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Inferring ^{222}Rn soil fluxes from ambient ^{222}Rn activity and eddy covariance measurements of CO_2

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Abstract. We present a new methodology, which we call Single Pair of Observations Technique with Eddy Covariance (SPOT-EC), to estimate regional-scale surface fluxes of ^{222}Rn from tower-based observations of ^{222}Rn activity concentration, CO_2 mole fractions and direct CO_2 flux measurements from eddy covariance. For specific events, the regional (^{222}Rn) surface flux is calculated from short-term changes in ambient (^{222}Rn) activity concentration scaled by the ratio of the mean CO_2 surface flux for the specific event to the change in its observed mole fraction. The resulting ^{222}Rn surface emissions are integrated in time (between the moment of observation and the last prior background levels) and space (i.e. over the footprint of the observations). The measurement uncertainty obtained is about $\pm 15\%$ for diurnal events and about $\pm 10\%$ for longer-term (e.g. seasonal or annual) means. The method does not provide continuous observations, but reliable daily averages can be obtained. We applied our method to in situ observations from two sites in the Netherlands: Cabauw station (CBW) and Lutfjewad station (LUT). For LUT, which is an intensive agricultural site, we estimated a mean ^{222}Rn surface flux of $(0.29 \pm 0.02) \text{ atoms cm}^{-2} \text{ s}^{-1}$ with values $> 0.5 \text{ atoms cm}^{-2} \text{ s}^{-1}$ to the south and south-east. For CBW we estimated a mean ^{222}Rn surface flux of $(0.63 \pm 0.04) \text{ atoms cm}^{-2} \text{ s}^{-1}$. The highest values were observed to the south-west, where the soil type is mainly river

clay. For both stations good agreement was found between our results and those from measurements with soil chambers and two recently published ^{222}Rn soil flux maps for Europe. At both sites, large spatial and temporal variability of ^{222}Rn surface fluxes were observed which would be impractical to measure with a soil chamber. SPOT-EC, therefore, offers an important new tool for estimating regional-scale ^{222}Rn surface fluxes. Practical applications furthermore include calibration of process-based ^{222}Rn soil flux models, validation of atmospheric transport models and performing regional-scale inversions, e.g. of greenhouse gases via the SPOT ^{222}Rn -tracer method.

1 Introduction

^{222}Rn is a radioactive noble gas (half-life 3.82 days) that is produced at a constant rate from ^{226}Ra (half-life 1600 years), which is relatively uniformly distributed in all soils. When released into the atmosphere, ^{222}Rn is transported and mixed in the atmosphere similar to all other gases emitted from, or close to, the surface. These features make ^{222}Rn an important tracer in atmospheric sciences. It has been used as a tracer to study transport processes in the atmosphere (e.g. Liu et al., 1984; Chevillard et al., 2002) and to evaluate or compare the transport component in atmospheric trans-

port models (Dentener et al., 1999; Gupta et al., 2004; Zaborowski et al., 2004). Another highly useful application of ²²²Rn is the direct inversion method commonly referred to as the ²²²Rn tracer method (Levin, 1987; Schmidt et al., 1996; van der Laan et al., 2014). With this method, the ratio of the ²²²Rn surface flux to a measured ²²²Rn activity concentration difference over time at a certain observation height can be applied to calculate the surface flux of another constituent (e.g. CO₂) from its concurrently observed mole fraction difference at the same measurement height. In all of these example applications, however, it is essential that the ²²²Rn surface flux is well known. This is especially true for the ²²²Rn tracer method as the resulting surface emissions, e.g. of CO₂, are directly proportional to the assumed regional ²²²Rn surface flux. But unfortunately ²²²Rn surface fluxes are still poorly known, especially on local and regional scales. One complicating factor is that, although the production of ²²²Rn is directly related to the uniformly distributed radium content in the soil and, therefore, relatively well known, its surface flux is highly sensitive to soil porosity, temperature and soil moisture content. Therefore, the ²²²Rn surface flux can be very heterogeneously spread on regional scales (e.g. because of different water table heights) and vary significantly (e.g. dropping from 100 % to almost zero emission) within hours, e.g. due to rainfall (Manohar et al., 2013).

Recently, several approaches have been applied to quantify ²²²Rn surface fluxes: (1) using gamma dose radiation as a proxy for ²²²Rn (Szegvary et al., 2007; Manohar et al., 2016) and (2) modelling the production and transport of ²²²Rn in soils (Hirao et al., 2010; Karstens et al., 2015a). These efforts have provided new tools for studying the driving mechanisms behind the ²²²Rn soil flux on relatively large spatial scales. Unfortunately, these methods are limited by the performance of the models, specifically related to the parameterisation of the underlying processes; hence they need to be validated independently. Currently, the only two methods for estimating the ²²²Rn surface flux directly are from observations of increasing activities in the soil (Dörr and Münnich, 1987) and in a soil chamber (Lehmann et al., 2004; Manohar et al., 2016). The chamber method, however, does not allow for continuous observations because it takes time to flush the chamber, for the concentrations to build up inside the box and to perform the actual analysis. Furthermore, the method is obviously limited in terms of spatial representation since it only observes the very small soil surface area of the chamber.

In this paper, we propose a novel approach that utilises and combines in situ measurements of atmospheric ²²²Rn activity concentration and CO₂ mole fractions as well as direct CO₂ flux from eddy covariance (EC) observations to determine the average ²²²Rn surface flux for a relatively large area defined by the footprint of the observations. We applied our method, which we call Single Pair of Observations Technique with Eddy Covariance (SPOT-EC), to data from two measurement stations in the Netherlands and compared our results to two recently published ²²²Rn soil flux maps for

Europe, as well as to in situ measurements from soil chambers at both sites. In the next section, we explain our method, together with a description of our data sets used and data selection applied. Our results are described in Sect. 3 followed by a discussion in Sect. 4 and our conclusions in Sect. 5.

2 Method

2.1 Theory

Our methodology for calculating the ²²²Rn soil flux is an adaptation of the ²²²Rn tracer method (Levin, 1987; Schmidt et al., 1996; Biraud et al., 2000; van der Laan et al., 2009a) where an assumed ²²²Rn soil flux is used together with combined observations of ambient ²²²Rn activity concentration and, for example, CO₂ concentrations at a certain measurement height, to calculate a regional CO₂ surface flux. More specifically, we modified the Single Pair of Observations Technique (SPOT) described by van der Laan et al. (2014). Compared to the commonly applied technique of using a linear regression fit on a bulk of observations, this version of the ²²²Rn tracer method is more suitable for estimating non-constant surface fluxes. The method is based on the concept that all species which are released from, or close to, the surface are transported and diluted in the atmosphere similarly. For example, when the atmosphere is well mixed, ambient concentrations are observed at (local) background levels and when the atmospheric stability subsequently increases, surface fluxes accumulate within the planetary boundary layer (PBL) and the concentrations increase as well. The relation between a surface flux and ambient concentrations during such an event of increasing concentrations can be mathematically described as follows (Biraud et al., 2000):

$$\frac{\Delta C_x}{\Delta t} = \int_{t_0}^{t_n} h(t)^{-1} \Phi_x(t) dt = \overline{h^{-1}} \cdot \overline{\Phi_x}. \quad (1)$$

Here the concentration change of an observed species x over time t (t_0 to t_n) is given by $\Delta C_x/\Delta t$, which is the result of its surface flux Φ_x accumulating within the PBL and diluted as a function of the mixing height h . Note that both Φ_x and $h(t)$ are time dependent. The overbar indicates averaging in space (i.e. the footprint) and time, that is, representing the average mixing height and the mean net surface flux during the observation period and for the observed area. Applying Eq. (1) to both ²²²Rn and one other gas species, for example, CO₂, then taking the ratio of $\Phi^{222}\text{Rn}/\Phi\text{CO}_2$ and rearranging for ΦRn yields an equation where the mixing height has been cancelled out, namely

$$\overline{\Phi\text{Rn}} = \frac{\text{Rn}(t_n) - \text{Rn}(t_0)}{\text{CO}_2(t_n) - \text{CO}_2(t_0)} \cdot \overline{\Phi\text{CO}_2}, \quad (2)$$

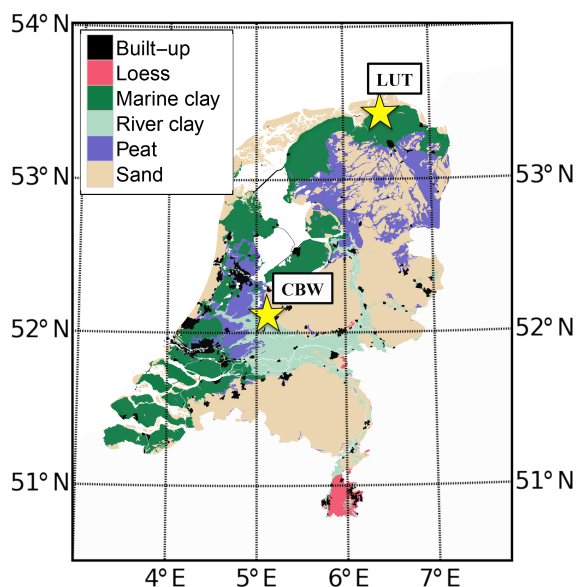


Figure 1. Aggregated soil map of the Netherlands developed from the initial soil map by Steur et al. (1985). Also shown are the locations of stations Lutjewad (53.405° N, 6.354° E) and Cabauw (51.971° N, 4.927° E).

where the resulting ²²²Rn soil flux is calculated from the observed concentration changes between local background levels at $t = t_0$ and (a pair of ²²²Rn and CO₂) observations at $t = t_n$. This methodology assumes equal vertical distribution for both species between surface and at intake, e.g. no sudden chemical loss or addition for one species. Vertical mixing (e.g. due to a changing PBL height) and dilution (e.g. due to mixing with the free troposphere) are assumed to be equal for both species; hence it is cancelled out. In the case of entrainment, we assume our observed background concentrations at $t = t_0$ are, to a good degree, representative of the free troposphere at the site location and potential mixing is equal for both species. Equation (2) is basically the inverse of the Single Pair of Observation Technique (SPOT) method described in van der Laan et al. (2014), where instead of using an assumed ²²²Rn soil flux to calculate the surface flux of CO₂, we use a measured CO₂ surface flux (obtained from EC measurements) to calculate the ²²²Rn soil flux. We will refer to this method as SPOT-EC for the remainder of this paper. The term “event” will be used for periods in time that are suitable for applying the SPOT-EC method and are further described in Sect. 2.3.

2.2 Measurement locations, instrumentation and data used

We applied our methodology on half-hourly-averaged ambient measurements of the ²²²Rn activity concentration and of CO₂ mole fractions as well as CO₂ surface flux measurements from eddy covariance (EC), at two sites in the Nether-

lands: Lutjewad (LUT) and Cabauw (CBW). Both stations are equipped for basic meteorological observations (air temperature, humidity, atmospheric pressure, wind speed and direction and solar radiation) and, via several air intakes on a sampling tower, ambient air is continuously flushed down to a laboratory for further analyses. Station-specific information is given below. Figure 1 shows a map of the Netherlands including the main soil types (Steur et al., 1985) and station locations.

2.2.1 Lutjewad station

LUT (53.405° N, 6.354° E, 1 m a.s.l.) is a coastal site in the north of the Netherlands about 30 km to the north-west of the city of Groningen (population ~ 200 000). To the north of the station, with its 60 m tall tower, a reclamation area and tidal flats merge into the North Sea whereas the south sector consists of agricultural area on sea clay soils; see also Fig. 1. The (intensely managed) water table is generally ~ 1.5 to 1 m (in winter) below the surface. The prevailing wind direction (> 31 % of the time) is between 195 and 255° and wind speeds between 6 and 9 m s⁻¹ are dominant (~ 35 % of the time) at the top intake height at 60 m above ground (van der Laan et al., 2009a). Ambient CO₂ mole fractions were measured from a height of 60 m with a modified Agilent HP 6890N gas chromatograph (van der Laan et al., 2009b) together with mole fractions of CH₄, N₂O, SF₆ and CO. Typically six analyses are performed per hour and the measurement precision is about ±0.08 ppm for CO₂. An eddy covariance system consisting of a LiCor 7500 open-path gas analyser and a Gill Windmaster Pro 3-axis ultrasonic anemometer is installed at a height of 50 m for direct surface flux estimates of CO₂ (as well as H₂O and sensible and latent heat fluxes) (Dragomir et al., 2012). For the EC CO₂ flux measurements at both LUT and CBW, we assumed a measurement uncertainty of about 10 % based on Kruijt et al. (2004).

Ambient ²²²Rn activity concentration is measured at both LUT and CBW using a dual-flow loop two-filter detector developed by the Australian Nuclear Science and Technology organisation (ANSTO) and described by Whittlestone and Zahorowski (1998). Unwanted aerosols and (radioactive) decay products are removed by a filter in front of the detector and the ²²²Rn decay products are sampled on a second filter at the exit of a 1500 L delay chamber, where their decays are counted by a photo-multiplier. This system uses a non-energy selective alpha particle counter to detect ²²²Rn progeny. In principle it also detects ²²⁰Rn (half-life of 55.6 s); however this is prevented by the relatively long residence time (~ 10 half-lives) of the air sample from the tower inlet to the detector. The total measurement uncertainty is about 11 % of the measured value at both sites (at an activity concentration of 1 Bq m⁻³) including measurement precision resulting from counting statistics (~ 3–4 %), accuracy of the source (~ 4 %), the coefficient of variability of valid monthly calibration coefficients (~ 2 %) and the background count vari-

ability ($\sim 10 \text{ mBq m}^{-3}$) (van der Laan et al., 2010; Popa et al., 2011; Schmithüsen et al., 2016). Ambient observations of CO_2 mole fractions, ^{222}Rn activity concentration and CO_2 surface fluxes for the period of November 2007–April 2010 at LUT are shown in Fig. 2a–c respectively.

For validation of our method, we use direct measurements of the ^{222}Rn soil flux with a soil chamber (surface area $\approx 0.03 \text{ m}^2$) located near the foot of the mast. This chamber system, which is described in detail in Manohar et al. (2016), uses a flow-through accumulator method (Zahorowski and Whittlestone, 1996) where the air is continuously circulated between the soil chamber and the detector (Lucas Scintillation Cell model 300A + Pylon AB-5 portable radon monitor, Pylon Electronics, Canada). Because of the relatively low radium activity and high soil moisture content at the site, and given the relatively high detection limit of the Pylon monitor, the chamber needs to accumulate for 4 h before each measurement which takes 7.5 h and is followed by a flushing period of 0.5 h (Manohar et al., 2016). In this way, two 4-hourly integrated observations are obtained per day. The system was extensively tested (Manohar et al., 2016) for saturation effects in the chamber and concentration increases were found to remain linear over time for at least 5 h for wet as well as dry soils. The soil chamber ^{222}Rn measurement uncertainty is estimated at $\sim \pm 20\%$ of the measured value including errors associated due to back diffusion.

2.2.2 Cabauw station

CBW (51.971° N , 4.927° E , 0.7 m b.s.l.) is located within a mainly agricultural area about 25 km south-west of the city of Utrecht (population $\sim 340\,000$); see also Fig. 1. To the south of the station, with its 213 m tall tower, the soil type is mainly river clay and to the north mostly peat or peat on clay (Arnold et al., 2010). Within a distance of about 400 m (and up to $\sim 2 \text{ km}$ for the WSW sector) the terrain can be classified as open pasture. The water table is generally $\sim 1 \text{ m}$ below the surface. Ambient CO_2 mole fractions are measured with a LiCor-7000 non-dispersive infrared analyser sampled from heights of 20 m (used in this study), 60, 120 and 200 m (Popa et al., 2011; Vermeulen et al., 2011). The measurement precision is generally $< \pm 0.1 \text{ ppm}$. Direct CO_2 fluxes are measured at heights of 3, 60 m (used in this study), 100 and 180 m with a similar EC system as at LUT consisting of a LiCor 7500 open-path gas analyser and a Gill R3 ultrasonic anemometer. Because of blockage from the tower, observations cannot be used when wind direction is between 280 and 340° . Ambient observations of CO_2 mole fraction, ^{222}Rn activity concentration and CO_2 surface fluxes for the period of January 2007–July 2013 at CBW are shown in Fig. 3a–c respectively.

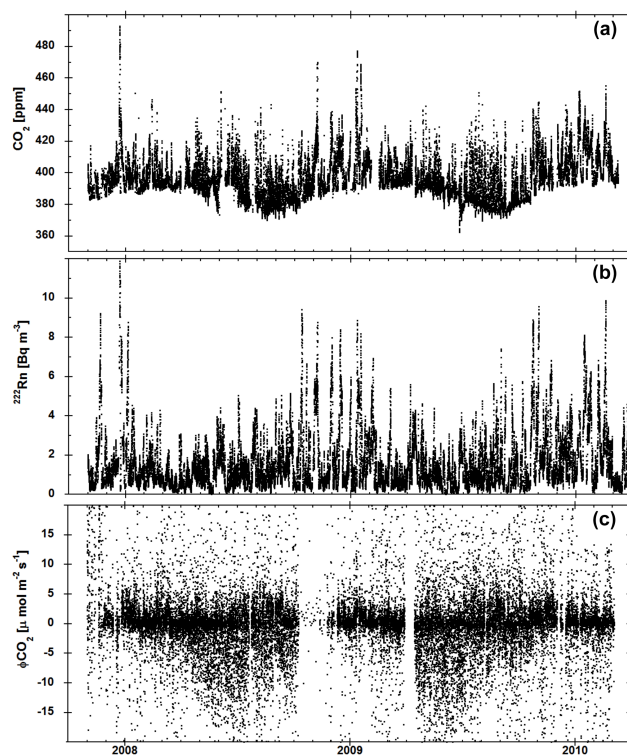


Figure 2. Ambient measurements of half-hourly-averaged CO_2 mole fraction (a), ^{222}Rn activity concentration (b) and CO_2 surface flux (c) from Lutjewad station. X axis tick labels indicate the beginning of the year stated.

2.3 Data selection

We selected “events” for both stations according to the (automated) method described by van der Laan et al. (2014). An example for CBW is given in Fig. 4. Events were selected based on the following criteria: the start of an event is detected when at least five out of eight consecutive half-hourly ^{222}Rn measurements are higher than the preceding measurement, and the first value (at $t = t_1$) is at least 0.3 Bq m^{-3} higher than the baseline (at t_0). Similarly, the end of the event is defined as the time when the maximum value is reached with at least five out of eight consecutive measurements lower than the preceding measurement before dropping back to background levels. The ^{222}Rn soil flux for the event is calculated with Eq. (2) for each measurement (at $t = t_n$) relative to the local background level at $t = t_0$. EC measurements were processed according to CarboEurope protocols (Aubinet et al., 2000) using EddySoft (Kolle and Rebmann, 2007) for LUT and ALTEDDY software (www.climatexchange.nl/projects/alteddy/) for CBW. A friction velocity (u^*) threshold (Papale et al., 2006) of $> 0.2 \text{ m s}^{-1}$ was determined for both stations and applied to ensure sufficient turbulence for the eddy-dependent EC measurements. Furthermore, the CBW measurements were rejected for wind directions between 280 and 340° because of tower blocking

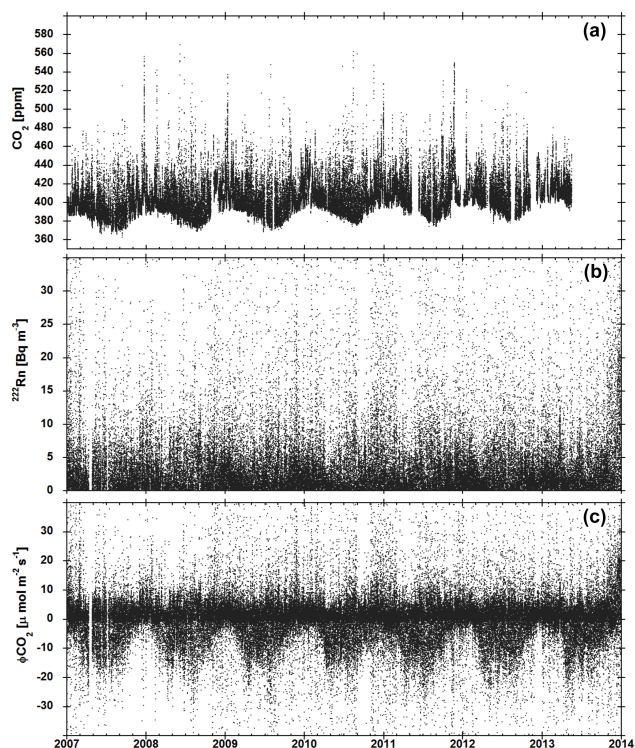


Figure 3. Ambient measurements of half-hourly-averaged CO₂ mole fraction (a), ²²²Rn activity concentration (b) and CO₂ surface flux (c) from Cabauw station. X axis tick labels indicate the beginning of the year stated.

and between 0 and 60° and 240–360° in the case of LUT to exclude the marine sector. As a rough strategy to ensure our results are predominantly locally influenced, results were only accepted for $t_n - t_0 < 4$ h. Furthermore, a maximum variation in wind direction of 25° was prescribed to ensure stationary conditions during the events. Results were only accepted for dry periods because rain affects the EC measurements of our open-path analysers and, finally, results were retained that had a relative uncertainty of $< \pm 75\%$ for CBW and, because of less data, $< \pm 100\%$ for LUT.

3 Results

3.1 LUT

For LUT, we find a mean ²²²Rn surface flux of (0.43 ± 0.05) atoms cm⁻² s⁻¹ and a median of 0.17 atoms cm⁻² s⁻¹ based on 209 events between January 2008 and January 2010 (Fig. 5a and Table 1). The error bars on Fig. 5a are calculated from error propagation of Eq. (2) using the measurement uncertainties described in Sect. 2.2.1 and 2.2.2. The statistical distribution of the ²²²Rn surface fluxes is shown in Fig. 6 (limited to < 2 atoms cm⁻² s⁻¹ for clarity), and from this we find that the mean value is much higher than the median

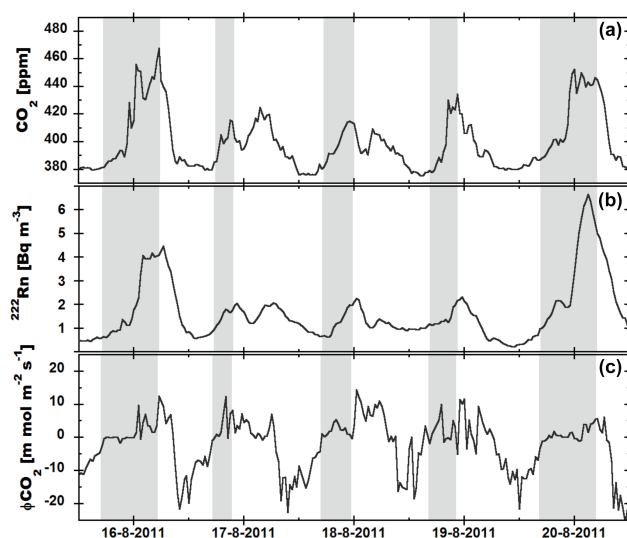


Figure 4. An example of diurnal events for CBW of CO₂ mole fraction (a), ²²²Rn activity concentration (b) and CO₂ surface flux (c) for 5 days in August 2011. The events identified by our event selection methodology are indicated by the grey shadings. X axis tick labels indicate the beginning of the day stated.

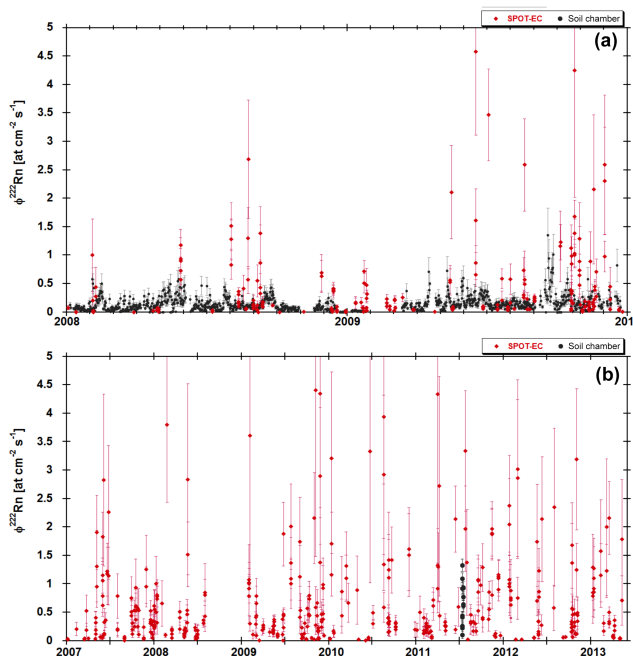
because of a few exceptionally large (i.e. much greater than 1.5 atoms cm⁻² s⁻¹) ²²²Rn surface fluxes. After excluding the 11 values > 1.5 atoms cm⁻² s⁻¹, we find a median value of 0.15 atoms cm⁻² s⁻¹ and a mean value of (0.29 ± 0.02) atoms cm⁻² s⁻¹. The latter is in fact equal to the mean value for the Netherlands of 0.29 atoms cm⁻² s⁻¹ proposed by Szegvary et al. (2007). This value was taken from a European ²²²Rn flux map based on using a gamma dose radiation as a proxy for ²²²Rn activity and has been used in previous studies for this site (van der Laan et al., 2009a, 2010). Note, however, that the coarse resolution of this map does not allow for any significant distinction between LUT and the mean value for the Netherlands.

Our mean result, even after discounting the 11 high values, is a factor of 2 higher than the mean value of (0.16 ± 0.01) atoms cm⁻² s⁻¹ based on soil chamber measurements (Manohar et al., 2016) and also higher than the model-based estimate of (0.19 ± 0.12) atoms cm⁻² s⁻¹ found by Manohar et al. (2013). The measurements from the soil chamber and our SPOT-EC method agree well for the majority of the events, but the higher values are not captured by the chamber method. In these cases, the soil underneath the chamber behaves differently to the average soil in our footprint as seen from the tower. This makes sense as the small chamber only “sees” a single soil type.

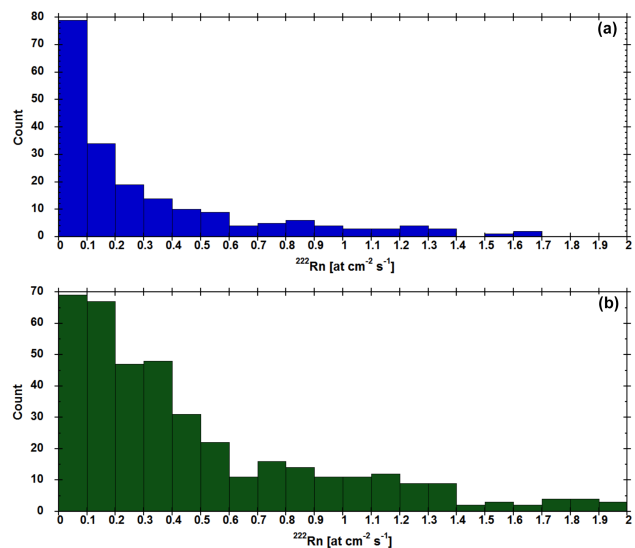
We also compared our results with results from a recently published process-based ²²²Rn flux map for Europe (Karstens et al., 2015a, b). Although the resolution of the map ($\sqrt{2}$, ERA-Interim/Land) is $0.083 \times 0.083^\circ$, resolution at coastal areas is limited by the availability of soil mois-

Table 1. ^{222}Rn soil flux for CBW and LUT estimated with SPOT-EC, soil chambers and models.

	Soil chamber	Model	SPOT-EC	Units
CBW	0.64 ± 0.09 (mean)	0.65 ± 0.14^a	0.63 ± 0.04 (mean)	$\text{atoms cm}^{-2} \text{s}^{-1}$
	0.62 (median)	0.59 ± 0.18^b	0.34 (median)	
	$N = 14$		$N = 422$	
	Period: July 2011 ^a		Period: Jan 2007–Jul 2013	
LUT	0.16 ± 0.01 (mean)	0.19 ± 0.12^a	0.43 ± 0.05 (mean)	$\text{atoms cm}^{-2} \text{s}^{-1}$
	0.11 (median)	$0.08\text{--}0.41 \pm 0.03^c$	0.17 (median)	
	$N = 1069$		$N = 209$	
	Period: Jun 2008–Jan 2010 ^a			
			0.29 ± 0.02 (mean) ^d	
			0.17 (median) ^d	
		Period: Jan 2008–Jan 2010		

^aManohar et al. (2013).^bValues taken from Karstens et al. (2015a) with latitude: 51.54°N , longitude: 4.88°E .^cValues taken from Karstens et al. (2015a) with latitude: 53.21°N , longitude: 6.38°E and: latitude: 53.13°N , longitude: 6.38°E .^dAfter excluding 12 values $> 1.5 \text{ atoms cm}^{-2} \text{s}^{-1}$ (see Sect. 3.1).**Figure 5.** ^{222}Rn surface fluxes calculated with Eq. (2) for LUT (a) and CBW (b). SPOT-EC results are in red and soil chamber results are in black. The error bars are calculated from error propagation of the measurement uncertainties as described in Sect. 2.

ture reanalysis ($0.75 \times 0.75^\circ$ in our case). For our sites' exact locations, therefore, ^{222}Rn fluxes are not available. We choose to report the mean values for (1) the first grid cell with ^{222}Rn fluxes directly to the south (53.21°N , 6.38°E) and (2) the cell south of that cell: (53.13°N , 6.38°E). For (1) we find a mean value of $(0.08 \pm 0.03) \text{ atoms cm}^{-2} \text{s}^{-1}$ and for (2) $(0.41 \pm 0.03) \text{ atoms cm}^{-2} \text{s}^{-1}$. The model-based results indicate the values from the grid box closest to the

**Figure 6.** Statistical distributions of ^{222}Rn surface fluxes for LUT (a) and CBW (b). Values $> 2 \text{ at cm}^{-2} \text{s}^{-1}$ (6% of the total) are omitted in the figures for clarity in the case for CBW.

tower are the lowest because of a higher soil moisture content, which is the main driver for the ^{222}Rn soil flux and a key variable in the model.

This spatial variability of the ^{222}Rn surface flux is also observed with our measurements and shown in Fig. 7a. This polar plot, generated with the “openair” package in R, depicts the wind direction vs. the maximum fetch range, calculated as wind speed times the duration of the event, vs. the ^{222}Rn surface flux. For clarity, data were limited to > 0.05 and $< 1.5 \text{ atoms cm}^{-2} \text{s}^{-1}$. In general, the values closest to our tower are around $0.3 \text{ atoms cm}^{-2} \text{s}^{-1}$. To the south-west and south-east values are observed around $> 0.5 \text{ atoms cm}^{-2} \text{s}^{-1}$.

The spatial variations are most likely due to different soil or crop types (i.e. affecting the soil moisture content and porosity) since the area around the tower is an agricultural region with rotation of several crop species, open pastures and an intensely managed water table to suit the needs of the agriculture and horticulture. Figure 8a shows the diel distribution of our events vs. the magnitude of the calculated ²²²Rn surface flux. Although the fraction of the day for which the atmosphere is generally well mixed (i.e. ~ 10:00 to 15:00) is undersampled due to too a small concentration gradient, we obtain a reasonable coverage over the day. More importantly, the magnitude of the flux does not seem to be correlated with the time of the day.

3.2 CBW

The results for CBW for the period January 2007–July 2013 are shown in Fig. 5b and both the mean and median ²²²Rn surface flux values are given in Table 1, which also shows values from the soil chamber measurements and model results. The error bars are calculated from error propagation in Eq. (2) using the measurement uncertainties described in Sect. 2.2.2. The mean value of (0.63 ± 0.04) atoms cm⁻² s⁻¹ ($n = 422$) compares very well with the results from the modelling work by Manohar et al. (2013), who reported a mean value of (0.65 ± 0.14) atoms cm⁻² s⁻¹. The results from the process-based model (Karstens et al., 2015a) are in the same range of (0.59 ± 0.18) atoms cm⁻² s⁻¹.

There is no ²²²Rn soil chamber programme at CBW. We organised a short field campaign from 12 to 16 July 2011 ($n = 14$) with a portable emanometer (Zahorowski and Whittlestone, 1996), the results of which are shown in Fig. 5b. The mean value of (0.64 ± 0.09) atoms cm⁻² s⁻¹ compares favourably with the results from our SPOT-EC method, but given the large variability this could simply be accidental. The median value of the SPOT-EC method, 0.34 atoms cm⁻² s⁻¹, is again almost a factor of 2 lower than the mean, which we attribute to the large variability of the fluxes. The statistical distribution of the regional ²²²Rn surface fluxes are shown in Fig. 6b, limited to 2 atoms cm⁻² s⁻¹ for clarity. The fluxes are clearly not normally distributed but rather follow a log-normal shape, which is as expected as the fluxes are unidirectional (van der Laan et al., 2009a). The large difference between the median and the mean values is a result of the very large temporal variability. Observed ²²²Rn surface fluxes can vary by orders of magnitude on hourly to diurnal scales because of changing wind direction or because of soil moisture and/or water table changes during rainfall. Figure 7b shows the spatial distribution of our ²²²Rn surface fluxes. Although part of this polar plot is masked because of tower blocking, it provides interesting information about the ²²²Rn surface fluxes in our footprint. ²²²Rn surface fluxes closest to the tower are on average between 0.4 and 0.6 atoms cm⁻² s⁻¹. Lower values are mostly observed from the north-east where the soil type is peat or peat on clay. The

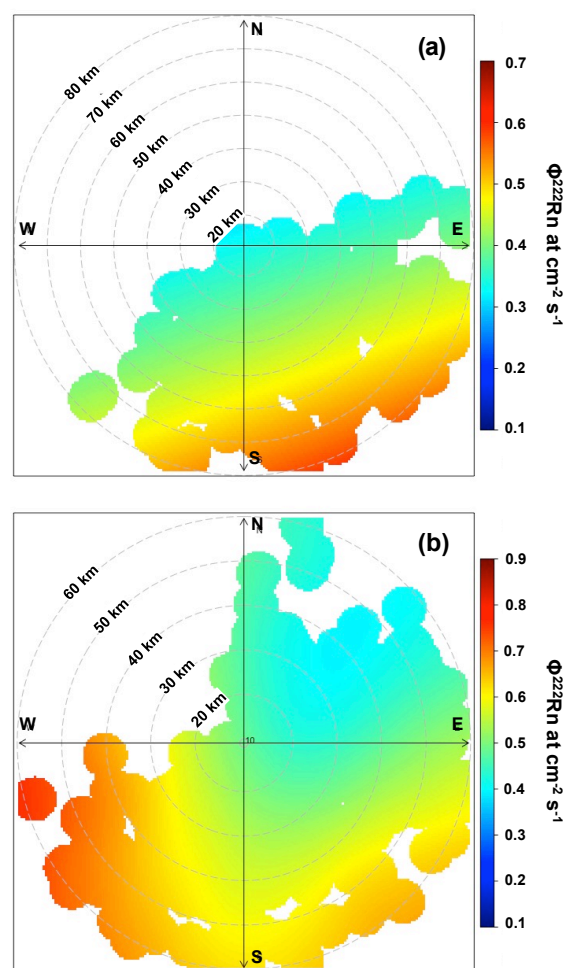


Figure 7. Spatial distributions of all analysed ²²²Rn surface fluxes for LUT (a) and CBW (b). The plots are generated with the openair package in R. The polar axis indicates the maximum fetch range calculated as wind speed times the duration of the event and is plotted against wind direction and the ²²²Rn surface flux. For clarity, data were limited to > 0.05 and < 1.5 atoms cm⁻² s⁻¹. Note that for LUT, the sector between 240° through 0 to 60° (between WSW and ENE) is not taken into account because of marine influences, and for CBW the sector between 280 and 340° (WNW–NNW) is blocked by the tower.

highest values are mostly observed in the south-west sector where the soil type is mainly river clay.

The diel distribution of the observed events vs. the ²²²Rn surface flux is shown in Fig. 8b. Similar to our findings for LUT, well-mixed periods are generally undersampled but a reasonable coverage over the day is obtained and the magnitude of the flux is not dependent on the time of the day.

4 Discussion

The method presented in this paper, SPOT-EC, allows for accurately estimating the ²²²Rn surface flux and its variability

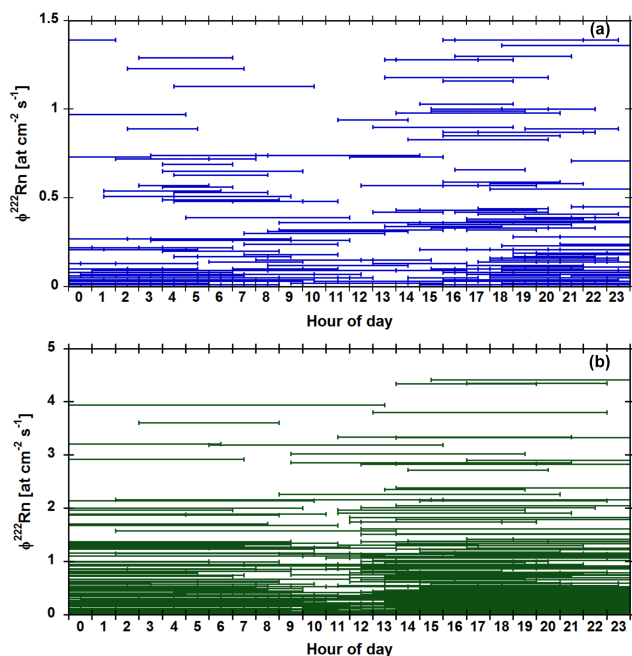


Figure 8. Distribution of all analysed events over the day for LUT (a) and CBW (b). Length and position of each line indicate the timing and duration of each event. No significant correlation is observed between the sampling time and the magnitude of the flux. Well-mixed periods are generally undersampled but a reasonable coverage over the day is obtained.

on a regional scale. The flux estimates are integrated in space and time, that is, averaged over the footprint and for the duration of an event (Sect. 2.3). Similar to the standard ^{222}Rn tracer inversion method, we use the ratio of a known surface flux to an observed concentration change over time as measured from a (tall) tower to determine the degree of atmospheric mixing and dilution. This factor is then subsequently applied to a concurrently observed concentration change of a species of interest to calculate its surface flux. In the case of the standard ^{222}Rn tracer inversion, the ^{222}Rn flux, which is assumed to be well known, is used together with ^{222}Rn activity concentration measurements to determine a factor representing the atmospheric mixing and dilution (to the free troposphere). This factor is subsequently used to determine the surface flux of a species of interest (e.g. CO_2). However, in practice, the ^{222}Rn flux (and its variability) is generally not well known and does not match the temporal resolution of the concentration measurements; therefore, it is assumed to be constant and homogeneously spread. Our results, however, indicate that even on regionally integrated scales the variability of ^{222}Rn surface fluxes can be relatively large and this potential source of uncertainty should be taken into account since the results of the ^{222}Rn tracer inversion are directly proportional to the assumed ^{222}Rn flux. We have shown that the long-term averaged results from our SPOT-EC method are in good agreement with those from three independent meth-

ods. We, therefore, assume that this potential uncertainty is mainly a concern when applying the ^{222}Rn tracer inversion for relatively short periods. For such studies we suggest either excluding observations during periods where the ^{222}Rn surface flux can be expected to be significantly variable such as for periods with rapidly varying soil moisture levels (e.g. during rainfall), or correct the applied ^{222}Rn flux estimates accordingly if possible. In the case of SPOT-EC, the above-named source of uncertainty is non-existent since the surface flux that is used to constrain the atmospheric mixing component is not assumed, but is actually measured (with an eddy covariance system).

We have shown the application of our SPOT-EC method for two sites in the Netherlands. For both sites, valuable information was obtained about both the temporal and spatial variability of the regional ^{222}Rn surface flux. For both sites, the experimental set-up could be further improved by reinstalling the EC systems to measure at the same height as the concentration measurements. This was not the case for the period covered in this paper due to practical reasons. In some cases, therefore, an increase or decrease in CO_2 mole fraction might not be fully reflected by the EC measurements. Therefore, and also because we wanted to compare our results with those from soil chambers, we tried to limit the footprint using strict selection criteria (Sect. 2.3). A coarse estimate based on the length of the selected events (i.e. $t_n - t_0$ in Eq. 2) and the mean wind speed yields a mean fetch range (i.e. maximum distance covered by the air mass) of ~ 60 km for LUT and ~ 45 km for CBW for our observations. The measurement uncertainty for each individually observed flux can be calculated relatively straightforward by error propagation of the measurement uncertainties for each variable. In general, the fluxes calculated from the largest concentration changes (Eq. 2) have the smallest uncertainty due to a better signal to noise ratio. For LUT, the uncertainties range from ± 17 to ± 100 % with a mean of ± 42 %. For CBW, the mean uncertainty was ± 45 % with individual values ranging from ± 13 to ± 75 %. The upper range, hence the mean value of the uncertainties, can be lowered by applying stricter event selection criteria, but at the cost of reducing the data set. The longer-term mean flux can be determined much more accurately provided there are enough observations, as its uncertainty is inversely proportional to the number of observations. For both sites, the error in the longer-term mean was about ± 15 % (Table 1), showing that our methodology is suitable for estimating seasonal and annual regional ^{222}Rn surface fluxes.

Although we calculate the ^{222}Rn soil flux from semi-continuous observations of the CO_2 mole fractions, ^{222}Rn activity concentrations and EC measurements, our method does not provide semi-continuous results for the ^{222}Rn fluxes. This is because the EC systems require relatively turbulent conditions (by definition), whereas the relative uncertainty of the measured concentration changes (i.e. numerator and denominator in Eq. 2) decreases with increasing concentra-

tion changes which are generally occurring during relatively stable conditions. In total 422 events were observed at CBW for the period of January 2007 to July 2013 and 209 events for LUT for the period of January 2008 to January 2010. Figure 8 shows that we do have a good data coverage throughout our observation period although events from autumn to spring are more common (Fig. 5) due to more atmospheric stable conditions. More importantly, there does not appear to be any correlation between the magnitude of the ²²²Rn surface fluxes and the time of the day. As shown in Table 1, for both sites the long-term mean results from four independent methods (SPOT-EC, soil chamber, radionuclides-based map and process based modelling) agree well. Considering that these sites have very different soil types and conditions, this is a very promising result as it suggests that the ²²²Rn surface flux can be relatively well constrained.

On shorter timescales, differences between SPOT-EC and the soil chamber are more pronounced, but because both methods integrate over a very different area, i.e. the surface of the chamber vs. the regional footprint of the EC system. The main driver for the variability of the ²²²Rn flux is expected to be soil moisture content which is not necessarily the same throughout the observed area. Since we measured the soil moisture content at LUT directly below the chamber at a depth of 0.3 m and did not observe any sudden increases, we attribute most of the soil-moisture-related variability to rainfall. Although both systems are capable of measuring the fluxes from wet soils, they do not provide measurements during rainfall. The lid of the chamber is closed during the measurement and the EC data are flagged out due to not being reliable. However, the measurements from the soil chamber might be affected by increasing soil moisture content during rainfall. Another potential discrepancy between the soil chamber and the tower observations is due to the fact that LUT is an intensive agricultural site and the soils are regularly disturbed (ploughed), leading to varying permeability and porosity and affecting the diffusion of ²²²Rn within the soil to the soil–atmosphere interface. Such variability, in particular high ²²²Rn surface fluxes, would not be seen with the soil chamber which is placed on undisturbed soil next to the tower. Another potential reason for the discrepancy between the very local and regionally integrated ²²²Rn surface fluxes is the use of ²²⁶Ra-containing phosphate fertiliser (Feichter and Crutzen, 1990). For example, Dörr (1984) measured a doubling of ²²²Rn from intensively used agricultural soils. Contrary to the chamber method, our SPOT-EC approach captures such variability integrated over a large area. The fact that our SPOT-EC method is able to measure the variability caused by reasons discussed here is a key advantage of SPOT-EC compared to chamber measurements.

The SPOT-EC method can be used in different applications. For example, the results from SPOT-EC provide valuable constraints to verify or calibrate ²²²Rn soil flux models and regional atmospheric transport models. They can also be applied to calculate fluxes of another species of interest us-

ing a ²²²Rn tracer inversion method such as SPOT (van der Laan et al., 2014). For example, SPOT-EC can be applied using eddy-covariance measurements of CO₂ to derive regionally integrated ²²²Rn surface fluxes which in turn can be applied to the SPOT method to estimate regionally integrated net emissions, e.g. of CH₄. If the same species are used for both SPOT-EC and the ²²²Rn tracer inversion method (e.g. SPOT), the assumption is made that ²²²Rn surface fluxes can be extrapolated in space and time. Note that the footprint of the SPOT-EC method is constrained by the eddy-covariance measurements; hence it is relatively small (~ 15 km distance at 60 m measurement height) compared to the much larger footprint (over 100 km distance) during purely stable atmospheric conditions for which SPOT is generally used. Although ²²²Rn fluxes are relatively homogeneously spread and, besides variability due to rapid changes in soil moisture content, relatively constant (as is commonly assumed with the ²²²Rn tracer inversion method) an uncertainty due to such extrapolation is obviously involved and needs to be taken into account. However, provided enough observations are available, a mean ²²²Rn flux can be determined, e.g. for each wind sector or soil moisture content (if monitored), or use a process model (e.g. Hirao et al., 2010; Karstens et al., 2015a) for extrapolating the flux after calibration with SPOT-EC.

5 Conclusions

We have described a new method, the Single Pair of Observations Technique with Eddy Covariance (SPOT-EC), to determine regional-scale surface fluxes of ²²²Rn from ambient measurements of ²²²Rn activity concentration, CO₂ mole fractions and CO₂ eddy covariance fluxes. SPOT-EC provides mean ²²²Rn fluxes at hourly resolution integrated in space (i.e. over the footprint) and time (i.e. the duration of a given event). Short-term fluxes (from single events) can be calculated with an uncertainty of about ±15 % and longer-term (e.g. seasonal/annual) mean fluxes with an uncertainty of about ±10 %. SPOT-EC does not provide continuous results; however good diurnal coverage was obtained and no significant correlation was observed between the sampling time of day and the magnitude of the flux.

We have applied our methodology to observations from two stations in the Netherlands, Cabauw and Lutjewad, and we compared our results with results from two independent modelling studies, as well as soil chamber measurements. For both stations, a good agreement was found between these four independent methods, suggesting that the ²²²Rn soil flux can be well constrained by our method.

For LUT we estimate a mean ²²²Rn surface flux of (0.29 ± 0.02) atoms cm⁻² s⁻¹. Fluxes > 0.5 atoms cm⁻² s⁻¹ were observed to the south and south-east. For CBW we estimate a mean ²²²Rn surface flux of (0.63 ± 0.04) atoms cm⁻² s⁻¹. Lowest fluxes (0.4 to 0.6 atoms cm⁻² s⁻¹) were generally observed from the

north-east and the highest values ($> 0.6 \text{ atoms cm}^{-2} \text{ s}^{-1}$) were observed to the south-west, where the soil type is mainly peat or river clay respectively.

Our methodology offers a powerful tool for calibrating process-based ²²²Rn soil flux models, validating regional atmospheric transport models and providing better constraints for regional inversions using the ²²²Rn-tracer method.

6 Data availability

Data are freely available upon request from the authors. Data from Cabauw station are also provided via the Cabauw Experimental Site for Atmospheric Research (Cesar, 2016) database: <http://www.cesar-database.nl/>. CO₂ mole fractions for both LUT as well as CBW are also made available through the Obspack product: available at <http://www.esrl.noaa.gov/gmd/ccgg/obspack/data.php> (ESRL, 2016). Model-based ²²²Rn soil fluxes for Europe (described in Karstens et al., 2015a) are available at doi:10.1594/PANGAEA.854715 (Karstens et al., 2015b).

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