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## Detection and understanding of natural CO<sub>2</sub> releases in KwaZulu-Natal, South Africa.

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### Abstract

Natural carbon dioxide (CO<sub>2</sub>) emanates from a number of sites along a N-S trend that coincides with a mapped fault near the village of Bongwana in KwaZulu-Natal, South Africa. In addition to the natural CO<sub>2</sub> seeps a groundwater well drilled on a farm in Bongwana encountered CO<sub>2</sub> and now leaks. Thus the Bongwana sites provide excellent analogues for failed CO<sub>2</sub> storage under the two primary leakage scenarios; 1) abrupt leakage through injection well failure or leakage up an abandoned well, and 2) gradual leakage, through undetected faults, fractures or wells. Here we present results from preliminary fieldwork undertaken in September 2015.

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**Keywords:** Natural CO<sub>2</sub> releases; Monitoring; Leakage; Geological CO<sub>2</sub> storage; Water quality

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## 1. Introduction

The safe and secure geological storage of CO<sub>2</sub> requires that monitoring technologies are deployed to establish existing baseline conditions and to be able to detect any potential leakage from the reservoir. Since each geological setting is unique, it is important to both test whether such monitoring technologies are suitable for leakage detection and also to understand any potential leakage pathway and their receptors so that appropriate monitoring programs can be implemented. The two leakage scenarios defined for CO<sub>2</sub> storage are: '(1) abrupt leakage, through injection well failure or leakage up an abandoned well, and (2) gradual leakage, through undetected faults, fractures or wells' [1]. At the Bongwana sites studied in KwaZulu-Natal Province, South Africa, diffuse CO<sub>2</sub> gas releases are present along a fault as well as discrete large fluxes from an abandoned well. Hence the sites provide an excellent opportunity for detecting CO<sub>2</sub> in an analogue for a failed CO<sub>2</sub> storage site under both leakage scenarios. This is of great importance since South Africa is currently investigating the potential of carbon capture and storage (CCS). Here, we present results from a field campaign conducted in late September 2015 to begin to ascertain the nature and magnitude of the CO<sub>2</sub> releases and discuss the implications for public acceptance of CO<sub>2</sub> storage.

## 2. Study Site

Natural CO<sub>2</sub> releases are present near the village of Bongwana in the KwaZulu-Natal Province, South Africa. The CO<sub>2</sub> release was first described in the early 20th century [2,3] and a commercial CO<sub>2</sub> bottling plant was established. Subsequently, additional sites of CO<sub>2</sub> release were identified along a N-S trend away from Bongwana that coincides with a mapped fault (Ntlakwe-Bongwan), including significant travertine deposition at Umtamvuna [3] and reported springs in the river at Manzimhlanga [2,3]. The Bongwana natural CO<sub>2</sub> releases thus appear to be controlled by an ~80km long N-S fault where CO<sub>2</sub> release occurs in distinct regions rather than along the whole trace of the fault (Figure 1). In addition a groundwater well drilled on the Baker farm near the trace of the fault encountered CO<sub>2</sub> at depth and following a vigorous release was subsequently plugged and abandoned. Fieldwork was conducted at three sites: 1) Baker Farm, 2) Umtamvuna, and 3) Manzimhlanga (Figure 1). At all the study sites, Dwyka Group tillite forms the surface lithology. The tillite is yellow-brown, soft and friable when weathered, but occurs as blue-grey, competent rock when fresh. At depth, the Dwyka Group is unconformably underlain by sandstones and subordinate shales of the Msikaba Formation and possibly Natal Group [4], which are further underlain by the basement granite and gneiss complex of the ~1200Ma Natal Metamorphic Province [5].

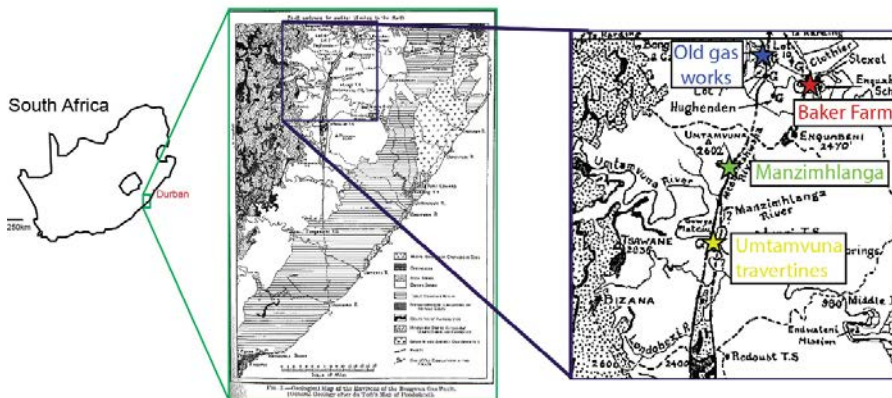


Figure. 1. Location map of the three fieldwork sites (Baker Farm, Umtamvuna travertines, Manzimhlanga). Map from Gevers [3]. Also shown is the location of the commercial bottling plant 'old gas works'.

## 2.1 Baker Farm

The Baker Farm in the village of Bongwana lies approximately 4km ESE of the old commercial bottling plant (Figure 1) and off the trend of the main fault. However, a splay of the fault mapped by Du Toit [6] is present at this location. Here a groundwater well drilled by the owner encountered CO<sub>2</sub> at approximately 60m depth. The well was plugged and abandoned by the owners shortly after drilling. Another groundwater well is in use on the property approximately 180m west of the abandoned well and has not encountered any CO<sub>2</sub>.

At Baker Farm a soil gas survey over a grid of 500 x 100m was conducted recording both gas content and flux. The soil gas survey was conducted once with the CO<sub>2</sub>-rich well un-plugged and once plugged. Water and gas (where present) samples were taken from the two wells and gas samples taken from the soil gas for subsequent analysis. Due to the agricultural nature and lack of outcrop no geological mapping was permitted.

## 2.2 Umtamvuna Travertines

The travertine cones and CO<sub>2</sub> springs along the Umtamvuna River on the border between KwaZulu-Natal and the Eastern Cape Provinces are well documented [3]. The springs occur ~14km SSW of Bongwana (Figure 1). The CO<sub>2</sub> spring site is underlain by Dwyka Group tillite on the northern tip of a large graben system where the Ntlakwe-Bongwan fault diverges into two splays with a downthrown central zone. The site is the southernmost of the known CO<sub>2</sub> emissions along the fault system, with four cones developed atop large mounds of travertine ~50-100m in diameter on either side of the river. The cones on the northern bank are by far the largest (~15m diameter), but the smaller cones on the southern bank are the most active. Both southern cones issue CO<sub>2</sub> gas and water, with the larger being steep-sided ~1m in diameter and 80cm high

At Umtamvuna a soil gas survey was undertaken following a transect line across the fault on the alluvial terrace of the northern bank of the river. Geochemical sampling of water and gases was conducted at each of the active travertine cones and in the river both up- and downstream of the inferred fault trace. Geological mapping and structural analyses of the structures present was also performed.

## 2.3 Manzimhlanga

A small CO<sub>2</sub> occurrence is mentioned [2,3] along the Manzimhlanga River ~8km south of Bongwana, however in each case no work was undertaken on this site as Young [2] never visited the site, and Gevers [3] writes that "At the time of the writers visits to the area in 1939 and 1940, no gas bubbles were to be seen here". In the field visit of 2015 slow and intermittent small streams of CO<sub>2</sub> bubbles were observed in the river at the base of the valley.

A soil gas survey was performed on the hillslope above the gas release and across the inferred fault trace. Water and gas samples for geochemical analyses were taken from the river directly in the CO<sub>2</sub> stream and both up- and downstream of the release. Geological mapping and structural analysis of the exposed fault zone was performed.

## 3. Methods

### 3.1 Structural analyses

Structural measurements of faults and fractures were collected digitally in the field. An iPad Air 2 was used for collection of the data. The iPad app utilises the magnetometer, gyroscope and accelerometer within the iPad's hardware for use as a compass clinometer, allowing measurements of fracture orientation and dip to be made and recorded directly on the iPad. Field maps pre-loaded onto the iPad, and open source aerial imagery were used to aid in the location of data which was augmented by GPS and GLONASS tracking with a Garmin GLO. The iPad app used allows the user to define locations, make field notes, and record located and oriented digital photographs through access to the iPad's digital camera

### 3.2 Geochemical analyses

Water samples for water quality analyses were taken at the three sites following the sampling recommendations by Weaver et al [7]. Field measurements were undertaken using an IN-SITU Aqua Troll 400 instrument to measure pH, temperature, electrical conductivity (EC) and dissolved oxygen (DO). The water quality samples were analysed at the Council for Geoscience (CGS) water laboratory for alkalinity, cation and trace element analyses by ICP-MS and a discrete analyser was used to measure anion concentrations. Sampling was undertaken using the following methods: For cation and trace elements analysis using ICP-MS a 100 ml plastic bottle was used. The sample bottle was rinsed three times with filtered (0.45  $\mu\text{m}$ ) sample water and then the aliquot is collected also filtered and acidified to  $\text{pH} < 2$  using  $\text{HNO}_3$ . For the anion analysis using the discrete analyser, 100 ml plastic bottles were used. The sample bottle was rinsed three times with filtered (0.45  $\mu\text{m}$ ) sample water and then the aliquot is collected also filtered but not acidified. For alkalinity, a 100 ml plastic bottle was used and the sample bottle was rinsed three times with the unfiltered sample water and an aliquot was then collected. Where gas emerges through water sampling of the  $\text{CO}_2$  was performed by connecting a funnel via hosing to 1L tedlar (septum) bags. In dry seeps (as at Baker Farm)  $\text{CO}_2$  was pumped from the soil probe direct to the tedlar bag using the BGS GA2000. In both cases tedlar bags were filled and emptied twice retaining a third sample to ensure no atmospheric contamination.

### 3.3 Soil Gas and content

Soil gas measurements were made using 8 mm diameter (4 mm internal diameter) stainless-steel tubes as probes. The probes are pounded into the soil via two solid steel cylinders welded to the tubes, which act as pounding surfaces. The probes are inserted, and removed, by hammering the probes into the soil to a depth of 85-90 cm. A tip fitted to the bottom of the probe prevents blockages during insertion. A Geotechnical Instruments GA2000 portable gas analyser was used to make in situ soil gas measurements of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , and  $\text{O}_2$  concentrations. Gas flux measurements of  $\text{CO}_2$  were taken using a West Systems portable flux meter with a LICOR LI-820 IR detector connected via Bluetooth to a PDA with built-in GPS. Soil gas flux measurements took 1–3 min to acquire depending on the flux rate, and flux was measured before soil gas to minimise disturbance of the flux. Calibration of the analytical equipment was completed before and after the fieldwork using certified calibration gases.

## 4. Results and Discussion

### 4.1 Baker Farm

Soil gas survey results indicated high  $\text{CO}_2$  values in soil gas concentrations (50%) which were confined to a narrow ~30m wide, north-trending zone at the farm. When the results are overlain on the geological map produced by Du Toit [6], the values correlate with a small fault system defined on the map by silicified breccia. Due to recent agriculture however the fault is now blind and cannot be identified at surface.  $\text{CO}_2$  values diminish rapidly away from the fault returning to background  $\text{CO}_2$  values. Repeat sampling with the  $\text{CO}_2$ -rich well closed to atmosphere (plugged) showed a variation in soil concentrations with values along the fault line increasing to 80%  $\text{CO}_2$  in two samples. Little variation was noted away from the fault zone with background values being obtained at similar points to the unplugged survey. At the  $\text{CO}_2$ -rich well itself  $\text{CO}_2$  concentration rose to >99% and estimated fluxes from the well alone almost matched the total emissions from the surrounding 36,250 $\text{m}^2$  surveyed area.

The geochemical field measurements of the two wells did show a noticeable difference, with the  $\text{CO}_2$ -rich well having a slightly lower pH and higher EC compared to the  $\text{CO}_2$ -absent well. The DO concentrations also showed a significant difference with the  $\text{CO}_2$ -absent well measuring an average of 2.5 mg/l compared to the 0.7 mg/l measured in the  $\text{CO}_2$ -rich well but the alkalinity concentration show the opposite with the  $\text{CO}_2$ -rich well almost double compared to the  $\text{CO}_2$ -absent well. All three water samples give a Na-Cl character when plotted on the Piper Diagram (Figure 2) however the  $\text{CO}_2$ -rich well has significantly higher  $\text{SO}_4^{2-}$  concentrations (almost 20-fold). In addition, the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$   $\text{HCO}_3^-$  and Fe concentrations are almost double that of the  $\text{CO}_2$ -absent well, which accounts for the higher EC measured. The water quality of all the Baker farm samples, except the Na and Fe of the  $\text{CO}_2$ -rich well, passed the

South African drinking water standards (SANS 241-2011) but since the CO<sub>2</sub>-well is not used for water supply purposes it does not pose a threat to users. Carbon isotope values of the CO<sub>2</sub> and oxygen to CO<sub>2</sub> gas ratios indicate an abiogenic source of the CO<sub>2</sub>.

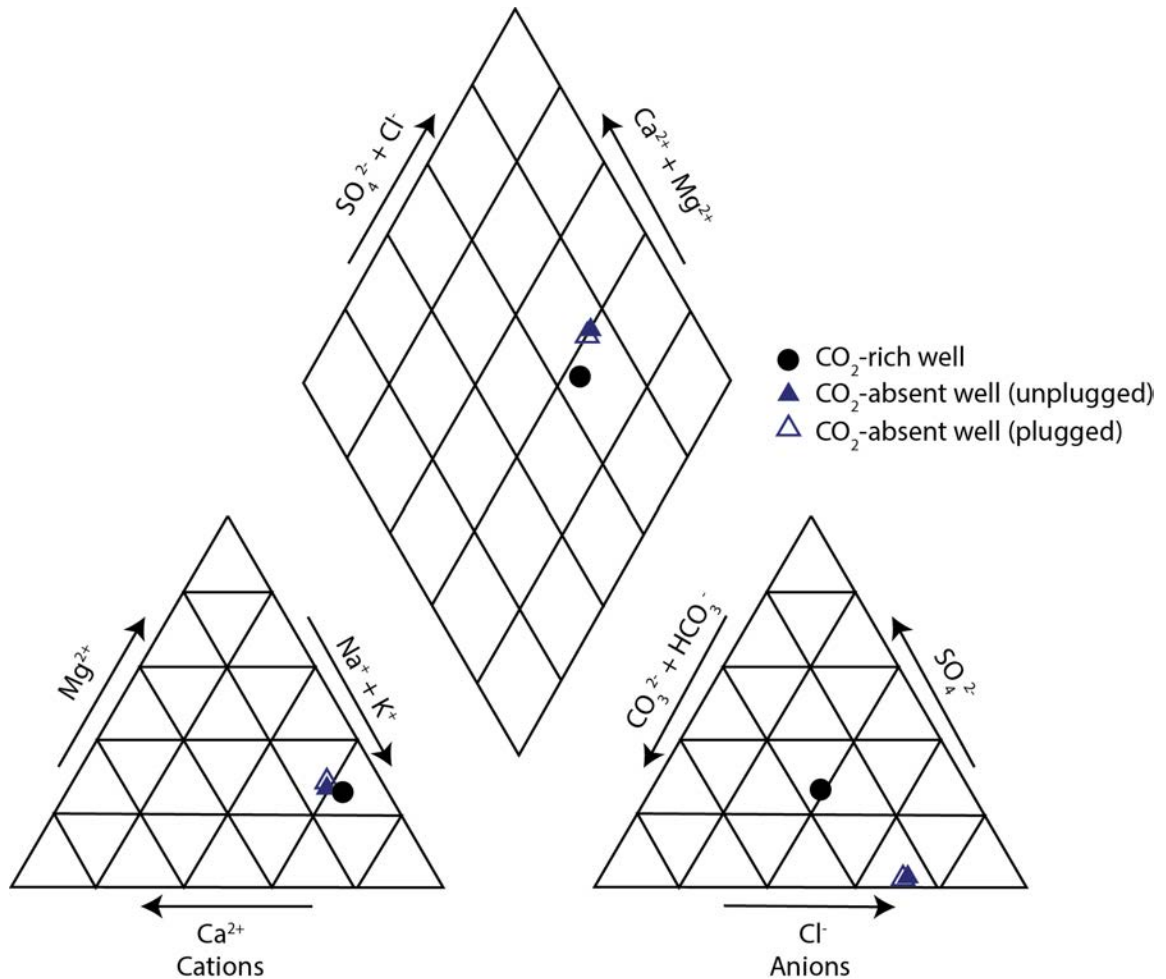


Figure 2. Piper diagram of the CO<sub>2</sub>-rich well and CO<sub>2</sub>-absent well (plugged and unplugged) on the Baker farm showing significant differences in the anion concentrations even though all three plot as Na-Cl water type.

#### 4.2 Umtamvuna

Soil gas surveys defined a sharp spike in CO<sub>2</sub> concentrations and flux in the soil across the fault trace [8], with concentrations attaining a maximum of 28% CO<sub>2</sub>. The CO<sub>2</sub>-rich waters sampled from the travertine cones and spring had significantly higher values of EC and alkalinity values compared to the river samples and the Baker Farm wells and also followed the trend of lower values of both DO and pH than the CO<sub>2</sub>-absent sites (Figure 3). Unfortunately, the Na concentrations in the sampled CO<sub>2</sub>-rich sites (i.e. the three travertines and spring) were found to be too high for the CGS' ICP-MS detection limits and the water quality results cannot be discussed further. Structural analysis of the site is described in Bond et al [8]. Here fractured and brecciated fault rock is apparent with the major trend of fracturation in a N-S direction.

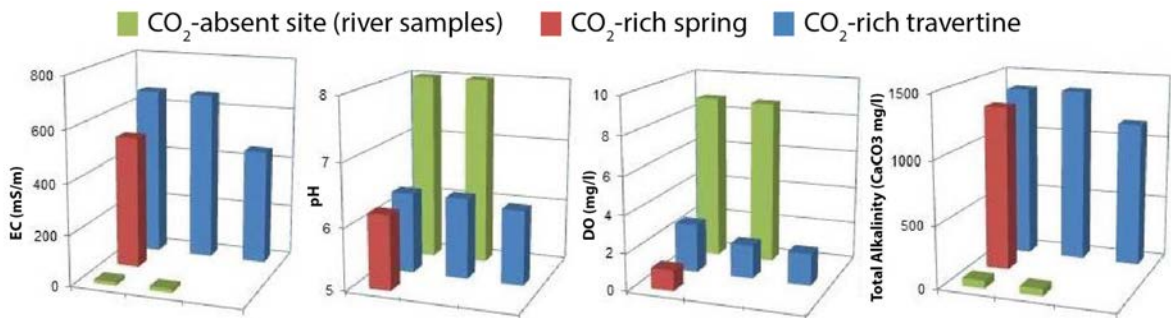


Figure 3. Variations in the water quality between the CO<sub>2</sub>-rich sites (i.e. travertines and spring) compared to the CO<sub>2</sub>-absent samples of the river (up- and down-gradient) at Umtamvuna.

#### 4.3 Manzihlanga

A soil gas sampling traverse was undertaken on the hillslope above the gas release identified in the river. Although CO<sub>2</sub> gas was identified in the river course, there appeared to be little to no variation in the soil gas concentrations in the region, suggesting that CO<sub>2</sub> gas flux was minimal along this portion of the fault system. Water samples in the river also showed little variation in geochemical parameters (i.e. pH, EC, DO, Alkalinity, cation/anion concentrations) irrespective of being up- or downstream of the CO<sub>2</sub> release. This is expected since the seepage is too small and any changes to water quality would be immediately diluted by the stream. As with Umtamvuna structural analysis of this site is described extensively in Bond et al [8]. To summarise, the fault core is exposed and here the tillite is highly silicified, brecciated with prominent fault parallel fractures sets evident.

#### 4.4 Impacts on public acceptance

Successful deployment of CCS as a climate change mitigation tool relies heavily on engaging a range of stakeholders with different perspectives. Not least of these is public perception of CCS that for local communities largely centres on the safety of CO<sub>2</sub> storage. Indeed public perception has been described as critical to the deployment of CCS [9] and examples exist of local communities successfully halting the deployment of storage sites e.g. Barendrecht, NL [10]. Benson and Cole [9] outline four key questions that are asked by all stakeholders:

1. Will geological reservoirs leak?
2. If leakage occurs what are the health, safety and environmental risks?
3. Can leakage be predicted, detected and quantified?
4. What can be done to stop or slow a leak, should it occur, and how much would it cost?

The work to-date at the Bongwana sites cannot answer all of these questions but provide the opportunity to address questions 2 and 3 in particular with detailed assessment of the mechanisms of natural CO<sub>2</sub> releases. Detection of leaking CO<sub>2</sub> at the Bongwana sites has been demonstrated. Impacts are found in soil gas concentrations and flux and on chemical parameters (e.g. pH, EC, alkalinity) in waters sampled in CO<sub>2</sub>-rich sites. Structural mapping shows a strong correlation between the leakage sites and the Ntlakwe-Bongwan fault with a fracture controlled permeable pathway for the CO<sub>2</sub> leakage. Significantly higher fluxes were found at the well than in the soil gas surveys and attribution of the source of CO<sub>2</sub> is demonstrated through soil gas ratios and isotope values. All of these results go some way to answering the questions of impacts to the environment and whether CO<sub>2</sub> can be detected, quantified and predicted. However much more work would be required to definitively answer all the questions that may be asked by stakeholders.

## 5. Conclusion

Results from all three sites indicate that relatively pure CO<sub>2</sub> gas is emanating from the releases and gas compositions and stable isotope results indicate a largely abiogenic source of the CO<sub>2</sub>. Both diffuse and abrupt leakage is detected and quantified at the combination of sites described. Fluxes are highest at the CO<sub>2</sub>-rich well and nearest to the trace of the fault with flux dropping away to minor amounts within 10s of meters of the fault. Significant differences in water chemistry (pH, EC, alkalinity, anion concentrations) are apparent between the CO<sub>2</sub>-rich and CO<sub>2</sub>-poor sites. Structural analyses and the delineation of the CO<sub>2</sub> release by the soil gas surveys indicate that the main control on natural migration (i.e. other than well drilling) is fracture permeability along zones parallel to the trend of the N-S main Ntlatkwe-Bongwana fault.

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