

# Ground Gas Monitoring: Implications for Hydraulic Fracturing and CO<sub>2</sub> Storage

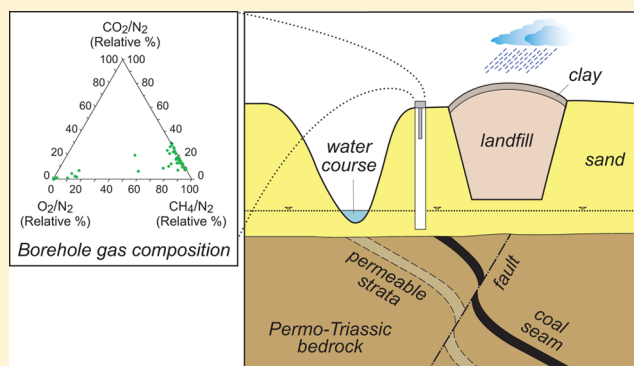
Christopher J. Teasdale,<sup>\*,†</sup> Jean A. Hall,<sup>†</sup> John P. Martin,<sup>‡</sup> and David A. C. Manning<sup>†</sup>

<sup>†</sup>School of Civil Engineering & Geosciences, Newcastle University, Newcastle upon Tyne, U.K., NE1 7RU

<sup>‡</sup>TerraConsult Ltd, Bold Business Centre, Bold Lane, Sutton, St Helens, Merseyside, U.K., WA9 4TX

## S Supporting Information

**ABSTRACT:** Understanding the exchange of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) between the geosphere and atmosphere is essential for the management of anthropogenic emissions. Human activities such as carbon capture and storage and hydraulic fracturing (“fracking”) affect the natural system and pose risks to future global warming and to human health and safety if not engineered to a high standard. In this paper an innovative approach of expressing ground gas compositions is presented, using data derived from regulatory monitoring of boreholes in the unsaturated zone at infrequent intervals (typically 3 months) with data from a high frequency monitoring instrument deployed over periods of weeks. Similar highly variable trends are observed for time scales ranging from decades to hourly for boreholes located close to sanitary landfill sites. Additionally, high frequency monitoring data confirm the effect of meteorological controls on ground gas emissions; the maximum observed CH<sub>4</sub> and CO<sub>2</sub> concentrations in a borehole monitored over two weeks were 40.1% v/v and 8.5% v/v respectively, but for 70% of the monitoring period only air was present. There is a clear weakness in current point monitoring strategies that may miss emission events and this needs to be considered along with obtaining baseline data prior to starting any engineering activity.



## INTRODUCTION

The exchange of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) between the geosphere and atmosphere is a key component of the global carbon cycle. At the advent of industrialization, atmospheric CO<sub>2</sub> concentration was 280 ppm and has subsequently increased so that it now exceeds 400 ppm.<sup>1</sup> This figure is projected to reach 600–800 ppm by the close of the century.<sup>1</sup> It is believed that the rise in CO<sub>2</sub> concentration in the Earth's atmosphere is linked to global climate change.<sup>2,3</sup> As well as CO<sub>2</sub>, CH<sub>4</sub> also occurs naturally in the ground. With a global warming potential (GWP) 21 times greater than CO<sub>2</sub>,<sup>4</sup> its emission to the atmosphere is considered to be one of the greatest environmental challenges of the 21st Century. In addition to emissions of CO<sub>2</sub> from the combustion of fossil fuels, which account for the major part of the post-industrial increase,<sup>5</sup> CO<sub>2</sub> exchange between the coupled plant–soil system and the atmosphere is a major control of atmospheric CO<sub>2</sub>.

Carbon Capture and Storage (CCS) is recognized by the Intergovernmental Panel on Climate Change (IPCC) and the United Nations Framework Convention on Climate Change (UNFCCC)<sup>6</sup> as a potentially important mitigation strategy against climate change due to CO<sub>2</sub>. Geological storage is technically feasible and under favorable conditions, CO<sub>2</sub> may be retained for millions of years.<sup>7,8</sup> Nonetheless, there are

accompanying risks of leaks as well as blowouts that can compromise the security of an operation.<sup>8</sup> Additionally, pumping CO<sub>2</sub> into deep geologic formations at high pressure may induce earthquakes and reduce groundwater pH, potentially enhancing contaminant mobility.<sup>9</sup> Monitoring for possible leaks is required to ensure the integrity of containment.

Hydraulic fracturing (“fracking”) associated with the production of natural gas has been highlighted as another environmental concern.<sup>10,11</sup> During the process, water containing chemical additives and a physical proppant is injected into shale formations through boreholes at high pressure. Liberation of gases trapped within the shale occurs as fractures spread. There is a possibility that CH<sub>4</sub> may leak from the subsurface via a number of pathways. In locations where groundwater is contaminated by CH<sub>4</sub>, there is scope for associated contamination of the overlying vadose zone.

For well-informed management of deep engineering processes that have the potential to affect greenhouse gas emissions, there is a need to understand the background levels

Received: May 23, 2014

Revised: October 30, 2014

Accepted: November 2, 2014

Published: November 3, 2014

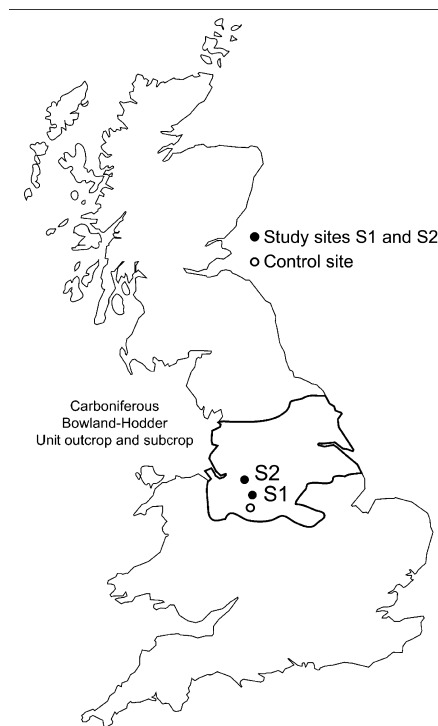
of  $\text{CH}_4$  and  $\text{CO}_2$  in soils, superficial unconsolidated sediment deposits and groundwater systems and, importantly, the extent of their temporal variability. In this paper, the compositions of gases (“ground gas”) within near-surface unconsolidated sands confined by a clay cover were investigated. Also, the implications of temporal variability for the design and interpretation of ground gas monitoring procedures are considered.

Emissions of gases from soils vary in their origin. Near surface fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  from biologically active soils occur in response to microbial respiration, and occur rapidly after the formation of the gas.<sup>12</sup> Concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  in soils dominated by plant roots and associated microbial systems are typically very low, below 1% v/v.<sup>13,14</sup> Below the biologically active soil, sedimentary geological processes produce  $\text{CO}_2$  and  $\text{CH}_4$ , whose proportions vary according to specific geological circumstances. Natural fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  to the atmosphere include contributions from both geological and biological sources. Artificial sources of gases within soil include sanitary landfill, where anaerobic microbial processes characteristically produce gas containing up to 70%  $\text{CH}_4$  and 30%  $\text{CO}_2$ .<sup>15</sup> Once formed, geological gases migrate through permeable and fractured formations until trapped or released to the atmosphere. Similarly, gases produced in landfills migrate, laterally as well as vertically, if containment systems fail. Monitoring systems in the vicinity of landfills are designed to detect migration so that appropriate action can be taken.

Specifically considered are the compositions of gases within shallow unconsolidated sands capped by glacial till. Landfills have been constructed in these formations within the UK and monitoring regimes are in place to assess the integrity of containment. Boreholes outside landfills are used to determine gas compositions. Thus, there is access to a resource of historical monitoring data that extends back many years.  $\text{CO}_2$  and  $\text{CH}_4$  in the sands may be derived from sources other than landfill, including natural migration from underlying strata, in this case, coal-bearing. Given that the sites lie within an area of search for shale gas (Figure 1), it is important to understand the origin of variability in gas compositions prior to any possible future deep engineering activities. Historic periodic and recent high frequency monitoring data obtained from outside landfill sites are compared, with reference to data from a site with a similar geological setting, but distant from landfill. The use of different temporal scales of observation has major implications for the planning and interpretation of ground gas monitoring procedures, with a wide range of applications.

## ■ DEEP GEOLOGICAL SOURCES OF GAS IN THE UK

Gas is a natural component of the geological subsurface, occurring within rock pores and fractures, and migrating in response to pressure gradients (i.e., generally to the surface, unless trapped). Geological gases have a wide range of compositions, depending on their origin. The focus of this paper is on  $\text{CO}_2$  and  $\text{CH}_4$ , which are formed naturally as a consequence of the decomposition (diagenesis) of organic matter within sediments and sedimentary rocks. In deep sediments, if geological factors are right, these gases accumulate in reservoirs which form the target of petroleum exploration. Current focus on unconventional sources of natural gas includes shale gas, tight gas and coal bed  $\text{CH}_4$ .<sup>16</sup> Production from these sources may require artificial fracturing, and there are concerns that “fracking” may cause gases to leak to shallow



**Figure 1.** Outline of the Bowland-Hodder Unit outcrop and subcrop (after Andrews<sup>23</sup>), with monitoring locations.

groundwater systems or to escape to the atmosphere through the soil.<sup>17,18</sup>

In addition to considering geological gas as a resource, CCS procedures require injection of  $\text{CO}_2$  into deep formations where it is to be stored.<sup>19–21</sup> Again, monitoring of ground gas compositions is required to ensure that there is no leakage from an underground store of captured  $\text{CO}_2$ .

In the UK, an evaluation of shale gas resources<sup>22</sup> identifies Carboniferous sequences in northern England as a priority area, and a more detailed study of the Bowland-Hodder unit is presented by the British Geological Survey.<sup>23</sup> Lower Carboniferous rocks that might be a source of shale gas extend from the Cheshire Basin north through Lancashire, and east to Yorkshire and Lincolnshire (Figure 1). Throughout this region, Carboniferous rocks occur at depth, beneath younger sedimentary rocks and superficial deposits, as well as outcropping.

This study considers locations (Figure 1) within the area of shale gas potential where gas monitoring data have been obtained before any investigation or exploitation of shale gas reserves. It provides baseline information that demonstrates the temporal variability of natural ground gas compositions for unconsolidated Quaternary sands capped by glacial till, which are below the root zone. These data represent ground gases that have accumulated in sands by migration from depth or by lateral movement, and that may be derived from artificial (such as landfill) or natural sources (such as coal-bearing rocks). Full details of the sites are provided as Supporting Information (SI).

## ■ DATA COMPILATION

**Data Sources.** Monitoring data were obtained for two landfill sites in Cheshire, UK (SI); the sites differ geologically and produce contrasting gas signatures. Site 1, a closed landfill, is situated in thick Quaternary deposits with no known

potential external (geological) source of  $\text{CH}_4$  or  $\text{CO}_2$ . Conversely, Site 2 is situated in Quaternary deposits overlying thin Permo-Triassic bedrock, with underlying Coal Measures (Carboniferous; Westphalian) which provide a potential source of geogenic gas. Additionally, Site 2 is adjacent to a second older landfill, constructed to a lower technical specification. The Control Site was chosen at a location with similar geology to Site 1, but with no associated landfill. Details of the ground conditions at each site are given in the SI.

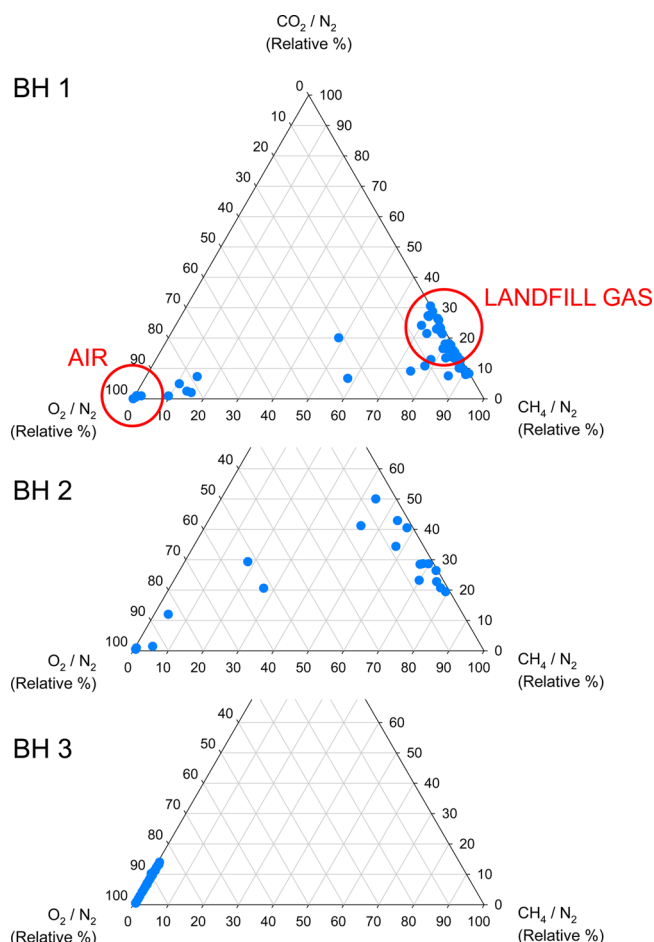
**Historic Measurement of Gas Composition.** Historically, gas composition has been measured in accordance with regulatory requirements using hand-held gas monitors, as frequently as daily (Site 2) to as infrequently as quarterly (Site 1). Measurements were made using a Geotech UK GA2000 Landfill Gas Analyzer until 2012, after which a Gas Data Ltd. GFM435 landfill gas analyzer was used. One of the limitations of changes of instrumentation over a period of several years is that data sets may not be directly comparable. Both gas monitoring instruments employ a dual beam infrared absorption method to quantify the concentration of  $\text{CH}_4$ ,  $\text{CO}_2$  and oxygen ( $\text{O}_2$ ) in a flowing gas. The balance is assumed to be nitrogen ( $\text{N}_2$ ). However, the instruments differ in their measurement of borehole flow. The GA2000 pressure transducer is equipped with a set resistor in order to minimize flow. It is argued that this will more closely reflect true borehole conditions as the act of opening the borehole valve will disrupt equilibrium conditions. Conversely, the GFM435 pressure transducer does not have this specification.

**Measurement of Gas Composition at High Temporal Resolution.** High temporal resolution data capture was achieved using a GasClam instrument, by which gas compositions can be recorded at intervals as short as 3 min.<sup>24</sup> The GasClam also records atmospheric pressure and temperature as well as gas composition, avoiding an additional limitation of hand-held gas monitors.<sup>25</sup> The instrument has, according to the manufacturer, a range 0–100% for  $\text{CH}_4$  and  $\text{CO}_2$ , with a stated detection limit of 0.1% for both gases. In practice, observed nonzero minimum concentrations for  $\text{CH}_4$  and  $\text{CO}_2$  were 0.4% and 0.1%, respectively, and observed maximum values were 57.1% and 10.8% respectively.

## ANALYSIS OF GAS MONITORING DATA

Two graphical approaches have been used to present the gas monitoring data. In the first, compositional data are compared in a ternary plot in terms of the measured  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{O}_2$  content normalised to  $\text{N}_2$  (assuming  $\text{N}_2$  to be the balance, i.e.,  $100 - \Sigma \text{CH}_4 + \text{CO}_2 + \text{O}_2$ ). This allows the relative proportions of  $\text{CH}_4$  and  $\text{CO}_2$  to be compared irrespective of any dilution by air, the  $\text{O}_2/\text{N}_2$  ratio indicating whether this has occurred and the extent to which  $\text{O}_2$  has been removed, as  $\text{N}_2$  can be regarded as non-reactive.<sup>15</sup> In a plot of this type, “end member” compositions can be identified, so that an array of observed data points can be explained as mixtures of gases from different sources, and the characteristics of one borehole can be compared with another. The second graphical approach is to show variation with time in absolute gas concentration (% v/v) measured at high frequency and how this is affected by atmospheric pressure conditions.

**Monitoring Wells Near a Landfill Where There Is No Known Input from Coal-Bearing Rocks.** Figure 2 shows the gas composition recorded over a period of 10 years at boreholes on Site 1. BH 1 is located on the southern boundary of the landfill (SI Figure S1), and produced a methane-rich gas



**Figure 2.** Gas compositions for monitoring wells on Site 1 (2003–2013), indicating (Figure 2a) expected plotting positions of landfill gas and air.

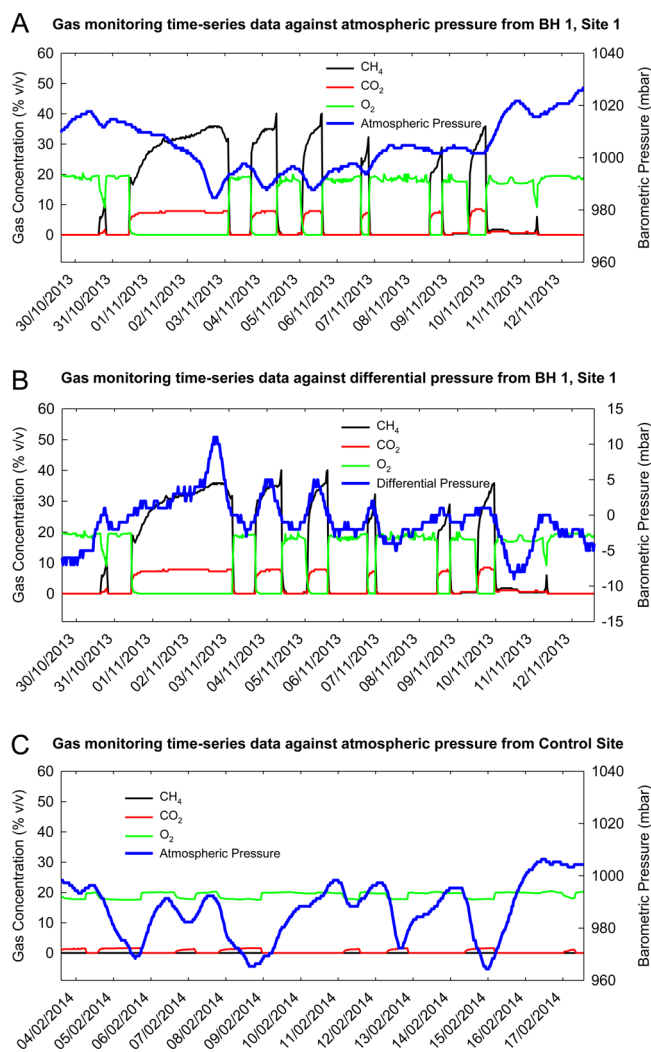
signature (70:30  $\text{CH}_4/\text{CO}_2$ ) which is attributed to landfill gas given the close proximity of the borehole to the edge of the landfill. Values recorded at 100%  $\text{O}_2/\text{N}_2$  correspond to air. There is some evidence of mixing between landfill gas and air at this location, but this was observed on few occasions (points between the two end member compositions).

BH 2 is approximately 25 m south of the landfill perimeter, and shows a more diffuse scatter of data. There is still a strong indication of the presence of landfill gas but the proportion of  $\text{CH}_4$  is lower (Figure 2), suggesting mixing with more  $\text{CO}_2$ -rich gas, or removal of  $\text{CH}_4$  by biological processes. BH 3, 100 m away from the landfill, records no landfill gas (Figure 2).

**High Frequency Monitoring.** Gas compositions were measured at Site 1, borehole BH 1, on a 30 min sampling frequency program with the instrument vent closed to ensure that borehole conditions were not disturbed during sampling. Figure 3 shows the results of sampling for a two week period starting Monday 29th October 2013.

During this period, there were three successive rises and falls in atmospheric pressure. The falls occurred on 2nd, 3rd, and 5th November, each with similar gradients. Accordingly, with each fall, corresponding peak concentrations of  $\text{CH}_4$  (up to 40%) and  $\text{CO}_2$  (up to 10%) were observed, the balance being  $\text{N}_2$ . As  $\text{CH}_4$  and  $\text{CO}_2$  appear in the borehole,  $\text{O}_2$  concentration decreases to 0% from atmospheric concentration (~20%). For the observed borehole, the change is very sensitive to





**Figure 3.** Gas monitoring time-series data collected from GasClam against atmospheric pressure and differential pressure (BH 1 Site 1), and gas monitoring time-series data against atmospheric pressure (control site).

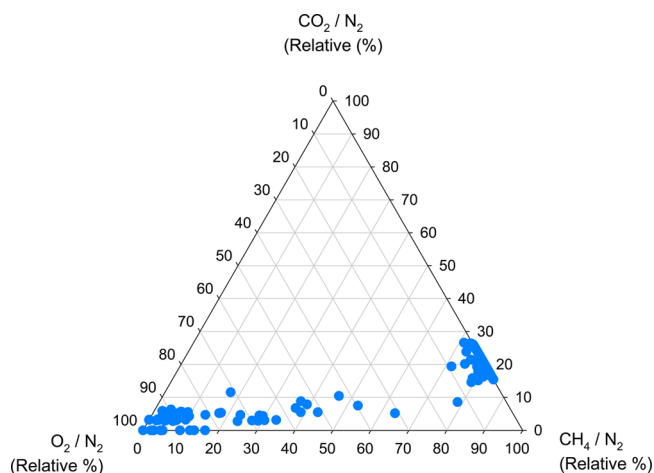
atmospheric pressure, usually occurring over 2–4 h and with as little as 3 mbar change in pressure. Concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  are lower than the expected composition of landfill gas, but have not been corrected for dilution by air or  $\text{N}_2$ .

Furthermore, when the time series data are plotted against the pressure difference between atmosphere and borehole (Figure 3), it is clear that under positive pressure difference (i.e., the borehole is “blowing”),  $\text{CH}_4$  and  $\text{CO}_2$  are elevated within the borehole. Conversely, when negative pressure difference conditions exist,  $\text{O}_2$  only (i.e., air) is measured in the borehole.

At the Control Site, gas monitoring data are not available for hand-held instruments. High frequency data were collected over a two week period, with the same instrument settings as at Site 1 (Figure 3). During the two week monitoring period, there were several winter storms (depressions) that crossed the UK, as shown by the pressure data. With each successive depression, the  $\text{CO}_2$  concentration in the Control Site borehole rose to a maximum 1.3% v/v. It is assumed that this corresponds with background  $\text{CO}_2$  that has entered the borehole from the sand formation, as a consequence of a rapid fall in atmospheric pressure. Hooker and Bannon<sup>26</sup>

observed that typical contributions to  $\text{CO}_2$  concentration from natural sources such as weathering of bedrock typically lie within the range 0–5% v/v. At a peak concentration of 1.3% v/v  $\text{CO}_2$ , the borehole  $\text{O}_2$  concentration dipped to approximately 18% v/v. No  $\text{CH}_4$  was detected. Typically, surface ground gas  $\text{CH}_4$  concentration varies between 0.2 and 1.6 ppm (mean concentration in air); with no external source of  $\text{CH}_4$ , the concentration is not expected to exceed 0.1% v/v.<sup>26</sup>

High frequency data for the two-week period from BH 1 at Site 1 are plotted (Figure 4) for comparison with monitoring



**Figure 4.** Ternary Plot of GasClam Data obtained from BH 1 Site 1 for the Period 29/10/2013–12/11/2013.

data for 10 years for the same borehole (as in Figure 2). In two weeks, a pattern of variation in gas composition is observed that covers the range of data observed during ten years of periodic monitoring. Additionally, mixing of air and landfill gas is more fully resolved, as demonstrated by the greater number of data points between the two end member compositions. Crucially, this demonstrates that occurrences of elevated emissions of  $\text{CO}_2$  and  $\text{CH}_4$  over a ten year period are much more frequent than suggested by measurement under the requirements of a normal regulatory regime.

#### Monitoring Wells Near a Landfill That Show Inputs to Ground Gases from Coal-Bearing Rocks.

At Site 2, which overlies Coal Measures, monitoring wells are located around the landfill perimeter. From hand-held monitor generated data, the  $\text{CH}_4/\text{N}_2$  ratio frequently exceeds 80%, suggesting a geogenic gas influence arising in two boreholes (BH 1 and BH 4). In BH 1, the array of data is consistent with mixing of air with predominantly geogenic  $\text{CH}_4$ , with some observations extending toward  $\text{CO}_2/\text{N}_2$  that may reflect a landfill gas component.

Boreholes BH 3 and BH 4 clearly show more variable gas compositions, with  $\text{CH}_4/\text{N}_2$  and  $\text{CO}_2/\text{N}_2$  ratios approaching 100% (Figure 5). Compared with Site 1, where gas composition was almost exclusively air or landfill gas (with some mixing in between), boreholes at Site 2 show a more complex pattern. The complication and greater mixing of gases is most likely to be due to additional sources, and the geological characteristics of the site are consistent with the presence of geogenic gas derived from the underlying Coal Measures.

Compared with the distributions that were observed at Site 1, Figure 5 clearly shows a more  $\text{CH}_4$ -rich gas composition mixed with air. A gas with such a high  $\text{CH}_4$  content is unlikely to be

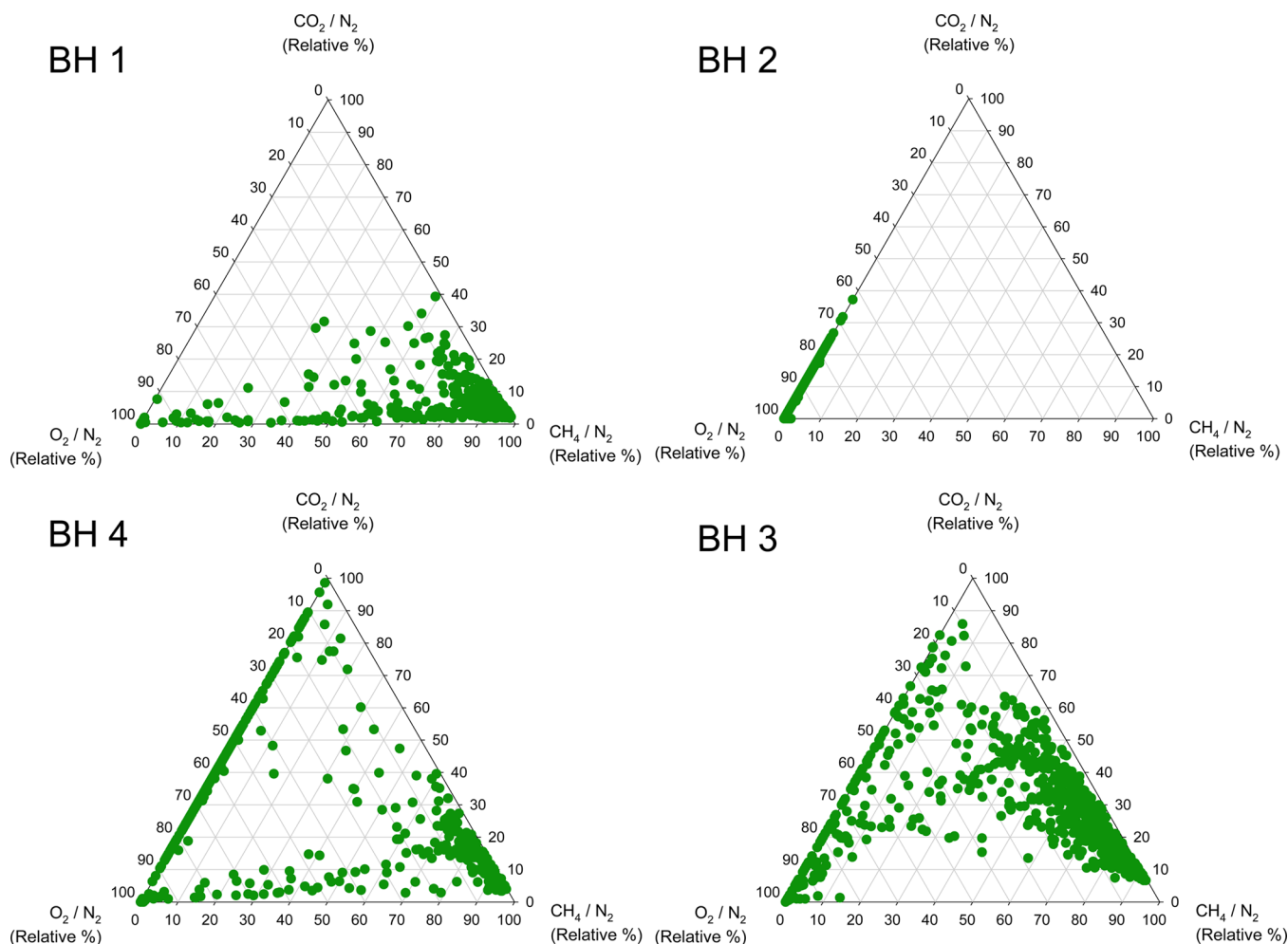


Figure 5. Gas compositions for monitoring wells at Site 2 (1998–2014).

derived from landfill (CO<sub>2</sub> is always present in landfill gas at these sites), and so is considered to originate from the underlying Coal Measures and to mix with landfill gas prior to entering the borehole. Migration and mixing of gas at the site can be achieved through sand lenses within glacial till, fissures and other voids (e.g., former boreholes). There is a population in the ternary diagram (Figure 5) for BH 3 around 60–70% CH<sub>4</sub> vs 30–40% CO<sub>2</sub> that likely indicates the presence of landfill gas in this monitoring well. BH 2 demonstrates a similar pattern to BH 3 at Site 1, dominated by air with a small concentration of diluted CO<sub>2</sub> (10–30% v/v range). Isotopic analysis of <sup>13</sup>C/<sup>12</sup>C ratios may clarify the origin of these gases.<sup>27</sup> However, routine monitoring protocols exclude routine collection of these data because of cost.

## DISCUSSION

The historical data measured using portable gas monitoring devices reveal patterns in gas composition that relate to the geology of the site and subsequent landfill activity, where appropriate. The high frequency monitoring of data allows temporal variability to be constrained, and indicates links with weather conditions. Taken together, these observations have significant implications for the understanding of ground gas emissions to the atmosphere with particular relevance for deep engineering activities that might perturb soil emissions,

including CCS and fracking, as well as for the design of monitoring programmes

**Ground Gas Emissions to the Atmosphere.** Figure 6 shows a conceptual model for the migration of gas from geological and non-geological sources through different pathways to the atmosphere at locations where glacial deposits

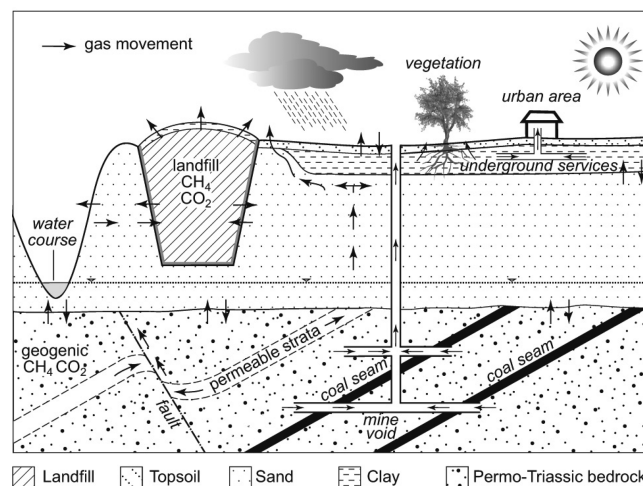


Figure 6. Conceptual model of CH<sub>4</sub> and CO<sub>2</sub> flows in the saturated and unsaturated zones.

overly coal-bearing rocks. This is a two-way process, as monitoring data clearly indicate that air enters boreholes (and other voids) in periods of high atmospheric pressure. Wherever permeable formations are exposed naturally (e.g. valley sides), air is also able to enter. Dilution of gases in a mixture by equivalent proportions occurs with the addition of one non-reactive gas component.<sup>28</sup> Thus, any CO<sub>2</sub> and CH<sub>4</sub> present are diluted by air (N<sub>2</sub> + O<sub>2</sub>) during periods of increasing atmospheric pressure.

The sources of ground gas can be distinguished from their compositions; taking a ratio to N<sub>2</sub> enables the relative proportions of CH<sub>4</sub> and CO<sub>2</sub> to be determined, allowing for dilution by air. In this study, gases derived from sands overlying coal bearing rocks are shown to be richer in CH<sub>4</sub> than those gases derived from landfill. Historical monitoring data shows evidence of mixing of ground gas and air, to extents that vary from occasion to occasion. Observations of gas compositions at a site with neither landfill nor coal-bearing sources show that the natural ground gas is air with a small proportion of CO<sub>2</sub>, and CH<sub>4</sub> below detection.

In Figure 6, CH<sub>4</sub> and CO<sub>2</sub> migration may be by either advective flow or diffusion, depending on the porosity and permeability characteristics of the subsoil. The relative importance of each is not considered here, although it is evident from borehole behavior that advective flow is important in the geological materials that they penetrate.

Faults and permeable strata in the bedrock act as natural conduits for gas flow in the subsurface. Similarly, mine shafts and other voids provide man-made channels for gas to flow to the surface. In the instance of abandoned mine shafts, the height of the water table becomes an important factor in gas movement. As groundwater recharges and fills the mine void, a piston effect is achieved that drives the gas toward the surface. However, as CO<sub>2</sub> is 58 times more soluble in water at standard temperature and pressure (STP) than CH<sub>4</sub>,<sup>26</sup> a proportion of this gas may be dissolved and so removed from the system.

Examining the high temporal resolution data, it becomes clear that in addition to the potential pathways that are available to CH<sub>4</sub> and CO<sub>2</sub> in the unsaturated zone, atmospheric pressure is a key controller of gas movement. As air pressure falls, gas is released from the unsaturated zone. With increasing atmospheric pressure, air is forced into the ground, thereby producing a diluting effect on the concentration of CH<sub>4</sub> and CO<sub>2</sub>. As was seen from the monitoring data, under a negative air pressure gradient, pressure in a borehole builds up and creates a positive borehole flow. In other words, the pressure in the borehole is greater than the atmosphere, giving a focused induced flow of gas from the ground to the atmosphere.

**Wider Implications: Design of Monitoring Programmes.** The data collected from continuous monitoring show considerable variation with time, and are consistent with the CH<sub>4</sub> and CO<sub>2</sub> data collected by hand-held meters. Using these, measurements are made at specific times/dates. If the periodicity of the sampling points is superimposed on the high frequency data series, gas composition is measured as a snapshot view of a highly variable system, and measured concentrations will vary considerably (as shown in Figures 2 and 3 in particular).

From a regulatory perspective, high temporal resolution allows a clearer understanding of the processes that are occurring in the near-surface ground gas regime. As has been noted, air pressure and depth of water table are key factors. Current UK practice is to take point measurements from all

monitoring wells on a site for a minimum investigation period of 6 weeks. It is required that at least one of the point measurements needs to be taken during falling atmospheric pressure.

The data presented here show high temporal variability. The periodicity of the cycling of gases can be as short as a few hours to as long as a few days. Under current regulatory practice, two point measurements would have been made during the selected two week period shown in Figure 3. For 70% of that monitoring period, only air (N<sub>2</sub> + O<sub>2</sub>) was present in the test borehole. Thus, there is a high likelihood of missing an emission event. To be certain of the ground gas regime for a site where CH<sub>4</sub> and CO<sub>2</sub> are likely to pose a hazard, a high temporal resolution data set may be required. Furthermore, a longer statutory monitoring period could be necessary to identify any longer-term seasonal variations in the ground gas regime.

#### **Wider Implications: CCS and Hydraulic Fracturing.**

The monitoring data reported here demonstrate the complex behavior of gases within the vadose zone, emphasizing the highly variable nature with time of exchanges of CO<sub>2</sub> and CH<sub>4</sub> between the soil and the atmosphere. Great care needs to be taken in the interpretation of ground gas data to distinguish variation arising from meteorological controls from those arising from changes in geogenic or anthropogenic inputs, which need to be recognized in any attempt to attribute an artificial cause for an emission. It is essential that the time period for monitoring is sufficient to capture meteorological events such as a rapid reduction in atmospheric pressure, and that the frequency of sampling is small enough to determine changes arising from these. Furthermore, other practices of continuous ground gas monitoring in relation to CCS have been discussed by Schlömer et al.<sup>29</sup> and Schlömer et al.<sup>30</sup> and outline the importance of establishing baseline conditions in the vadose zone before and during operations to determine any leakages of CO<sub>2</sub> from geologic formations.

It is clear that from the development of a conceptual model of the ground gas regime, the principles that are applied to landfill sites are equally applicable to gas emissions from other subsurface activities including CCS and hydraulic fracturing. It is possible that leakages occur along undetected faults and fractures coupled with changes in atmospheric pressure. Without rigorous monitoring, there is potential for low intensity leakages to go undetected for prolonged periods of time.<sup>31</sup> For example, Klusman<sup>32</sup> estimated that approximately 170 tons of CO<sub>2</sub> was lost per annum through leakage from deep storage to the atmosphere at an enhanced oil recovery/CO<sub>2</sub> sequestration site at Rangely, CO. In order to establish baseline levels of CO<sub>2</sub>, monitoring programmes are required, before injection (with respect to CCS) and continuing through operations for safety, public acceptance and model calibration.<sup>33</sup>

Importantly, the data presented in this paper demonstrate that ground gas compositions vary greatly with time. Conventional monitoring protocols are likely to fail to detect some emission events, and so it is important that high frequency measurements are made as part of a monitoring regime that is underpinned by a sound conceptual model of the geological characteristics of the location of interest.



## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Email: [c.j.teasdale1@newcastle.ac.uk](mailto:c.j.teasdale1@newcastle.ac.uk)

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank EPSRC for financial support in the form of a DTA studentship to CJT.

## ■ REFERENCES

- (1) IPCC. *IPCC Fourth Assessment Report: Climate Change 2007 (AR4)*; Cambridge, United Kingdom, 2007; p 996.
- (2) Hansen, J.; Sato, M. Greenhouse gas growth rates. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101* (46), 16109–16114.
- (3) Hansen, J.; Johnson, D.; Lacis, A.; Lebedeff, S.; Lee, P.; Rind, D.; Russell, G. Climate impact of increasing atmospheric carbon dioxide. *Science* **1981**, *213* (4511), 957–966.
- (4) Nosalewicz, M.; Brzezinska, M.; Pasztelan, M.; Sypryn, G. Methane in the environment: A review. *Acta Agrophys.* **2011**, *18* (2), 355–373.
- (5) Hofmann, D. J.; Butler, J. H.; Tans, P. P. A new look at atmospheric carbon dioxide. *Atmos. Environ.* **2009**, *43* (12), 2084–2086.
- (6) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon dioxide capture: Prospects for new materials. *Angew. Chem., Int. Ed.* **2010**, *49* (35), 6058–6082.
- (7) Abu-Khader, M. M. Recent progress in CO<sub>2</sub> capture/sequestration: A review. *Energy Sources, Part A* **2006**, *28* (14), 1261–1279.
- (8) Wilson, E. J.; Johnson, T. L.; Keith, D. W. Regulating the ultimate sink: Managing the risks of geologic CO<sub>2</sub> storage. *Environ. Sci. Technol.* **2003**, *37* (16), 3476–3483.
- (9) White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. Separation and capture of CO<sub>2</sub> from large stationary sources and sequestration in geological formations—Coalbeds and deep saline aquifers. *J. Air Waste Manage. Assoc.* **2003**, *53* (6), 645–715.
- (10) Howarth, R. W.; Santoro, R.; Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim. Change* **2011**, *106* (4), 679–690.
- (11) Howarth, R. W.; Santoro, R.; Ingraffea, A. Venting and leaking of methane from shale gas development: Response to Cathles et al. *Clim. Change* **2012**, *113* (2), 537–549.
- (12) Maier, M.; Schack-Kirchner, H. Using the Gradient method to determine soil gas flux: A review. *Agric. For. Meteorol.* **2014**, *192*, 78–95.
- (13) Hirano, T.; Kim, H.; Tanaka, Y., Long-term half-hourly measurement of soil CO<sub>2</sub> concentration and soil respiration in a temperate deciduous forest. *J. Geophys. Res.: Atmos.* **2003**, *108* (D20).
- (14) Yavitt, J. B.; Fahey, T. J.; Simmons, J. A. Methane and carbon dioxide dynamics in a northern hardwood ecosystem. *Soil Sci. Soc. Am. J.* **1995**, *59* (3), 796–804.
- (15) Bergamaschi, P.; Harris, G. W. Measurements of stable isotope ratios (<sup>13</sup>CH<sub>4</sub>/<sup>12</sup>CH<sub>4</sub>; <sup>12</sup>CH<sub>3</sub>D/<sup>12</sup>CH<sub>4</sub>) in landfill methane using a tunable diode laser absorption spectrometer. *Glob. Biogeochem. Cycle* **1995**, *9* (4), 439–447.
- (16) McGlade, C.; Speirs, J.; Sorrell, S. Unconventional gas—A review of regional and global resource estimates. *Energy* **2013**, *55*, 571–584.
- (17) Davies, R. J. Methane contamination of drinking water caused by hydraulic fracturing remains unproven. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108* (43), E871–E871.
- (18) Davies, R. J.; Mathias, S. A.; Moss, J.; Hustoft, S.; Newport, L. Hydraulic fractures: How far can they go? *Mar. Pet. Geol.* **2012**, *37* (1), 1–6.
- (19) Bachu, S. Screening and ranking of sedimentary basins for sequestration of CO<sub>2</sub> in geological media in response to climate change. *Environ. Geol.* **2003**, *44* (3), 277–289.
- (20) Bachu, S.; Bonijoly, D.; Bradshaw, J.; Burruss, R.; Holloway, S.; Christensen, N. P.; Mathiassen, O. M. CO<sub>2</sub> storage capacity estimation: Methodology and gaps. *Int. J. Greenhouse Gas Control* **2007**, *1* (4), 430–443.
- (21) Eccles, J. K.; Pratson, L.; Newell, R. G.; Jackson, R. B. The impact of geologic variability on capacity and cost estimates for storing CO<sub>2</sub> in deep-saline aquifers. *Energy Econ.* **2012**, *34* (5), 1569–1579.
- (22) Department of Energy and Climate Change. The Unconventional Hydrocarbon Resources of Britain's Onshore Basins—Shale Gas. [https://www.og.decc.gov.uk/UKpromote/onshore\\_paper/UK\\_onshore\\_shalegas.pdf](https://www.og.decc.gov.uk/UKpromote/onshore_paper/UK_onshore_shalegas.pdf) (accessed October 2013).
- (23) Andrews, I. J. *The Carboniferous Bowland Shale Gas Study: Geology and Resource Estimation*; British Geological Survey for the Department of Energy and Climate Change: London, UK, 2013.
- (24) IonScience GasClam. Continuous Ground Gas Monitor. [www.ionscience.com/products/gasclam-portable-gas-monitor](http://www.ionscience.com/products/gasclam-portable-gas-monitor) (accessed 01 March 2012).
- (25) Morris, P.; Todman, M.; Boulton, S. *Improved Ground-Gas Risk Prediction Using In-Borehole Gas Monitoring*; Helmholtz Centre Environmental Research-Ufz: Leipzig, 2008; p 36–44.
- (26) Hooker, P. J.; Bannon, P. *Methane: Its Occurrence and Hazards in Construction*; Construction Industry Research & Information Association (CIRIA); London, UK, 1993; p 137.
- (27) Widory, D.; Proust, E.; Bellenfant, G.; Bour, O. Assessing methane oxidation under landfill covers and its contribution to the above atmospheric CO<sub>2</sub> levels: The added value of the isotope (δ<sup>13</sup>C and δ<sup>18</sup>O CO<sub>2</sub>; δ<sup>13</sup>C and δD CH<sub>4</sub>) approach. *Waste Manage.* **2012**, *32* (9), 1685–1692.
- (28) Romanak, K. D.; Bennett, P. C.; Yang, C. B.; Hovorka, S. D. Process-based approach to CO<sub>2</sub> leakage detection by vadose zone gas monitoring at geologic CO<sub>2</sub> storage sites. *Geophys. Res. Lett.* **2012**, *39*, 6.
- (29) Schlömer, S.; Furche, M.; Dumke, I.; Poggenburg, J.; Bahr, A.; Seeger, C.; Vidal, A.; Faber, E. A review of continuous soil gas monitoring related to CCS—Technical advances and lessons learned. *Appl. Geochem.* **2013**, *30*, 148–160.
- (30) Schlömer, S.; Müller, I.; Furche, M. Baseline soil gas measurements as part of a monitoring concept above a projected CO<sub>2</sub> injection formation: A case study from Northern Germany. *Int. J. Greenhouse Gas Control* **2014**, *20*, 57–72.
- (31) Harvey, O. R.; Qafoku, N. P.; Cantrell, K. J.; Lee, G.; Amonette, J. E.; Brown, C. F. Geochemical implications of gas leakage associated with geologic CO<sub>2</sub> storage—A qualitative review. *Environ. Sci. Technol.* **2013**, *47* (1), 23–36.
- (32) Klusman, R. W. Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. *Appl. Geochem.* **2003**, *18* (12), 1825–1838.
- (33) Korre, A.; Imrie, C. E.; May, F.; Beaubien, S. E.; Vandermeijer, V.; Persoglia, S.; Golmen, L.; Fabriol, H.; Dixon, T. Quantification techniques for potential CO<sub>2</sub> leakage from geological storage sites. In *10th International Conference on Greenhouse Gas Control Technologies*, 2011; Vol. 4, pp 3413–3420.