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Atmospheric monitoring of carbon capture and storage leakage using radiocarbon

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ABSTRACT

We outline the methodology for detection of carbon dioxide (CO_2) leaks to the atmosphere from carbon capture and storage (CCS) using measurements of radiocarbon in CO_2. The radiocarbon method can unambiguously identify recently added fossil-derived CO_2 such as CCS leaks due to the very large isotopic difference between radiocarbon-free fossil derived CO_2 and natural CO_2 sources with ambient radiocarbon levels. The detection threshold of 1 ppm of fossil-derived CO_2 is comparable to other proposed atmospheric detection methods for CCS leakage. We demonstrate that this method will allow detection of a 1000 ton C yr^{-1} leak 200–300 m from the source during the day and more than 600 m away at night. Using time-integrated sampling techniques, long time periods can be covered with few measurements, making the method feasible with existing laboratory-based radiocarbon measurement methods We examine the method using previously published observations and new model simulations for a case study in Taranaki, New Zealand. Plant material faithfully records the radiocarbon content of assimilated CO_2 and we show that short-lived grass leaves and cellulose from tree rings provide effective time-integrated collection methods, allowing dense spatial sampling at low cost. A CO_2 absorption sampler allows collection at controlled times, including nighttime, and gives similar results.

1. Introduction

Carbon capture and sequestration (CCS) is widely recognized as a feasible strategy for mitigating the impact of fossil fuel combustion on atmospheric carbon dioxide (CO_2) levels (e.g. Pacala and Socolow, 2004; IPCC, 2005; Bruckner et al., 2014). Yet leakage of sequestered CO_2 back into the atmosphere is of concern. Leaks of large enough magnitude could be a health hazard, and even small leaks return CO_2 to the atmosphere, reducing or altogether negating the effectiveness of the CCS process in mitigating climate change. Thus monitoring, attribution and quantification of any CO_2 leaks back to the atmosphere is an important component of the CCS process (e.g. European Commission, 2007; NETL, 2007; Dixon and Romanak, 2015), and is already required by regulation in some regions (e.g. European Commission, 2009).

Numerous methods for detecting CCS leaks into the atmosphere have been proposed. All of these methods make measurements of the locally measured trace gas mole fraction or isotopic composition of a trace gas to estimate the local atmospheric mole fraction of CO_2 due to the CCS leak (CO_2CCS). The observed CO_2CCS mole fraction is dependent both on the magnitude of the leak and on atmospheric transport of that leak to the measurement location.

Measurement of CO_2 mole fractions is the most obvious method, but suffers from a major challenge in that CCS leaks are likely to be small relative to the large and variable CO_2 background (Leuning et al., 2008; Loh et al., 2009; Jenkins et al., 2011, 2016; Barr et al., 2011). This background variability is primarily due to natural diurnally varying CO_2 sources and sinks from photosynthesis and respiration which can result in a 40 part per million (ppm) range in CO_2 mole fraction at a single location in a single day [e.g. Miles et al., 2012]. Thus the detection limit using CO_2 measurements alone is ~4 ppm in CO_2CCS mainly due to the large variability and uncertainty in the CO_2 background (Loh et al., 2009). Nonetheless, this method can be successful when measurements are made very close to the source (Jenkins et al., 2016; van Leeuwen et al., 2013).

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CO_2 from CCS will have no impact on atmospheric oxygen and hence the oxygen to nitrogen (O_2/N_2) ratio in the atmosphere, whereas the other land based CO_2 sources, biogenic CO_2 exchange (respiration and photosynthesis) and fossil fuel combustion, will both alter the O_2/N_2 ratio. Thus concurrent CO_2 and O_2/N_2 measurements can positively identify CCS leaks (Keeling et al., 2011). The O_2/N_2 method likely has a detection limit of about 3 ppm CO_2CCS (van Leeuwen and Meijer, 2015; Keeling et al., 2011).

The ^{13}C content of CO_2 is another potential tracer for CCS leakage, as long as the CO_2CCS has a ^{13}C content substantially different from that of the atmosphere and that of nearby biogenic and fossil CO_2 sources (e.g. Moni and Rasse, 2014; Garcia et al., 2012; Fessenden et al., 2010; Krevor et al., 2010; McAlexander et al., 2011). The ^{13}C content is usually described as δ^{13}C, the deviation of the ^{13}C content from that of a standard material in units of ‰. The detection threshold of this method depends on the isotopic difference between the CO_2CCS, the ambient atmosphere and any other CO_2 sources, and the degree to which the δ^{13}C of the CO_2CCS is well known. The current atmosphere has δ^{13}C of about −8‰ (Derek et al., 2014) and biogenic CO_2 ranges from −12 to −30‰ (Tans, 1981). CO_2CCS derived from natural gas will usually be the most readily detectable since it has a typical δ^{13}C range of −40 to −50‰ (Tans, 1981), although some studies have suggested a much wider range of −28 to −75‰ (Milkov, 2005; Palstra and Meijer, 2014). CO_2 derived from biogenic sources and then sequestered ("biogas") will have a similar range of values (Palstra and Meijer, 2014). Coal and oil (−20 and −24‰, respectively (Tans, 1981)) derived CO_2CCS may be more difficult to distinguish particularly in areas with strong biogenic CO_2 fluxes. Even so, under many circumstances the δ^{13}C method is likely slightly better than using CO_2 mole fractions alone, and has a detection limit of about 3–5 ppm (Keeling et al., 2011; Moni and Rasse, 2014).

It is also possible to inject "correlate" trace gasses into carbon reservoirs along with CO_2 and monitor leakage of these gasses (Hurry et al., 2016; Susanto et al., 2016; Garcia et al., 2012; Pekney et al., 2012; Watson and Sullivan, 2012; Wells et al., 2009). The correlate gas can be intrinsically associated with a particular CO_2 source used for CCS, or deliberately added. If the leak rate of the correlate gas can be determined and the ratio of correlate to CO_2 in the CCS reservoir is known and is not altered between injection and leakage, then the CO_2 leak rate can also be calculated. For example, in the Otway project, the CO_2 injected into the reservoir naturally contained high levels of methane. The leaked methane was more readily detectable in the atmosphere than leaked CO_2 since the magnitude of the CH_4 leak was much larger relative to the CH_4 background (Loh et al., 2009). Some care must be taken with tracer methods since the tracer gas may have flow pathways and leak rates depending on the particular gas and the sequestration environment. Use of added tracers such as perfluorocarbons (PFCs) can be an extremely sensitive detector of leaks but the volume of PFCs required likely makes the method impractical for routine monitoring (Watson and Sullivan, 2012).

Here we will consider the radiocarbon (^{14}C) method as a tracer for CO_2CCS. ^{14}C, the radioactive isotope of carbon, is entirely absent in fossil derived CO_2 (CO_2ff) whereas natural CO_2 sources contain ^{14}C at levels similar to the atmosphere. This makes the radiocarbon method an unambiguous detector of recently added CO_2ff in the atmosphere, and in principle an ideal tracer for CO_2CCS (Dixon and Romanak, 2015; van Leeuwen and Meijer, 2015). We discuss the principles of the radiocarbon method, the different field sampling technologies and their advantages and disadvantages, and the detection limits of the radiocarbon method.

Our objective in this paper is to demonstrate the utility of the ^{14}C method in detecting CO_2CCS. We repurpose previously published observations of CO_2ff determined from ^{14}C observations to provide an analog for CO_2CCS and combine these observations with new model simulations to test the sensitivity and detection limit of the ^{14}C method. We aim to demonstrate the ability to *detect* CCS leaks with *quantification* of the magnitude of the leak being of only secondary concern. Our main observational dataset is from the Kapuni natural gas processing plant in rural Taranaki, New Zealand (Turnbull et al., 2016, 2014) and we also use results from other similar studies (Donders et al., 2013; Cook et al., 2001). Although these datasets are previously published elsewhere, we include explanations of the sampling methods and calculations to illustrate the ^{14}C method. The Kapuni observations were initially designed to test how well point source CO_2ff emissions can be quantified from atmospheric observations. Here we use them as an analog, along with new atmospheric transport model simulations, to understand how the method could be scaled to detect CCS leaks.

2. Radiocarbon method

^{14}C is produced naturally in the upper atmosphere and rapidly converts to radiocarbon monoxide (^{14}CO) and then to radiocarbon dioxide ($^{14}CO_2$) over a period of weeks to months. $^{14}CO_2$ then exchanges throughout the carbon cycle. ^{14}C is radioactive with a half-life of 5730 ± 40 years (Karlen et al., 1968). Thus fossil fuels, which have been out of contact with the atmosphere for millions of years, contain no ^{14}C, whereas natural CO_2 sources which exchange carbon with the atmosphere on timescales of a few years, such as biogenic respiration, contain ^{14}C at levels similar to that of the atmosphere. $^{14}CO_2$ is therefore now widely recognized as the best tracer for recently added fossil fuel CO_2 (CO_2ff) in the atmosphere (Levin et al., 2003; Ciais et al., 2010; Balter, 2012). Most CCS sites will sequester fossil fuel derived CO_2, so the radiocarbon method would be widely applicable to most CCS leaks. Like $^{13}CO_2$ measurements, the $^{14}CO_2$ content is intrinsic to the injected CO_2, and thus there are no problems with differential transport of the tracer species relative to CO_2CCS itself, nor requirements for special treatment of the CO_2 prior to injection.

The major challenge with the radiocarbon method is the difficulty of measurement. Currently, in situ $^{14}CO_2$ measurement is not possible (although new laser-based methods are being developed and in situ atmospheric $^{14}CO_2$ measurement may become possible some years in the future once several technical challenges are overcome [e.g. Galli et al., 2013]). Instead, $^{14}CO_2$ measurement is typically done by collecting CO_2 from air and processing in a laboratory setting. CO_2 is extracted from whole air and the resulting CO_2 is reduced to graphite followed by measurement of the ^{14}C content by accelerator mass spectrometry (AMS) (e.g. Turnbull et al., 2007; Graven et al., 2007). Two alternative methods use radiometric counting (gas or liquid scintillation counting), whereby the particles generated by radioactive decay of ^{14}C are measured. These methods can achieve similar measurement precision to AMS when long counting times are used and require three orders of magnitude more CO_2 (Levin et al., 2003). Costs for all methods are a few hundred US dollars per measurement. It is of particular note that unlike $^{13}CO_2$, isotopic fractionation is not a concern for $^{14}CO_2$ measurement. The Δ^{14}C notation used to represent ^{14}C content (and described further in Section 2.2) includes a correction based on the measured ^{13}C content for any fractionation that has occurred naturally or during sample collection and processing (Stuiver and Polach, 1977).

2.1. Integrated sample collection methods

CO_2 can be collected from air for radiocarbon measurement in a number of different ways, depending on the particular application. Here we focus on time-integrated sampling techniques, whereby CO_2 or a proxy is collected from a single site averaged over a period