USE OF ISOTOPIC ANALYSIS TO DISTINGUISH BETWEEN BIOLOGICAL AND GEOTHERMAL SOIL CO_2 FLUX AT TAUHARA AND TE MIHI GEOTHERMAL AREAS

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ABSTRACT

Soil CO_2 flux measurements allow the identification of faults and near surface heat flow in geothermal areas. As CO_2 is the major component of typical geothermal gases, and is readily detectable, it is the most appropriate component to focus on. However, a current limitation of the CO_2 flux technique is the overlap between the magnitude of biological and geothermal CO_2 flux in survey areas; this overlap makes the two sources difficult to distinguish and can give ambiguous survey results. This study demonstrates the use of a laser-based optical absorption technique (Cavity Ring-Down Spectroscopy, Picarro G2132) to determine the stable carbon isotope composition of gas samples collected from the accumulation chamber of a portable soil diffuse CO_2 flux meter (West Systems, Italy). Isotope samples were collected from the accumulation chamber during normal CO_2 flux surveying at the Tauhara and Te Mihi geothermal areas, Taupo. This allowed both the magnitude of CO_2 flux, and the relative proportions of biological and geothermal CO_2 present to be determined. This combination of measurements provides a powerful approach to distinguish geothermal from biological CO_2 flux where the magnitude of CO_2 flux alone is ambiguous.

1. INTRODUCTION

1.1. Soil diffuse CO_2 flux and geothermal exploration

Soil gas flux measurements allow the identification of faults and near surface heat flow, assuming that those faults allow greater fluid flow than elsewhere. As CO_2 is the major component of typical geothermal gases, and is readily detectable, it is the most appropriate component to focus on.

In any survey of CO_2 flux a key task is the identification of the biological component in the CO_2 flux measurements, so this ñbackgroundò can be accounted for (or quantified).

1.2 Approaches to identify the biological background component

A review of volcanology and geothermal publications shows that three approaches are commonly used to identify and quantify background flux (Harvey et al., 2014). These approaches include: (i) the graphical statistical approach (GSA) that partitions separate log-normally distributed populations using cumulative probability plots (Chiodini et al., 1998; Fridriksson et al., 2006), (ii) taking a background control set of measurements at some distance from areas of visible surface thermal activity, where no magmatic CO_2 flux is expected (Chiodini et al., 2007; Viveiros et al., 2010), and (iii) evaluation of background on the basis of the carbon (^{13}C) isotopic signature (Viveiros et al., 2010; Rissmann et al.,2012).

This study investigates the use of a laser-based optical absorption technique (Cavity Ring-Down Spectroscopy, Picarro G2132) to determine the carbon ($^{13}CO_2$) isotopic signature of gas samples collected from the accumulation chamber of a portable soil diffuse CO_2 flux meter (West Systems, Italy). Isotope samples were collected from the accumulation chamber during normal CO_2 flux surveying at the Tauhara and Te Mihi geothermal areas, and at Kinloch (non-geothermal control area) near Taupo.

The aim of the study is to determine if geothermally sourced CO_2 flux can be distinguished from biological sourced CO_2 flux where the magnitude of CO_2 flux alone is ambiguous.

2. METHODS

2.1 Field methods

Soil CO_2 flux measurements were made using a calibrated West Systems portable soil gas flux meter (accumulation chamber method). The accumulation method calculates CO_2 flux by placing a 200 mm diameter accumulation chamber on the soil surface and pressing it into the soil to obtain a seal. Gases flowing into the chamber are pumped to an infrared gas analyser and the increase in CO_2 concentration inside the chamber over time is recorded by the instrument. The rate of concentration increase is proportional to flux.

Samples for $^{13}CO_2$ isotope analysis were collected from the accumulation chamber during flux measurement using a syringe; the syringe accesses the accumulation chamber via a septum on top of the chamber. The contents of the syringe were then then introduced into 0.5 L Tedlar bags. Soil CO_2 samples were withdrawn from the accumulation chamber after 2 to 30 min. Samples were also collected from the atmosphere to provide an atmospheric end-member, which allows mixing trends to be analysed. The samples were analysed for CO_2 and CH_4 concentrations and $^{13}CO_2$ using an isotopic CO_2 analyser (G2131-i Isotopic Carbon Analyser, Picarro Inc., Santa Clara, CA, USA).

2.1 Experimental Control Study design

Isotope samples were collected from forest and grass pasture at a farm at Kinloch, a non-geothermal area located 7km west of the Wairakei geothermal system boundary (resistivity boundary) (Figure 1).

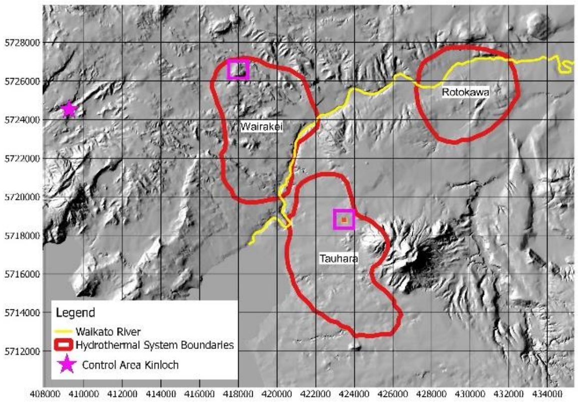

Figure 1: Map of Taupo area showing study locations at Te Mihi (North Wairakei) and Tauhara (magenta rectangles) and experimental control area (magenta star) outside the approximate Wairakei-Tauhara system boundary (white boundary line). Map datum: WGS84.

Isotope samples were collected from forest, grass and scrub (low vegetation), the three main vegetation types. Isotope sampling was repeated (winter and summer) to determine if any seasonal variation occurred.

Measurement locations were marked with survey pegs, so that the exact location can be revisited over the course of one year. CO_2 flux and soil temperature (30cm) were measured at each location.

3. RESULTS AND DISCUSSION

3.1 CO2 Flux data

CO_2 flux populations from Te Mihi, Tauhara and the Control Set are compared as percentiles (Table 1), and box and whisker plots (Figure 2). It is clear that the central 50% of biological flux measurements (25^{th}ï 75^{th} percentiles) overlap with lower halves (Ò50^{th} percentile) of measurements from geothermal areas at both Te Mihi and Tauhara (boxes in Figure 2). Te Mihi shows the greatest overlap with the control set.

Accordingly, assuming the lower halves of CO_2 flux measurements at Te Mihi and Tauhara are (at least partly) geothermally sourced, the magnitude of CO_2 flux alone cannot be used to distinguish biological and low (Ò40 g m^{-2} d^{-1}) geothermal measurements.

The following sections present the results of isotopic analysis to verify CO_2 flux measurements at Te Mihi and Tauhara are (at least partly) geothermally sourced, and the Control Set biologically sourced.

3.2 Control Measurements

Isotopic results from the biological control set are presented as a Keeling plot (Figure 3). The plot shows a clear mixing line (R^2=0.97) between ambient atmospheric CO_2 (-8.5ă) and biogenic soil CO_2 flux (-26.4ă). -26ă is typical of biogenic soil CO_2 flux (Smith et al. 2003). Accordingly, the biological origin of soil CO_2 flux is at Kinloch is confirmed.

One geothermal sample is also shown on the plot (Figure 3ï red dot). The geothermal sample is enriched in $^{13}CO_2$ (-6.8 ă) relative to the biogenic samples (-26 ă), as expected for a magmatic source in the Taupo Volcanic Zone (Lyon, & Hulston, 1984).

3.3 Tauhara

CO_2 flux results at Tauhara show a clear relationship between the central area of bare thermal ground and highest geothermal CO_2 flux measurements (Figure 4).

Isotopic results at the Tauhara geothermal area are presented as a Keeling plot (Figure 5). The mixing line from the Kinloch control measutments is provided as a reference (blue dash line - Figure 3 and Figure 5), and shows that strong CO_2 flux measurements (CO_2 flux is labelled in Figure 5) are located nearer to the centre of the bare thermal ground. These measurements are also strongly enriched in the heavier isotope ŭ^{13}C (Figure 5).

Measurement from peripheral grass areas (i.e. adjacent to the bare thermal ground), are also enriched but to a lesser extent than the bare thermal ground measurements. Measurement from dry outer grass (farthest from the bare thermal ground) are least isotopically enriched, with a minor geothermal component possible.

Three member mixing analysis allows each sample collected from the chamber to be expressed quantitatively as the relative additions of the three end-members (ambient atmosphere, biogenic and geothermal)(Hanson et al., 2014). The proportion of geothermally sourced CO_2 end-member in the chamber is clearly related to the intensity of CO_2 flux (Figure 6) and is highest on the bare thermal ground (Figure 7).

3.4 Te Mihi

CO_2 flux results at Te Mihi show a clear relationship between the central area of thermal ground (magenta boundary) and highest geothermal CO_2 flux measurements (Figure 8).

Isotopic results at the Te Mihi geothermal area are presented as a Keeling plot (Figure 9). The mixing line from the Kinloch control measutments is provided as a reference (blue dash line - Figure 3 and Figure 9), and shows that strong CO_2 flux measurements (CO_2 flux is labelled in Figure 9) located nearer to the centre of the bare thermal ground are also strongly enriched in the heavier isotope ŭ^{13}C.

Measurement from areas covered with Prostrate Manuka (thermally tolerant vegetation), and grass areas at the periphery of the thermal area, are also enriched but to a lesser extent than the central bare thermal ground measurements. Measurement from the peripheral grass areas (farthest from the bare thermal ground) are least isotopically enriched (Figure 9).

Three member mixing analysis allows shows the proportion of the geothermally sourced CO_2 end-member in the accumulation chamber is clearly related to the intensity of CO_2 flux (Figure 10), and is highest within the main thermal area (Figure 11). A significant proportion (>8%) of geothermally sourced CO_2 is present in all but 2 measurements (Figure 9 and Figure 10).

Table 1 Percentiles showing overlap for CO_2 flux data sets: Te Mihi, Tauhara and Control Set (g m^{-2} d^{-1}).

	n	5%	25%	50%	75%	95%
Hot Hill	116	7	18	28	51	198
Tauhara	164	9	25	40	95	1237
Control	171	11	14	17	26	37

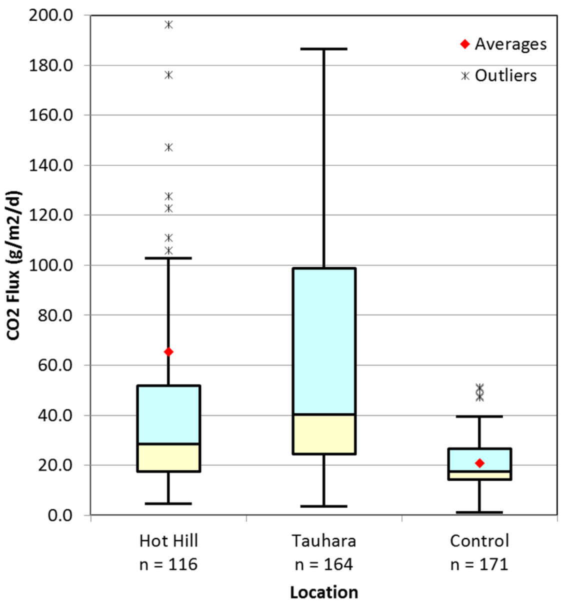

Figure 2 Box and Whisker plot showing overlap between CO_2 flux data sets: Te Mihi, Tauhara and Control Set.

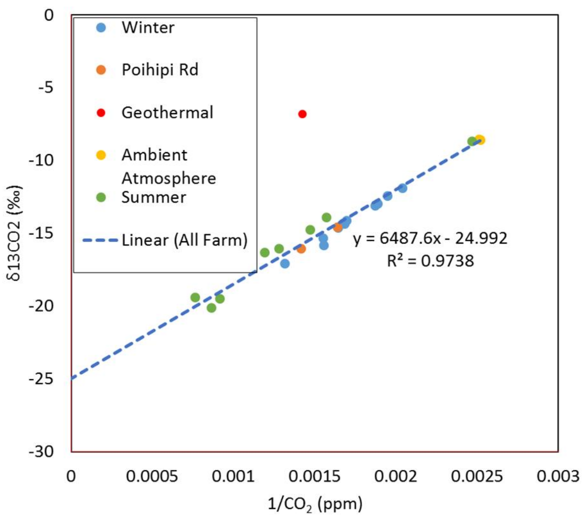

Figure 3 Keeling Plot showing ‰ $^{13}CO_2$ sampled from accumulation chamber at Kinloch (grass control area) where no geothermal CO_2 is expected.

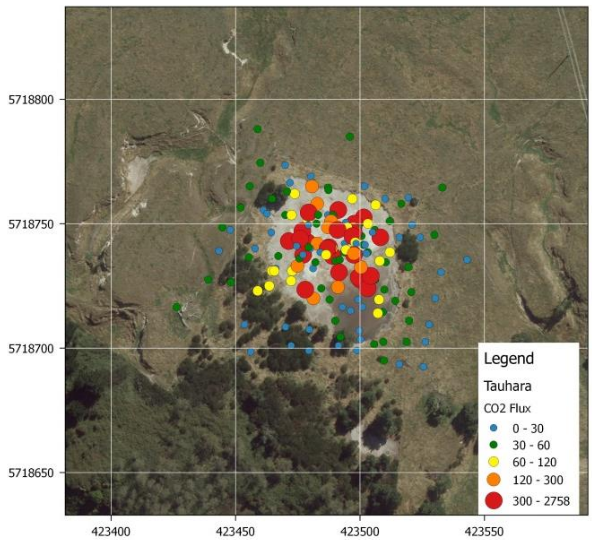

Figure 4 Tauhara CO_2 flux distribution (g m^{-2} d^{-1}).

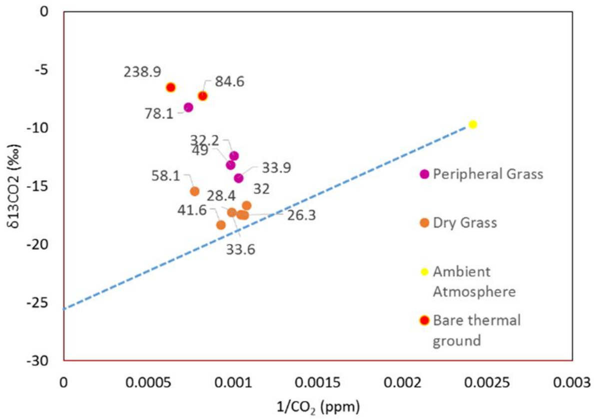

Figure 5 Keeling Plot showing ‰ $^{13}CO_2$ sampled from accumulation chamber at Tauhara. Purple mixing line from control set (Figure 3) shown as a reference. Points are labeled with CO_2 flux (g m^{-2} d^{-1}).

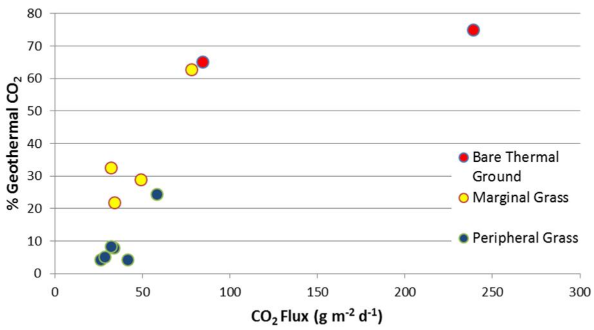

Figure 6 Tauhara CO_2 flux versus proportion of Geothermal CO_2 in the accumulation chamber (%).

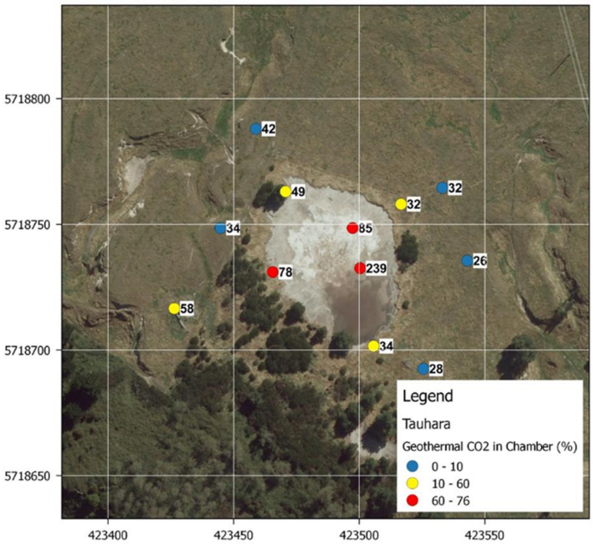

Figure 7 Tauhara Proportion of Geothermal CO_2 in the accumulation chamber (%). Points are labelled with CO_2 flux (g m^{-2} d^{-1}).

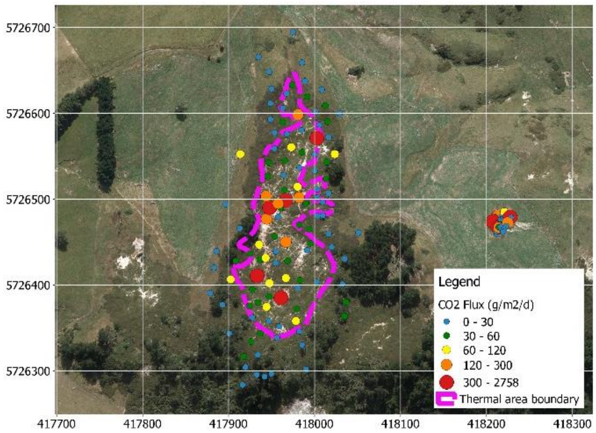

Figure 8 Te Mihi CO_2 flux distribution (g m^{-2} d^{-1}).

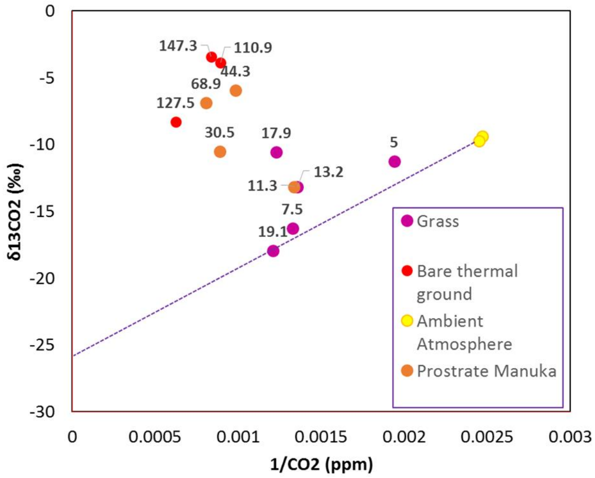

Figure 9 Keeling Plot showing ‰ $^{13}CO_2$ sampled from accumulation chamber at Te Mihi. Purple mixing line from control set (Figure 3) shown as a reference. Points are labeled with CO_2 flux (g m^{-2} d^{-1}).

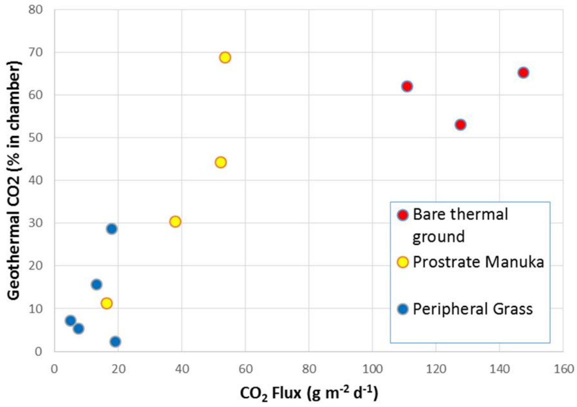

Figure 10 Te Mihi CO_2 flux versus proportion of Geothermal CO_2 in the accumulation chamber.

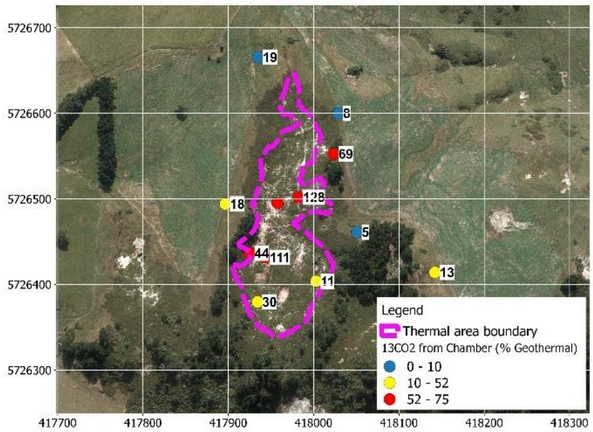

Figure 11 Te Mihi proportion of Geothermal CO_2 in the accumulation chamber (%). Points are labelled with CO_2 flux (g m^{-2} d^{-1}).

4. CONCLUSIONS

Our results show the use of $^{13}CO_2$ isotope analysis is a highly effective tool to discriminate between geothermally sourced and biologically sourced CO_2. The technique will be critical in vegetated areas where levels of biological CO_2 flux are similar to, or dominate geothermal CO_2 flux; without ^{13}CO2 isotope analysis, the overlap between geothermally sourced and biologically sourced CO_2 provides ambiguous survey results.

The practical value of this research is to remove the ambiguity of CO_2 flux results when surveying a prospect in the early exploration phases of a geothermal project. Thermal areas are obvious and often the focus of well targeting. The real potential of the CO_2 flux technique lies outside the thermal areas; to reliably identify blind faults, or confirm faults have degassing geothermal fluids at depth.

The use of $^{13}CO_2$ isotope analysis effectively raises the sensitivity of the CO_2 flux technique, and likewise is expected to expand the utility of CO_2 flux surveys to locate faults for well targeting.

Finally, the practicalities associated with $^{13}CO_2$ isotope analysis have only recently improved to the point where a typical commercial CO_2 flux survey could include the type isotope analysis undertaken here. Cavity Ring equipment for isotope analysis is now commercially available, semi-portable and rugged.

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REFERENCES

Chiodini, G., Baldini, A., Barberi, F., Carapezza, M. L., Cardellini, C., Frondini, F., & Ranaldi, M. (2007). Carbon dioxide degassing at Latera caldera (Italy): evidence of geothermal reservoir and evaluation of its potential energy. *Journal of Geophysical Research: Solid Earth (1978–2012)*, *112*(B12).

Chiodini, G., Caliro, S., Cardellini, C., Avino, R., Granieri, D., & Schmidt, A. (2008). Carbon isotopic composition of soil CO2 efflux, a powerful method to discriminate different sources feeding soil CO2 degassing in volcanic-hydrothermal areas. *Earth and Planetary Science Letters*, *274*(3), 372-379.

Fridriksson, T., Kristjansson, R., Armannsson, H., Margretardottir, E., Olafsdottir, S., Chiodini, G. (2006). CO_2 emissions and heat flow through soil, fumaroles, and steam-heated mud pools at the Reykjanes geothermal area, SW Iceland. Applied Geochemistry, 21(9): 1551-1569.

Hanson, M.C., Oze, C., and Horton, T.W. (2014) Identifying blind geothermal systems with soil CO2 surveys. *Applied Geochemistry, 50,* 106ï 114.

Harvey, M.C., Britten, K., and Schwendenmann, L. (2014). A review of approaches to distinguish between biological and geothermal soil diffuse CO2 flux. New Zealand Geothermal Workshop 2014 Proceedings, November 2014, Auckland, New Zealand.

Lyon, G. L., & Hulston, J. R. (1984). Carbon and hydrogen isotopic compositions of New Zealand geothermal gases. *Geochimica et Cosmochimica Acta*, *48*(6), 1161-1171.

Rissmann, C., B. Christenson, C. Werner, M. Leybourne, J. Cole, and D. Gravley (2012), Surface heat flow and CO< sub> 2 emissions within the Ohaaki hydrothermal field, Taupo Volcanic Zone, New Zealand*, Appl. Geochem., 27*, 223-239.

Viveiros, F., Cardellini, C., Ferreira, T., Caliro, S., Chiodini, G., & Silva, C. (2010). Soil CO2 emissions at Furnas volcano, São Miguel Island, Azores archipelago: Volcano monitoring perspectives, geomorphologic studies, and land use planning application. *Journal of Geophysical Research: Solid Earth (1978–2012), 115*(B12).