finally, authors say (Line 279) that they used an ANSTO scale to calibrate their instrument. Unfortunately ANSTO instruments, running at several ICOS stations, are calibrated using their own source which is located within each instrument. This means that there is not a primary standard or a second transfer standard instrument to harmonize these instruments and using a ANSTO scale does sound correct to be used. The lack of a ambient radon measurement metrology was one of the main aims of the traceRadon project. For example, in Grossi et al., 2020 the correlation of the same ARMON (Grossi et al., 2012) with two ANSTO monitors (located respectively at Saclay (100 m.a.g.l.) and at Orme de Marisier (5 m.a.g.l.)) had slopes of 0.97 ± 0.01 and 0.96 ± 0.01 with intercepts of 0.01 ± 0.06 and 0.01 ± 0.06, respectively. Schmithüsen et al., 2017 found a correlation, at the Heidelberg station, between the HRM and the ANSTO instrument of 1.22 ± 0.01 with an intercept of 0.42 ± 0.04.

Section 3: Results

*Paragraph 3.5***:** The comparison of STILT based and RTM based results of the $CH_4/^{222}Rn$ slopes is obtained, if I understood correctly, comparing the ratios between CH_4 and ^{222}Rn concentrations simulated using the STILT model in forward mode and using, as emissions, the radon flux climatology output from the model presented in Karstens et al., 2015 with the ratios of measured $CH_4/^{222}Rn$. Is it correct? Authors said that these comparison seems to work properly. May this due to the fact that RTM is used only applying a constant radon flux values over the time and area where here the forward simulation is run with spatial radon flux climatology?

Discussion and Conclusion: Authors may revisit the discussion and conclusions sections taking into account the previous comments expressed by the reviewer.

Minor and technical comments / suggestions

- Please use radon or ^{222}Rn instead of ^{222}Radon within the manuscript. The same nomenclature for ^{226}Radium and ^{214}Polonium.
- Line 384 mBq instead of Bq.

References to be included

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