Enrichment of Radon and Carbon Dioxide in the Open Atmosphere of an Australian Coal Seam Gas Field

Douglas R. Tait,[†,*] Isaac R. Santos,[†] Damien T. Maher,[†] Tyler J. Cyronak,[†] and Rachael J. Davis[†]

[†]Centre for Coastal Biogeochemistry, School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore, NSW, Australia, 2480

ABSTRACT: Atmospheric radon (^{222}Rn) and carbon dioxide (CO_2) concentrations were used to gain insight into fugitive emissions in an Australian coal seam gas (CSG) field (Surat Basin, Tara region, Queensland). ^{222}Rn and CO_2 concentrations were observed for 24 h within and outside the gas field. Both ^{222}Rn and CO_2 concentrations followed a diurnal cycle with night time concentrations higher than day time concentrations. Average CO_2 concentrations over the 24-h period ranged from ~390 ppm at the control site to ~467 ppm near the center of the gas field. A ~3 fold increase in maximum ^{222}Rn concentration was observed inside the gas field compared to outside of it. There was a significant relationship between maximum and average ^{222}Rn concentrations and the number of gas wells within a 3 km radius of the sampling sites (n = 5 stations; $p < 0.05$). A positive trend was observed between CO_2 concentrations and the number of CSG wells, but the relationship was not statistically significant. We hypothesize that the radon relationship was a response to enhanced emissions within the gas field related to both point (well heads, pipelines, etc.) and diffuse soil sources. Radon may be useful in monitoring enhanced soil gas fluxes to the atmosphere due to changes in the geological structure associated with wells and hydraulic fracturing in CSG fields.

INTRODUCTION

The past decade has seen a dramatic increase in unconventional gas extraction worldwide. Unconventional gas differs from conventional gas in that conventional gas is trapped in natural pores or fractures in sedimentary layers while unconventional gas can also be adsorbed to the sediment itself. One of these unconventional gases is coal seam gas (CSG), also known as coal bed methane. Production of CSG relies on the extraction of water, which reduces pore pressures and thereby allows gases to desorb and flow through fractures and micropores in a coal seam. Technological advances such as directional drilling and hydraulic fracturing (i.e., the injection of fluid and proppants under pressure into the wellbore to fracture geological strata), have allowed greater access to these gas reserves through increasing the connective matrix in subsurface sediments. Initial studies have shown that unconventional shale gas extraction may increase groundwater–methane concentrations in the vicinity of gas production wells.[1] However, there is also the potential for unintentional or "fugitive" emissions produced through the CSG mining process to be released into the atmosphere.

Fugitive emissions are gases that are unintentionally lost to the atmosphere through the gas extraction, collection, processing and transportation processes. These emissions can emanate from point sources (e.g., venting, equipment leaks, and distribution) and enhanced diffusion of gas from soils. Emissions include greenhouse gases (GHG) such as carbon dioxide (CO_2) and methane (CH_4). While not harmful to human health at low concentrations, these emissions should be accounted for when estimating the net greenhouse gas footprint of CSG operations. The release of methane is of particular interest as it is a powerful greenhouse gas with a global warming potential 25 times that of CO_2 over a 100-year time horizon.[2] Importantly, the atmospheric presence of these gases may suggest the release of other gaseous substances, such as volatile organic carbons[3,4] which may be harmful to human health.[5] Without a quantitative knowledge of the gases produced and their sources and sinks, it is difficult to unequivocally estimate gas fluxes through modeling approaches.[6]

Monitoring of radon (^{222}Rn) has been undertaken for decades in enclosed spaces such as mines and dwellings where the build-up of the gas can be harmful to human health.[7] Enhanced radon concentrations in groundwater and the atmosphere have also been linked to earthquakes.[8] Radon is a radioactive (half-life = 3.84 days) noble gas that is produced in the ^{238}U decay chain.[9,10] Since uranium is present in nearly all rocks and sediments, soil-gas exchange represents a nearly continuous source of radon to the atmosphere. Radon is an excellent natural soil gas tracer because it is unreactive and its short half-life prevents any significant build-up in the atmosphere over long time scales. Therefore, the presence of ^{222}Rn in the atmosphere requires a nearby source. In addition,
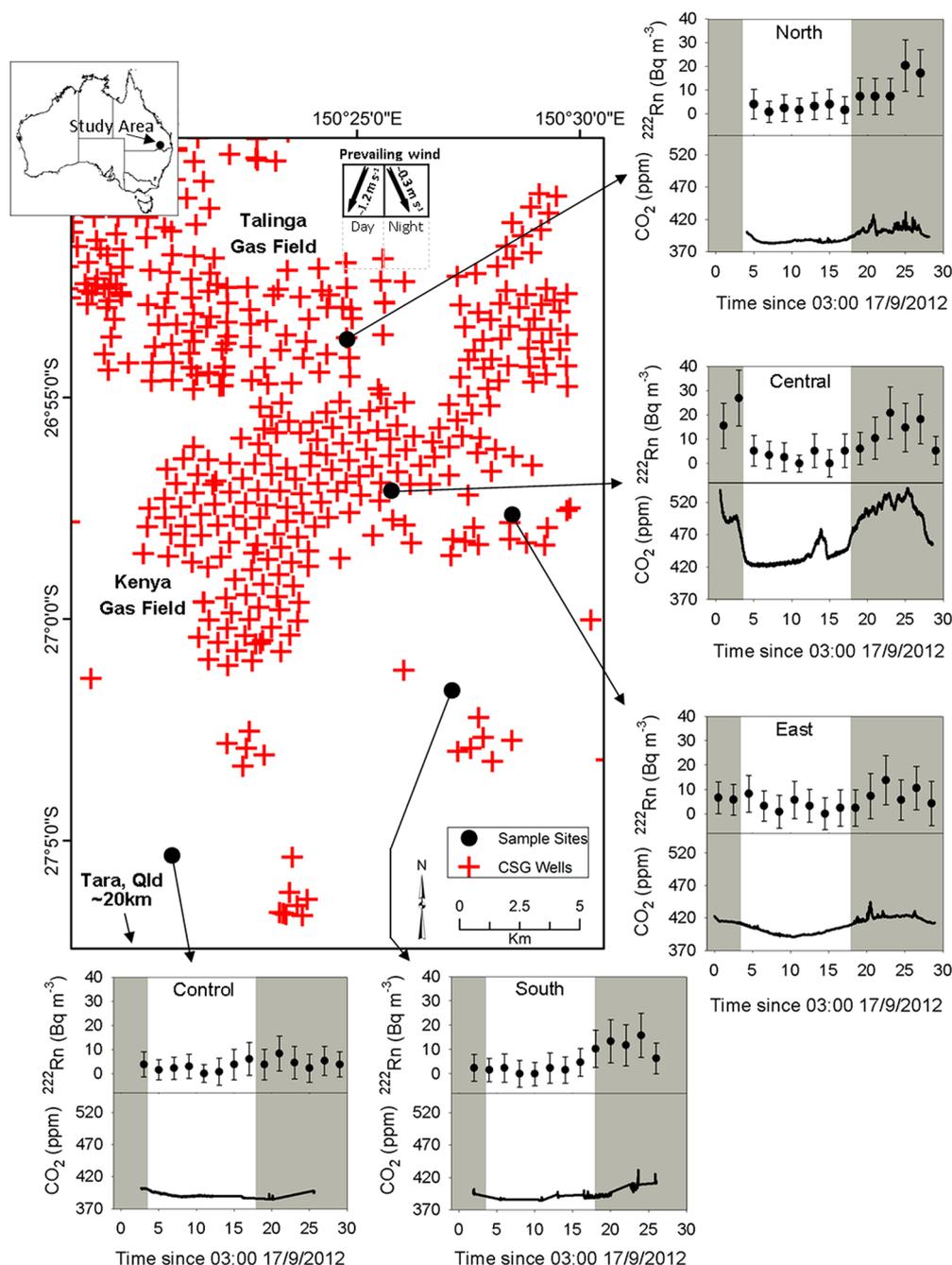
Figure 1. The study site in the Surat Basin, Tara region, Queensland. Gas wells are indicated by a red cross (data from http://mines.industry.qld.gov.au/geoscience/interactive-resource-tenure-maps.htm, accessed 24 October 2012). The red crosses may represent more than one well if they are in close proximity. CO_2 (ppm) and ^{222}Rn (Bq m^{-3} $\pm 2\sigma$) concentrations over a ~24-h period are indicated for each site. The gray areas represent night-time, while the white areas represent daytime.

radon can be easily detected by portable instruments that can be deployed in the field.

We hypothesize that measurement of atmospheric ^{222}Rn concentrations may provide a simple and effective way to gain insight into fugitive emissions from CSG mining activities. The aim of this study was to assess whether atmospheric ^{222}Rn and CO_2 concentrations are enriched within an Australian CSG field relative to nearby areas outside the CSG field. We postulate that a relationship between gas concentrations and the number of nearby CSG wells will emerge if CSG extraction processes represent a significant source of ^{222}Rn and CO_2 to the atmosphere.

■ EXPERIMENTAL SECTION

This study was performed in a CSG field near Tara, Queensland, Australia (~26°50′0″S, 150°20′0″E). The area has two main gas fields, the Talinga and the Kenya gas fields, with wells in varying states of exploration and production. The production and exploration of CSG in the area is associated with the extensive Walloon Coal Measures, which are relatively permeable (>4.93 x10^{-13} m^2 in some seams) and generally shallow (near surface to <400 m).[11] The water table in the area is typically at a depth of ~40 m,[12] however there is little historical water level monitoring information available.

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We deployed 24-h time-series stations to measure atmospheric ^{222}Rn and CO_2 at three locations within the gas fields and two stations outside of the gas fields (Figure 1). A gas intake was positioned at 2 m above the ground at each station. The first station (hereafter referred to as North) was adjacent to an open wheat field approximately 3 km north of the Kenya gas field and to the east of the Talinga gas field. The second site was located on a roadside reserve in the central part of the Kenya gas field (Central). The third site was located directly south of a large water holding pond in the Kenya gas field (East). The fourth site was located approximately 3 km south of the Kenya gas field (South). The fifth site was located approximately 8 km from the southern boundary of the Kenya gas field (Control). For each site, the distance to the nearest well and the number of nearby wells are indicated in Table 1.

Table 1. Position and Proximity of Sampling Sites to CSG Well Heads[a]

site	lat/long	~distance to nearest gas well (m)	wells within 1 (km)	2 (km)	3 (km)	4 (km)
north	26° 53′S, 150° 24′E	60	4	15	27	51
central	26° 57′S, 150° 25′E	500	4	17	36	63
east	26° 57′S, 150° 28′E	250	1	9	19	27
south	27° 1′S, 150° 27′E	1500	0	2	5	7
control	27° 5′S, 150° 20′E	4400	0	0	0	0

[a]The location of well heads was obtained from www.mines.industry.qld.gov.au/geoscience/interactive-resource-tenure-maps.htm, accessed 24 October 2012.

Measurements of ^{222}Rn concentrations were performed using a commercially available continuous radon-in-air monitor (RAD-7, Durridge Company), with two-hour averaging intervals to ensure acceptable counting statistics. CO_2 measurements were taken using two nondispersive infrared gas analysers (Li-cor 820) and two nondispersive differential gas analysers (Li-cor 7000) recording at one minute intervals. Water vapor was removed from air sample streams using a Drierite column in-line with the analysers. All CO_2 analysers were calibrated using 0 and 502 ± 10 ppm certified reference gases (Coregas Australia). The uncertainty of individual CO_2 detectors was less than 2%, well below the natural variability in the region. For CO_2 concentrations at the South site and the final 12 h at the Control site, CO_2 was measured every four hours using a cavity ringdown spectrometer (Picarro G2201-i CRDS). The spectrometer calibration was within 10 ppm of the Li-cor CO_2 analysers. The radon monitors were calibrated by the manufacturer (±5%). A cross-calibration check just before deployment resulted in agreement within the calibration uncertainty. Automated weather stations (Davis Vantage Pro) were deployed on six-meter poles at the South and Control sites to determine wind, temperature and humidity fluctuations. To compare averages, one-way ANOVA and regression analyses were done using SPSS with p values ≤0.05 considered significant.

■ RESULTS AND DISCUSSION

Time Series Observations. Calm winds occurred during our experiment. During the day, winds were predominantly from the NNE and averaged ~1.2 m s^{-1}. At night, wind speeds approached zero. Over the 24 h period, temperatures ranged from 10 to 25 °C. Humidity ranged from 25% during the day to 90% at night. There was no significant difference in the average atmospheric pressure during the day and night (1008.5 ± 3.9 mbar and 1008.9 ± 1.1 mbar respectively).

Concentrations of ^{222}Rn and CO_2 followed similar diurnal patterns with lower concentrations during daylight hours (Figure 1). CO_2 concentrations varied from day to night by over 60 ppm at the Central site and by as little as 5 ppm at the Control site. Concentrations of ^{222}Rn increased at night by ~5 fold at the Central and South sites and approximately doubled at the Control site. This is probably due to the formation of a temperature inversion layer at night, trapping any emissions closer to the surface and causing the accumulation of gases released from soils or CSG infrastructure. The release of radon at the soil-air interface has been shown to follow a diurnal pattern with variations governed by temperature and wind speeds,[13] which is consistent with our observations. The effects of night-time inversion layers on ^{222}Rn concentrations has been previously described for non-CSG regions.[14] Lower wind speeds and a lower atmospheric mixing height at night may allow the accumulation of soil gas in the atmosphere. These are important considerations for assessing CSG fugitive emissions as the time of sampling could significantly alter the concentration of gases in the atmosphere, and as such sampling of full 24-h cycles is essential. A distinct spike in CO_2 and ^{222}Rn concentrations occurred at the Central site approximately 13.5 to 15 h after the start of monitoring. This spike corresponded to a distinct shift in winds from NNE at ~1.3 m s^{-1} to easterly at ~0.5 m s^{-1} before returning to a NNE direction.

The highest average CO_2 concentration during the 24-h period was measured at the Central site (~468 ppm) while the lowest was at the Control site (~391 ppm) (Figure 2). There
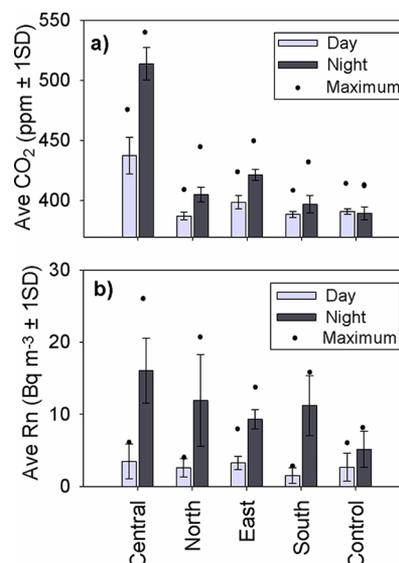
Figure 2. Average CO_2 (a) and ^{222}Rn (b) concentrations ±1 SD at different sampling sites. The maximum CO_2 (a) and ^{222}Rn (b) concentrations during the day and night are indicated with a solid circle.

were significantly higher night-time average CO_2 concentrations at sites within the gas field (North, Central and East) ($p < 0.01$) than at sites outside (South and Control), while the Central and East sites had significantly higher CO_2 concentrations during the day compared to the other sites ($p < 0.01$). The only significant difference in ^{222}Rn concentrations between sites occurred at night between the Central site and the Control site ($p = 0.04$). This was caused by the relatively large standard deviations due to the steady increase in ^{222}Rn concentrations during the night coupled with the long averaging times used (2 h).

Correlations between Gas Concentrations and Number of CSG Wells. There was a significant relationship between the number of wells within 3 km of sampling sites and the maximum radon concentration over the 24 h period ($r^2 = 0.81$, $p = 0.04$) (Figure 3a). If we use the average radon
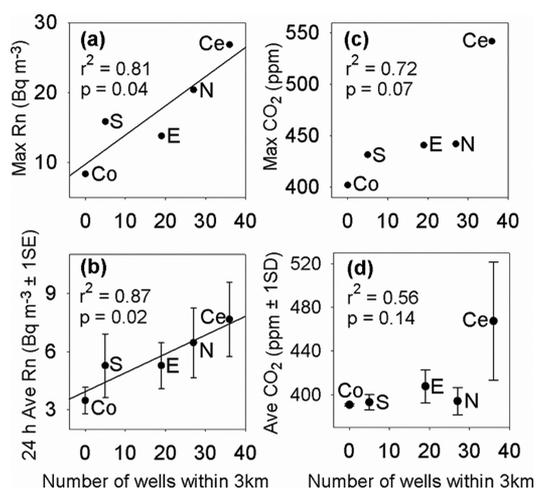
Figure 3. Regression plots of the number of CSG wells within 3 km of study sites and maximum ^{222}Rn (a), average ^{222}Rn (b), maximum CO_2 (c), and average CO_2 (d) concentrations. Control (Co), South (S), East (E), North (N), and Central (Ce) study sites are indicated.

concentration, then the r^2 value is higher ($r^2 = 0.87$, $p = 0.02$) (Figure 3b). It is difficult to estimate the exact area influencing gas concentrations at each station. If we use the number of wells within 1 km, then the correlations illustrated in Figure 3a are weaker ($r^2 = 0.74$, $p = 0.06$), while if we use the number of wells within 4 km of each monitoring station, the correlations are similar but slightly lower ($r^2 = 0.83$, $p = 0.03$). There was no significant relationship between the number of wells at 3 km and the average day ($r^2 = 0.30$, $p = 0.34$) and average night ($r^2 = 0.65$, $p = 0.10$) ^{222}Rn concentrations largely due to the ^{222}Rn concentrations at the south site being comparably low during the day (1.48 ± 1.07 bq m^{-3}) and high at night (11.21 ± 4.17 bq m^{-3}).

There was a positive, but statistically nonsignificant relationship between the number of wells within 3 km of sampling stations and the maximum CO_2 concentration at each station ($r^2 = 0.72$, $p = 0.07$) (Figure 3c). A weaker (but still positive) correlation was found when the average CO_2 concentration at each site was used ($r^2 = 0.56$, $p = 0.14$) (Figure 3d). The Central site, which had the highest CO_2 concentrations, was located approximately 30 m from a service road in the central part of the Kenya gas field (Central). No short-term CO_2 spikes similar to what would be expected from passing vehicles was observed. The relatively low concentrations of CO_2 at the

North site may be partially due to the location of the station in relation to the prevailing wind direction. The North site had a much smaller number of wells upwind compared to the Central site. However, similar patterns of low ^{222}Rn concentrations at the North site were not observed. The diurnal variations in CO_2 concentrations was likely driven by ecosystem metabolism, leading to a reduction in CO_2 through plant uptake during the day and an increase in CO_2 at night due to respiration. The relatively higher background CO_2 concentration in the atmosphere associated with a longer residence time than radon may also have prevented stronger correlations from emerging as a larger source could be needed to significantly alter CO_2 concentrations in the atmosphere. CO_2 is only a small fraction (<1%) of the CSG in the Surat Basin[15] and therefore CO_2 release through fugitive emissions is potentially masked by biological processes on the surface. Alternatively, if enhanced diffusive soil fluxes occur within the CSG field, part of the methane (which accounts for >98% of Walloon Coal CSG[16]) may be oxidized to CO_2, and account for the general trend observed. For example CH_4 oxidation rates, and first-order rate constants, of 45 g m^{-2} d^{-1} and -2.37 h^{-1} respectively have been reported for CH_4-rich landfill soils.[17]

In contrast to CO_2, uptake and release of atmospheric ^{222}Rn by vegetation can be considered negligible due to its low reactivity as a noble gas as supported by experiments with plants growing in soils containing high uranium concentrations.[18] This, along with the nearly constant production of ^{222}Rn in soils and short residence time (several days) makes ^{222}Rn an excellent tracer of physical processes that drive soil gas exchange. Radon has been extensively used to assess gas exchange in conventional coal mines[19,20] and soils.[21] In the open atmosphere, ^{222}Rn has been used in conjunction with $^{14}CO_2$ to quantify CO_2 emissions from fossil fuels in Europe.[6,22] However, the present study is the first to use ^{222}Rn concentrations to assess potential emissions from a CSG production field.

Conceptual Model. We hypothesize that the high concentrations of ^{222}Rn and CO_2 measured inside a CSG field during this study are derived not only from gas extraction infrastructure, but also from the depressurization (horizontal drilling, hydraulic fracturing, groundwater extraction) of the coal seams which may increase diffuse soil emissions (Figure 4). The changes to subsurface strata influencing gas exhalation processes before an earthquake may be conceptually similar to the changes imposed by CSG extraction. Variation in ^{222}Rn concentrations in groundwater[23] and the open atmosphere[24] has preceded large earthquakes. This is likely due to increased subsurface stress which alters sediment pore spaces and opens or closes cracks in the strata which releases ^{222}Rn. For example, an approximate 5-fold increase in atmospheric ^{222}Rn concentrations in the five months leading up to an earthquake was observed in Kobe, Japan.[8]

The groundwater level in the general Tara region is predicted to drop as a result of CSG extraction[12] and has been reported to drop by approximately 100 m in certain locations since the commencement of widespread CSG mining.[25] This would increase the unsaturated soil volume, which may increase gas exchange with the atmosphere. The depressurization of aquifers can change the geological structure of the soil profile and create cracks and fissures that may enhance gas exchange. Maximum hydraulic fracture heights of ~588 m have been reported in stimulated hydraulic fractures in U.S. shales,[26] however no data
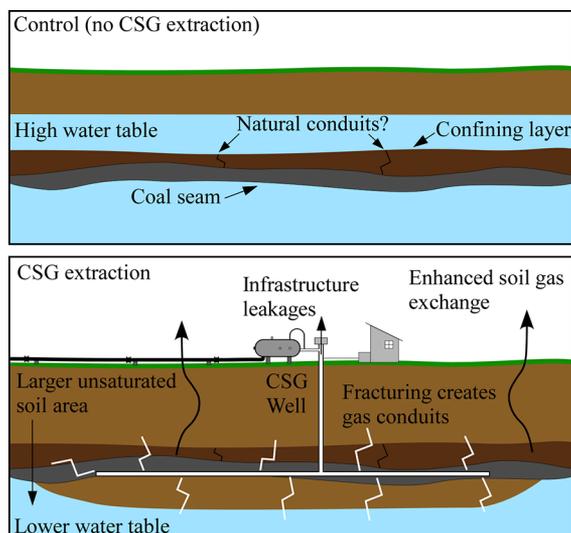
Figure 4. Conceptual model of the potential alteration to gas pathways through CSG extraction. We hypothesize that the lowering of the water table and the alteration of subsurface strata creates enhanced soil gas exchange, which results in higher radon concentrations near CSG wells.

are available on the stimulated fracture dimensions from CSG fields in Australia. As the coal seam targeted for CSG production in the Tara region is relatively shallow (near surface to <400 m)[11] and CSG wells are reported to be as shallow as 65 m,[27] diffuse surface emissions may be enhanced.

While our conceptual model (Figure 4) appears to be the most reasonable explanation for the patterns observed, we highlight that other hypotheses need to be assessed. The lack of baseline studies prevents us from determining unequivocally whether the radon enrichments are a response to CSG, or CSG companies simply choose to drill wells in an area of naturally elevated radon concentrations. In addition, different atmospheric mixing heights at the different sampling stations could mask our source assessment. However, a spatially heterogeneous atmosphere is unlikely considering the proximity of our stations (<25 km apart) and the flat regional topography. The atmospheric modelling of total gas fluxes is necessary to test this hypothesis. Longer term observations and further sampling of radon-in-soil-gas and radon-in-groundwater measurements may further support our hypothesis. Distinguishing the relative contribution of point infrastructure and diffuse soil sources is paramount because reducing infrastructure gas leakages is likely to be less challenging than restoring the original soil structure. In order to distinguish point and diffuse sources, future studies may need to employ detailed baseline studies or alternatively, use the isotopic signature of gases to try to elucidate the pathways driving changes in atmospheric chemistry.

Implications. Quantifying fugitive emissions from CSG is an important consideration in determining the greenhouse gas footprint of CSG compared to traditional hydrocarbons such as coal. Past studies have suggested that nonconventional gas has less GHG emissions than coal.[28−30] However, these studies overlooked the fact that CSG activities may change the geological structure and enhance diffuse soil gas exchange processes. In addition, these studies used a global warming potential value for methane which is now believed to be too low.[31] Using the more recent global warming potential value, fugitive emissions as low as 2% to 3% of production may make

the GHG footprint of CSG higher than that of oil and coal.[32] Howarth et al.[32] estimated fugitive emissions from the high-volume hydraulic fracturing of shale formations to be between 3.6% and 7.9%, and Pétron et al.[3] estimated a similar range of between 2.9% and 7.7%, indicating the greenhouse gas footprint for unconventional gas mining maybe 20−100% greater than coal on a 20-year horizon. However, some of these results have been disputed.[33] This controversy highlights the need for development of better methods to quantify fugitive emissions from CSG.

This study showed that ^{222}Rn may be used as a tracer to qualitatively describe fugitive emissions from a CSG field. Importantly, this study highlights that single measurements may not give a reliable indication of atmospheric gases and that continuous sampling over full diurnal cycles is necessary. Further studies that quantify fugitive emission over the entire lifecycle of gas fields using combinations of carbon isotope ratios of CH_4 and CO_2, ^{222}Rn, and volatile organic carbon should be undertaken to fill the current gaps in knowledge concerning fugitive emissions from CSG and other unconventional natural gas resources. The monitoring of atmospheric gases at more sampling locations and over longer time scales may give more confidence to our proposed conceptual model. Monitoring atmospheric radon before and after the development of a CSG field could help to reveal whether CSG mining enhances soil gas fluxes over the long-term.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: +61 2 6620 3000; fax: +61 2 6621 2669; e-mail: douglas.tait@scu.edu.au.

Notes
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