**egusphere-2024-1370**
**Title: Estimation of seasonal methane fluxes over a Mediterranean rice paddy area using the Radon Tracer Method (RTM)**
**Author(s): Roger Curcoll et al.**

**Comments to the second review by Scott Chambers**

The authors have clearly put a lot of effort into this study, and revision of the original manuscript, which is to be commended given the significance of needing to characterize changing methane missions related to agricultural practices and other anthropogenic activities. The primary goal of the study is to characterize the seasonality in methane emission specifically from the rice paddy growing area of the Ebro River Delta region. After revision however, I still have reservations that the RTM is an appropriate method to achieve the intended goals. I outline my main concerns below.

Application of the RTM to this particular scenario challenges many of the fundamental assumptions on which the technique is based (some of which are reviewed by the authors in Section 2.3 of the revised MS). The fluxes of radon and CH4 over the contributing footprint should ideally be relatively consistent and similarly distributed (or, if not, randomly correlated on small spatial scales of heterogeneity, Levin et al 2021), the radon flux in particular should be well characterized for the period of measurement, accumulation amounts over the nocturnal window should well exceed instrument uncertainty, and for such a restricted study region, strictly stable nocturnal conditions should be adhered to.

First of all, the authors want to thank the third reviewer for his accurate work and his time. However, the authors think that most of the concerns of the reviewer were already addressed during the first round of this revision process. Considering that the other two reviewers already accepted the document after the first round, here authors make an extra effort to clarify the different points to the third reviewer.

As it was already explained during the first round of revisions, an harmonized protocol for the application of the Radon Tracer Method is not yet available for the scientific community and studies like the present one are essential to understand its limitations and strengths for better addressing future improvements.

For the preparation of this document the authors benefited from three recent publications (two of which are currently under revision) that explore themes related to RTM application, the reliability of radon flux models, and a comparison of the ARMON and ANSTO 200L instruments. These publications include: Yver-Kwok et al (https://egusphere.copernicus.org/preprints/2024/egusphere-2024-3107/); Maier et al. (https://egusphere.copernicus.org/preprints/2025/egusphere-2025-477/); Röttger et al. (https://www.sciencedirect.com/science/article/pii/S2665917424006846). This is important not only for demonstrating that the methodology of the present manuscript is supported by existing literature, but also for emphasizing the ongoing discussions in this research field and the importance of this study for future developments.

It is true that a homogeneous distribution of radon and target gas fluxes over the area of interest is an important factor for applying the RTM. However, in a region such as the Ebro River Delta (where there are essentially no other significant target gas emissions besides those under study, primarily due to the high methane emissions from rice paddies) the analysis of variability and the application of the RTM become significantly more straightforward.
The Ebro River Delta, with a surface of 320 km$^2$, cannot be considered a point source, also taking into account the low height of the station tower (only 10 meters above the ground).

Finally, as suggested by both reviewers in the first round of revision, stable nocturnal conditions were taken into account by filtering the study to include only low wind speed events.

So far, based on RTM assumptions, past studies were conducted primarily in relatively 'simple' areas of Central Europe, where radon and target gas concentrations are lower and quite homogeneous over time and space. The present study, however, is particularly challenging as it applies the RTM in an 'extreme' region (i.e. one where radon flux models and atmospheric transport models do not operate as smoothly). Such regions exist across Europe, especially in Mediterranean and Oceanic stations in the south, and emissions must also be quantified there.

Despite the challenges, the results obtained here are remarkable, as noted by both reviewers and the editor. The agreement between RTM-based estimates and manual accumulation chamber measurements (which are time- and cost-intensive) is striking. For instance, in October RTM-based results estimated a median flux of 13.9 mg $CH_4$ $m^{-2}$ $h^{-1}$, closely matching fluxes from static chambers, which were calculated as 14.7 ± 4.2 mg $CH_4$ $m^{-2}$ $h^{-1}$.

The average difference between RTM-based $CH_4$ fluxes obtained using the Flex-WRF-ERA5 and Flex-WRF-GLDAS models was only 0.1 ± 0.2 mg $CH_4$ $m^{-2}$ $h^{-1}$, and this difference remained stable regardless of whether the wind threshold of 1.5 m $s^{-1}$ was applied.

This study shows the great potential that RTM offers for emission budget analysis, with the theoretical, modeling and experimental efforts done by authors contributing to robust and reliable results. While uncertainties exist and must be acknowledged, they provide valuable insights for future research in this field.

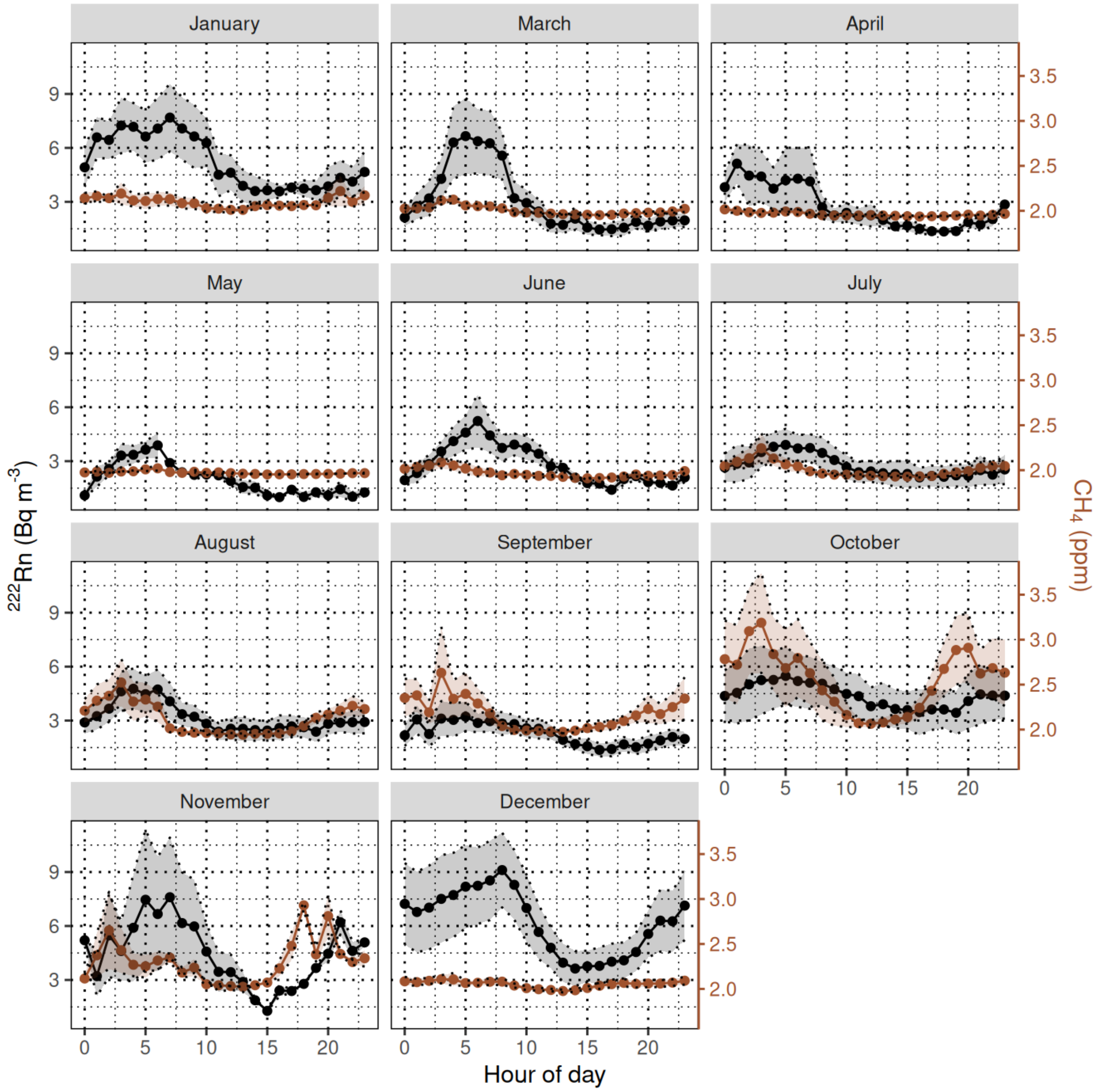
A key finding of this study is that the EDGAR v7.0 inventory, which accounts for emissions from agricultural soils, does not consider rice paddy field emissions at ERD. This is evident form the fact that the agricultural soil emissions assigned to ERD pixels are reported as below 0.02 mg $CH_4$ $m^{-2}$ $h^{-1}$.

The radon tracer method provides a footprint-weighted average estimate of (in this case) the $CH_4$ flux. Of the estimated contributing footprint region (Fig 10), the authors indicate that 50% constitutes the ERD (~65% of which are rice fields), 35% is ocean and 15% are other regions of NE Spain (with relative contributions from each of these regions changing seasonally). Each of these 4 contributing regions are characterised by substantially different radon and $CH_4$ emission characteristics (roughly speaking, according to the MS and supp material provided):
NE Spain: moderate to high Rn flux, moderate $CH_4$ flux (~15%).
Ocean:almost zero radon flux (~0.2 mBq m-3), assumed zero $CH_4$ flux (~35%).
Non-rice ERD:low radon flux, low to intermediate $CH_4$ flux (~20%).
Rice fields: seasonally varying radon flux from near zero to moderate, seasonally varying $CH_4$ flux from low to high (~30%).
Even if the oceanic contribution can be ignored as the authors suggest, the rice field region could represent slightly less than half of the contributing fetch region in the reported results. Contributions to CH4 emissions from the non-rice paddy regions may well be small (as the authors suggest), but I suspect not entirely negligible. Given the prevalence of high winds in the region (which will "flaten" diurnal cycles), it would have been informative to see composite diurnal cycles (e.g. Fig 5) for just the days of each month where the RTM had been applied, to better assess this assertion. Also, having half of the non-oceanic contributing fetch region for the reported results characterised by a smaller CH4 flux, wouldn't this result in an underestimation of the actual CH4 flux coming from the rice fields? After all, the estimated flux from the RTM is assumed to have been uniformly contributing to concentrations within the "idealised box" of the model for each hour of the accumulation window.

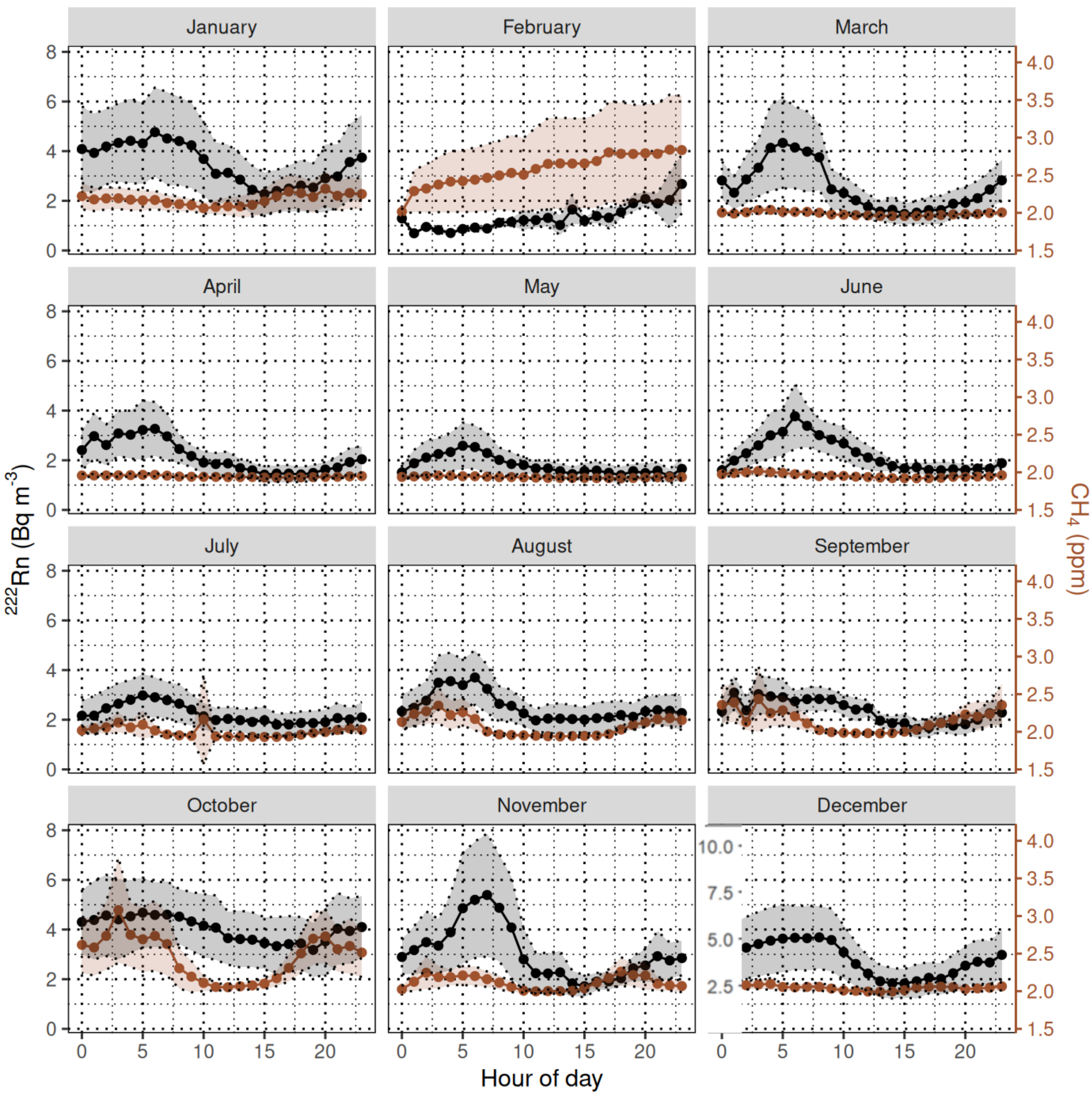
The authors thank the reviewer for this comment. Before addressing the response, we would like to clarify that in this study radon and methane concentrations measured at the station are used within the RTM, together with the effective radon flux observed at the station. The effective radon flux is derived from the weighted contribution of initial radon flux maps considering the residence time of FLEXPART back trajectories.

Regarding the potential presence of other methane sources within the station footprint, our analysis, which is consistent with the EDGAR emission inventories, Corine Land Cover map, and other bibliographic studies, indicates that their contributions are not significant compared to emissions from rice paddies. Specifically, methane fluxes over the footprint area, when rice paddies are dry, range between 0.3 and 0.6 mg $CH_4$ $m^{-2}$ $h^{-1}$, whereas our results, corroborated by literature (Martínez-Eixarch et al., 2018) and other studies in rice fields (Wang et al., 2018), show that methane fluxes from rice fields exceed 3 mg $CH_4$ $m^{-2}$ $h^{-1}$ between July and November. Considering this difference, the external contribution to the rice paddies methane emissions can be considered uncertain within a range of 10 % to 15 %.

As suggested by Dr. Chambers, the following figures show diurnal cycles of radon and methane concentrations for each month considering only the days when RTM was applied. The first figure presents the RTM dataset with a wind speed threshold of 1.5 m/s, and the second figure shows the dataset without this threshold. No important differences are observed between these figures and the results obtained using the complete dataset (Figure 5 of the manuscript), except for February, where deviations are due to the limited amount of available data.




*Radon and methane composite diurnal cycles for just the days of each month where the RTM was applied and with a wind speed threshold of 1.5 m/s.*



*Radon and methane composite diurnal cycles for just the days of each month where the RTM was applied and with no wind speed threshold.*

Regarding the footprint area, the reviewer may consider that nocturnal winds may be overestimated by the atmospheric transport model based on WRF (see Figure 7), which may, in turn, lead to an overestimation of the footprint area. Moreover, it is well known that the WRF model does not accurately reproduce the height of the nocturnal boundary layer. As for methane fluxes, as the reviewer says, they may indeed be underestimated because the footprint region is larger than the Ebro Delta. However, as clarified in the methodology section of the manuscript, the use of the FLEXPART transport model allowed the calculation of the footprint area for each selected RTM night.

Equation (3) of the manuscript shows how (for similarly distributed fluxes), the flux of $CH_4$ can be retrieved by scaling the slope of the co-measured trace gases with the radon flux. It also highlights that any uncertainty or error in the estimate of the radon flux is directly proportional to subsequent error / uncertainty in the CH4 flux. The radon flux estimates for this study, derived from the Karstens and Levin (2023) flux map with different soil moisture reanalyses, account for typical seasonal variability of soil moisture within the footprint weighted fetch region, but do not account for saturation (or worse, complete inundation). In most studies, saturation alone is considered to severely inhibit (or stop) radon emission (e.g., Griffiths et al 2010, doi:10.5194/acp-10-8969-2010).
Information provided in this MS indicates that the rice fields could be flooded for around 7 months of the year. Radon fluxes from open water bodies such as oceans are near zero (~0.2 mBq m-3; e.g.,

Zahorowski et al. 2013, htp://dx.doi.org/10.3402/tellusb.v65i0.19622). For conditions of complete inundation (8 – 15 cm deep), since the water is shallow compared with an ocean, and a limited amount of radon transfer through crop stems may be possible, a slightly larger radon flux may be expected. Even assuming a factor of 4 increase in radon flux for inundation conditions (i.e., 0.8 mBqm-3), this flux is still an order of magnitude less than the flux assumed in this study for the target area. Assuming that the derived radon fluxes derived for the non-inundation periods are representative (which I believe they are), if the flux estimates presented were actually predominantly representative of only the rice-paddy region (L447-448 revised manuscript), the CH4 flux estimates derived in this study for the inundated periods would necessarily be ~10 times higher than they actually are, on account of the overestimated radon flux.

Thanks again to the reviewer for this comment. Before addressing the response, we would like to emphasize that the radon flux used in Equation 3 is calculated for each RTM night using radon flux maps (Karstens and Levin, 2023) and weighting them according to the residence time of air masses arriving at DEC station. This means that the radon and methane concentrations measured at the station each night are due to the contribution not only from rice fields but also from other regions where air masses have been in contact with the surface gas emissions.

The key point here is that, in the case of radon, the difference between dry and water-saturated areas within the ERD is relatively small, whereas methane emissions from rice fields during straw incorporation are significantly higher in comparison with other sources. The strong agreement between our results and those obtained by Martínez-Eixarch et al. (2018) using an independent methodology support the reliability of our study.

Additionally, we acknowledge that uncertainty in traceRadon radon flux maps is high and may be further improved as reported by Maier et al. (2025). Although radon maps have seen significant improvements over the last decades, there are still lots of uncertainties. For example, a recent study on the uncertainty of radon fluxes obtained from the two available maps (ERA5-Land and GLAS-Noah) showed that, in central Europe, fluxes estimated with GLDAS-Noah could be twice as high as those estimated using ERA5 during certain periods (see Curcoll's PhD dissertation (2024) and Maier et al. (2025) work).

The authors are fully aware of the large uncertainties associated with these results. A new section, reproduced here below, has been added in the manuscript in order to assess the uncertainty associated in this work. We also recognize the importance of carrying out new studies to quantify and minimize these uncertainties.

#### 3.5 Uncertainty and representativeness of the RTM-based $CH_4$ fluxes at DEC

One of the simplifications considered for the application of the RTM is that fluxes should be homogeneous around the station, as strong point sources could affect the concentrations measured at the station and the regional flux estimation. Although the ERD is relatively small compared to other areas where the RTM has been applied (Schmidt et al. 1996, Levin et al. 2021), the short height of the sampling tower and the homogeneity of the ERD makes this area well-suited for the application of the RTM.

The difficulty of the application of the RTM in this study is sure but the evaluation of both meteorological and atmospheric transport models for the area and periods of interest, the comparison of the RTM based methane fluxes results with national inventories and other independent experimental studies from the bibliography add useful highlights for the research in this field and improvement of the RTM application protocols.

As seen in section 3.2, the WRF model in regions like ERD does not always simulate correctly the nocturnal accumulation and the wind speeds, deriving to important bias in concentration simulations. The advantage of the work exposed here is that due to the short height of the sampling point, the footprint of the station is quite small, within a few kilometers, and thus, the footprint is more reliable. Moreover, by applying the 1.5 m/s wind speed threshold for selecting RTM-feasible night events, we ensure minimal advection from continental sources. In agreement with EDGAR emission inventories, Corine Land Cover map, and other bibliographic studies, there are no significant contributions to the methane emissions compared to those from rice paddies. Methane fluxes over the footprint area and when rice paddies are dried are between 0.3 and 0.6 mg CH4 $m^{-2}$ $h^{-1}$, while our results, corroborated by literature (Martínez-Eixarch et al., 2018) and other studies in rice fields (Wang et al., 2018), show methane fluxes due to the rice fields above 3 mg $CH_4$ $m^{-2}$ $h^{-1}$ between July and November. Considering these differences, the external contribution to the rice paddies methane emissions may be assumed with an uncertainty between 10-15%.

One of the elements that produces more uncertainty in the calculus of the methane flux using the RTM is the uncertainty of real radon flux distribution over the footprint area of the measurement station (Vogel et al., 2012, Levin et al., 2021). In Eq. (3), the radon flux is directly proportional to the estimated methane flux. Therefore, an error in the radon flux will proportionally produce an error in the estimated methane flux. For this reason, until the radon flux maps in the area over the DEC station could be sufficiently validated, the global annual methane flux estimated with the RTM should be carefully accepted assuming a certain uncertainty. On the other hand, the integration, in this work, of data from several years, makes the result more robust than if using data from a single year.

One of the limitations of the RTM is that only the nocturnal emissions are monitored. In the case of rice fields, it is well known that the gross ecosystem photosynthesis (GEP) and the soil temperature are drivers of $CH_4$ flux variability (Hatala et al., 2012). Although diel fluxes and nocturnal fluxes keep a strong correlation (Wassmann et al., 2018), methane emissions in the early afternoon can be between 10% and 20% higher than the nocturnal emissions during the productive months (Alberto et al., 2014; Dai et al., 2019; Minamikawa et al., 2012). This difference may lead to an underestimation, ranging between 10% (Weller et al., 2015) and 20 % (Wassmann et al., 2018), of diel fluxes if considering only the nocturnal emissions.

Another assumption of the RTM is that the fluxes of radon and the tracer species are similarly distributed – here, for 7 months of the year – there is a high CH4 flux from the primary region of interest, and a radon flux close to zero. This is another challenge for the suitability of the technique for this purpose, and the claimed specificity of the results.

The ERD area has homogeneously distributed emissions. As already mentioned, based on RTM assumptions, previous studies obtained results in 'simple' areas of central Europe where radon and target gas concentrations are lower and quite homogeneous over time and space. Our study was challenging because, for the first time, we applied RTM in a 'extreme' region and, despite the challenge, the results were stunning.

Some further concerns regarding the fetch/flux distribution over the study region. A fundamental assumption of the simplified model used to derive the RTM (Equation 3) is that observed concentrations within the "idealised accumulation volume" over the accumulation window are a function ONLY of the surface flux and atmospheric mixing depth. Looking at a picture of the site location on the Ebro River Delta peninsula (Figure S1), north and east of the site there is rice paddy fetch for about 2 km, south of the site there is around 8 km of rice paddy fetch, and west of the site, approximately 15-18 km of rice paddy fetch. Beyond these bounds the authors consider CH4 fluxes to be zero or close to negligible. Bearing in mind that according to L511, the decision was made NOT to restrict nocturnal wind speeds to below 1.5 m s-1 for the final results, even at a best-case scenario of 1.5 m s-1, air would move from the ocean to the site (from the north or east) in 30 minutes (about 35% of the time according to Fig 10). From the south, air masses would transit the rice-paddy fields in 90 minutes, and from the west (atier passing over interior Spain), the air masses would transit the rice-paddy fields in 3 hours. Given that the chosen nocturnal accumulation period for this study was 6 hours, it is quite clear that the amount of CH4 accumulating in the "idealised box" will also be a strong function of wind direction (violating a basic assumption of the method), and that rice-paddy CH4 sources would influence observed concentrations for typically less than half of the chosen accumulation window. It is therefore quite likely that a large proportion of the observed positive correlations between radon and CH4 during selected RTM events were either due to influences on the air mass that happened much further upstream of the ERD or based on CH4-to-Rn slopes derived from only 2 or 3 measurement points.

Authors are not really sure to understand which is the point of the discussion here. As the reviewer may see in the first round of comments, the authors DID apply the threshold criteria of low wind speeds, and the comparison of the results shows basically no differences between the full dataset and low winds dataset. On this basis, the decision of carrying on the analysis with the full dataset was to ensure a robust statistic for the results. The correlation criteria, on the other hand, was applied to only select nights where the increase of the radon and methane concentrations was proportional.

The linearity of the CH4-to-Rn slope (on which equation 3 is based) reflects the degree to which the source functions of the gases in question are similarly distributed (a requirement of the technique). The diurnal cycles of CH4 and radon shown in Fig 5 indicate substantially different accumulation behaviour between the two gases in this study – presumably related to substantial difference in source distributions. The majority of contemporary RTM studies adopt a linearity threshold of 0.6 ≤ R2 ≤ 0.8 in an atempt to minimise contributions to results from conditions that don't meet the assumptions of the technique. In this study an R2 threshold of only 0.5 was adopted, which has implications for the derived flux uncertainties.

Thanks to the reviewer for this comment but it was already clarified during the first round of comments that the use of an $R^2 \geq 0.5$ was already been acknowledged in past scientific studies. Authors agree on the fact that a higher $R^2$ would give more robust results. On the contrary it will also give a smaller dataset which will lead to higher statistical uncertainty. The compromise between robust statistics and reliable data was here considered a priority.

Another contributing factor to the low R2 threshold adopted in this study is likely to have been the signal-to-noise ratio for the ARMON's radon detection in this coastal and otien water-logged environment. Fig 5 of the revised MS indicates typical whole-night radon accumulation of 1.5 – 3 Bq m-3. On the more stable nights, Fig 8 indicates maximum nocturnal radon accumulations over a whole night of 2 – 4 Bq m-3 (less for the 6-hour accumulation window used for this study). As part of the recently completed EMPIR 19ENV01 traceRadon Project, the performance of an improved model of ARMON (relative to the one used in this study) was tested over radon concentrations between 0 – 40 Bq m-3 under controlled conditions. In this idealised case, the standard deviation of hourly measurements was ~3 Bq m-3 (see below, from Rötger et al. 2024; XIV IMEKO World Congress "Think Metrology", 26-29 Aug, Hamburg Germany), which is large compared with hourly radon accumulation rates of 0.3 – 0.6 Bq m-3. This type of instrument would be beter suited to sites with larger nocturnal radon accumulation ranges (e.g., Grossi et al. 2018, htps://doi.org/10.5194/acp-18-5847-2018).

Thanks to the reviewer for this comment. Looking at the bibliography we can see that Figure 2b from Grossi et al. (2020) shows an intercomparison between the ARMON instrument (red circles), used in the present study, and other radon and radon progeny monitors. One of them is the ANSTO monitor (blue circles) provided and sold in Europe by Dr Chamber, the reviewer of the present manuscript. This figure clearly shows the ability of the ARMON to measure increments of concentration lower than 3 Bq $m^{-3}$.

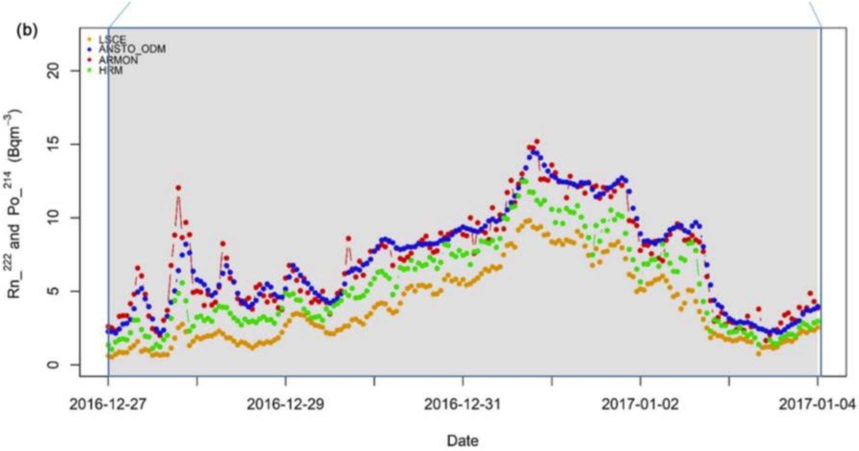



**Figure 2. (a)** Hourly time series of the atmospheric $^{222}$Rn and, in the case of LSCE and HRM data, $^{214}$Po activity concentration, measured at the Orme de Mérisiers (ODM) station during Phase I (between 25 November 2016 and 23 January 2017) by the ARMON (red circles), ANSTO_ODM (blue circles), HRM (green circles), and LSCE (orange circles) monitors. **(b)** Hourly time series of the atmospheric $^{222}$Rn and $^{214}$Po measured between 27 December 2016 and 4 January 2017.

In a study published by Curcoll et al. (2024), the authors showed that for a typical radon concentration of 5 Bq $m^{-3}$ the total uncertainty of the ARMON instrument was about 10% (k=1), that is an uncertainty of about 0.5 Bq $m^{-3}$. This result confirms that the instrument (nowadays commercialized by Radonova, a leading company in radon measurements) is able to capture radon concentrations increases similar to the ones observed in the present study at the DEC station during the nocturnal accumulation periods. In the case of the ANSTO, for example, Maier et al. (2025) shows that using this instrument may lead to an overestimation of the radon concentration due to its intrinsic background. This means that a full metrology is needed (and is under construction) for atmospheric radon measurements in Europe.

Finally, in the same study suggested by the reviewer (Röttger et al., 2025), it can be observed that the ARMON instrument has a high linear response with a very low standard deviation of the scatter (0,77%), which is much better than the one from other commercially available radon and radon progeny atmospheric monitors. Röttger et al. (2025) also underlines the very quick response of the ARMON monitor to a concentration pulse. This makes the instrument quite suitable to measure small concentrations variations over short time periods. Below you can see the figures from the cited manuscript.

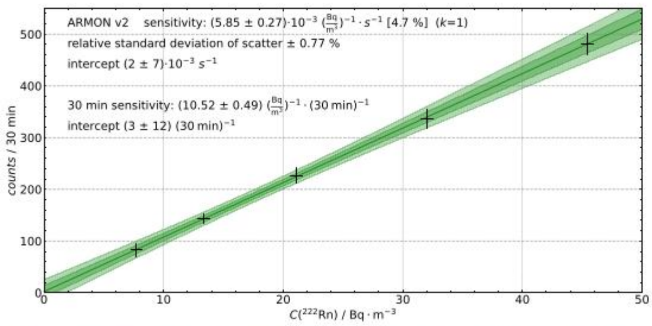



*Figure 6: Results for the calibration factor of the ARMON v2 detector applying all sources and combinations measured, taking correlated and uncorrelated contributions of the source characterisation into account.*

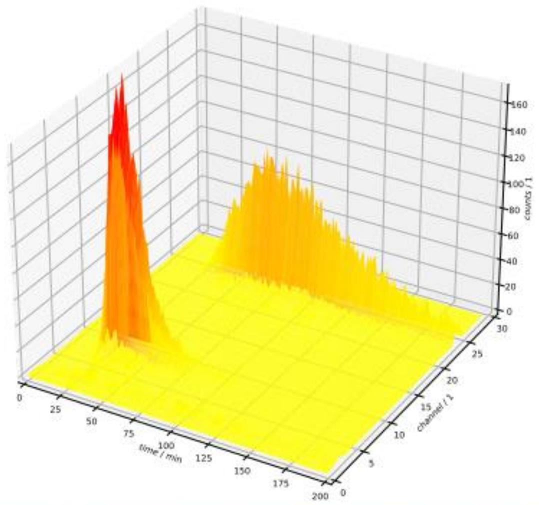



*Figure 7: 3-dimensional representation of the time and energy (channel) resolved response of the ARMON v2 detector for a defined $^{222}Rn$ pulse applied at time 0 at the air inlet of the detector. At the lower channels (5-10) $^{218}Po$ represents the faster response of the detector and channel (20-30) the slower response of $^{214}Po$ is visible.*

Including nights for RTM calculations on which positive correlations between radon and CH4 are observed, but wind speeds are significantly above 1.5 m s-1, greatly increases the risk of incorporating flux contributions from (i) large distances upstream (not representative of the study region), or (ii) synoptic scale fetch change influences (which violate important assumptions of the RTM).

Thanks to Dr Chambers for this comment. However, the authors already answered to this comment in the first revision and in this document. Again, they declare that winds above 1.5 m/s have been ONLY included for the calculation of the annual methane emission, and it has been done because the difference in methane flux between the two data series in the months with enough data were smaller than 15%.

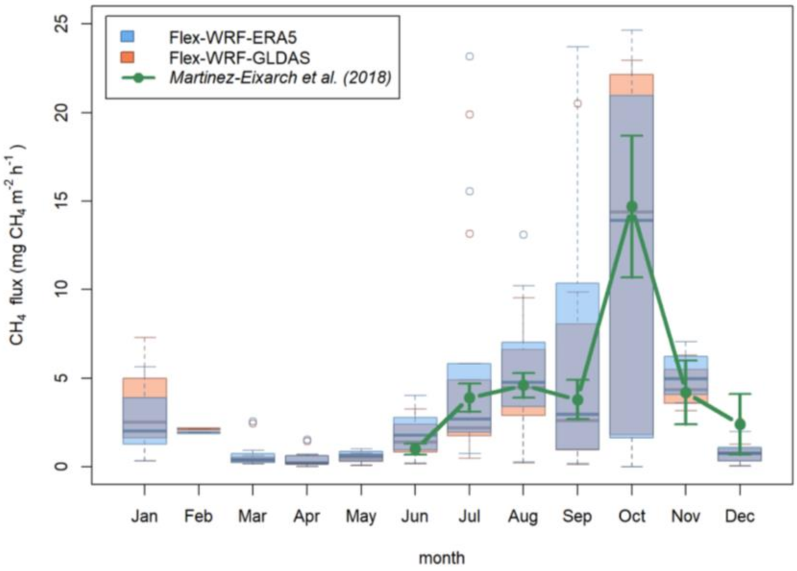
Separate to their derivation of a contributing footprint region for this study, the authors have equated a measurement height of 10 m agl with observing only local influences (e.g., L447-448 of revised manuscript). Certainly, under convective daytime conditions, the dominant measurement fetch is usually within <100 times the measurement height. Under stable nocturnal conditions however, a requirement for the application of the “local” implementation of the RTM, as described by Conen et al (2002; GRL, 10.1029/2001GL013429), a column of air will move across the surface at the average near surface wind speed, accumulating influences of surface fluxes over which it passes.

At wind speeds of only 1.5 m s-1, over a 6-hour nocturnal accumulation window, the observed air mass will have been influenced by a fetch of at least 32 km. Over this distance, at this study site, air masses could easily pass over 4 regions with entirely different surface emission characteristics. As previously mentioned, a fundamental assumption of the nocturnal accumulation implementation of the RTM is that over the accumulation window concentrations within the “idealised atmospheric column” are purely a function of a near-constant source of both gases (per night) and a changing mixing depth.

As commented before, the use of back trajectories coupled with the radon flux maps allow to pinpoint the area of influence. The use of these back trajectories and the limitation of 1.5 m $s^{-1}$reduce the influence of the regions outside the ERD. The continental influence has been already estimated to be around 15%.

For all the reasons above I am not convinced that Fig 12 represents the true seasonal variability of CH4 fluxes specifically from the rice-paddy region of the ERD.

The authors of this study really regret that one of the three reviewers of the study has still concerns about the methodology and the results obtained and shown in this manuscript. The authors believe that the methodology of the RTM has been here adjusted and applied in the best way. Additionally, despite the uncertainties coming with the results (mainly due to the application of radon flux maps and atmospheric transport models in frontier region such as the delta of a Mediterranean river), the amazing agreement between the methane fluxes, their seasonal variability, as well as their absolute mean values, obtained in this study and those obtained by Martínez-Eixarch et al. (2018) using a completely independent method is stunning. This result, together with the comparison with official emission inventories, confirm the importance of this study and its publication. Research results are never perfect, but they are milestones to build and to improve knowledge.




485 **Figure 12. Boxplot of the methane RTM based fluxes over the DEC station calculated using Flex-WRF-ERA5 (blue) and Flex-WRF-GLDAS (red) for every month of the year (period 2013-2019), and methane fluxes over ERD using static chambers (green points**