

A REVIEW OF APPROACHES TO DISTINGUISH BETWEEN BIOLOGICAL AND GEOTHERMAL SOIL DIFFUSE CO₂ FLUX

Mark C. Harvey¹, Karen Britten² and Luitgard Schwendenmann¹

¹School of Environment, University of Auckland, Auckland, New Zealand

²GNS Science, New Zealand

mhar098@aucklanduni.ac.nz

Keywords: carbon, stable, isotopes, soil, respiration, data base, exploration, biogenic, energy, prospecting.

ABSTRACT

Soil diffuse CO₂ flux (also called soil CO₂ efflux or soil respiration) is of interest to a number of research disciplines (e.g. geology, ecosystem ecology, climate and atmospheric science). While ecologists and soil scientists are primarily concerned with near surface, organic carbon flux, geologists are usually interested in CO₂ originating from deeper layers associated with magmatism. From the geological perspective, in any survey of CO₂ flux a key task is the identification of the biogenic component of the total CO₂ flux, so this “background” can be accounted for. Conventional approaches for identification of the biogenic CO₂ flux component include i) statistical methods, ii) experimental control sampling in non-geothermal areas, and iii) isotopic (¹³C) analysis of soil CO₂. In this literature review we compile past estimates of biogenic CO₂ flux from the geothermal and volcanology literature and compare these to values reported in the soil respiration database (SRDB), a freely available compendium of published biological soil respiration (RS) data. For many studies of geothermal CO₂ flux, biogenic fluxes are observed to be very similar to soil respiration reported in the SRDB database. Preliminary results from an experimental control design in the Taupo Volcanic Zone are presented.

1. INTRODUCTION

1.1 Soil diffuse CO₂ 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 CO₂ 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 CO₂ flux a key task is the identification of the biological component in the CO₂ flux measurements, so this “background” 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. 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 CO₂ flux is expected (Chiodini et al., 2007; Viveiros et al., 2010), and (iii) evaluation of background on the basis of the carbon (¹³C) isotopic signature (Viveiros et al., 2010; Rissmann et al., 2012).

1.3 Global Database of Soil Respiration Data (SRDB)

A comprehensive review of CO₂ flux studies from the ecological and soil sciences was previously undertaken by Bond-Lamberty & Thomson (2010) and complied as the Soil Respiration Database (SRDB). Although the included publications were not concerned with geothermal emissions, they provide an independent evaluation of the biological component.

The SRDB includes results from 1021 published studies that report CO₂ flux data measured in the field (not laboratory), usually as mean annual or seasonal flux. Because some of the studies contain multiple years or locations, there are 4387 records in the database. As the name suggests, the SRDB contains only studies concerned with biogenic flux. Accordingly, it is assumed that mean values in the SRDB contain negligible volcanogenic flux component, and the database provides an excellent resource providing representative biological flux values for a variety of ecosystems. The SRDB is a freely available MS Excel® spreadsheet that can be easily sorted by the particular environmental characteristic of a survey area (e.g. mean annual temperature, mean annual precipitation, biome, etc.) (<http://dx.doi.org/10.3334/ORNLDAC/1235>).

In this literature review we compile past estimates of background flux from the volcanology and geothermal literature, and compare these to values reported in the SRDB. We also present preliminary results from an experimental control design for evaluating spatial and temporal variations in biogenic CO₂ flux in the Taupo Volcanic Zone (TVZ).

2. ESTIMATES OF BIOGENIC CO₂ FLUX

2.1 Volcanology and geothermal literature

Table 1 provides a summary of studies where the biogenic component of CO₂ flux was determined in order to quantify the geothermal (magmatic) component. Table 1 divides studies according to climate, as this is expected to be a strong determinant of mean flux.

The most common method to estimate the biogenic component of CO₂ flux is the GSA method (BKs Table 1.), utilized in nearly all studies. Use of a control set of measurements has been applied in about 1/3 of the studies

(BKc Table 1). Use of ^{13}C isotope signature is restricted to only 4 studies published after 2005.

Mean biogenic CO_2 flux varies from $9.3 - 20.5 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, depending on the method of estimation and climate; mean flux for tropical soils is greatest, temperate soils is lowest. 2.2 Soil Respiration Database (SRDB)

Summary data from the SRDB, includes number of studies (n), mean (μ) and standard deviation (s.d) for biogenic CO_2 flux (Table 2). Mean fluxes from Table 1 are provided for comparative purposes, and show the same order of mean flux where tropical soils are greatest, and temperate soils are lowest. SRDB mean fluxes are comparable but slightly lower than values from Table 1.

2.3 Urban and Modified Areas

Neither Table 1 nor Table 2 consider land use (although the SRDB does), but this can be an important factor, particularly where vegetation is managed and artificially fertilised, or where the shallow sub-surface contains buried waste that may be generating high CO_2 and CH_4 fluxes (landfills) (Mazot et al., 2013).

3. EXPERIMENTAL CONTROL DESIGN

An experimental control design is presented in order to evaluate spatial and temporal variations in biogenic CO_2 flux in the Taupo Volcanic Zone (TVZ) (Figure 1, 2).

3.1 Study design

The design includes 4 measurements at each area (forest, grass and scrub) (Figure 1). Forest, grass and scrub (low vegetation) allows representative biogenic CO_2 flux to be established for three main vegetation types. The design also allows for seasonal variation of CO_2 flux by resampling the same locations in each season, and diurnal variation by repeated sampling at each measurement location 5 times over the course of one day.

Measurement locations are marked with survey pegs, so that the exact location can be revisited over the course of one year. At each location, CO_2 flux is measured along with soil temperature and soil moisture at 0-30 cm soil depth.

To assess the isotopic signature two samples of soil CO_2 are collected at each location along with ambient air. 300mL ambient air samples are collected using a syringe and then transferred into 1 L Tedlar bags. Two 300 mL soil CO_2 samples are collected from the accumulation chamber using a syringe; the first after 4 minutes, and the second after 10 minutes of gas accumulation. Samples were contained in 1 L Tedlar bags.

Samples were analysed for CO_2 and CH_4 concentrations and $\delta^{13}\text{CO}_2$ using a Cavity Ring-Down Spectroscopy analyser (G2131-i Isotopic Carbon Analyser, Picarro Inc., Santa Clara, CA, USA).

The above design was applied in winter, 2014 at a farm located 7km west of the Wairakei geothermal system boundary (resistivity boundary) (Figure 2).

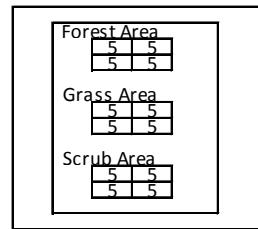


Figure 1: CO_2 flux experimental control design. Each site is marked by a survey peg and is measured five times per day to capture diurnal variability. Survey is repeated in winter, spring, summer and autumn.



Figure 2: Map of Taupo area showing locations of the CO_2 flux experimental control area outside the approximate Wairakei-Tauhara system boundary (white boundary line).

3.2 Preliminary Results

The mean of preliminary control measurements from Taupo forest ($11.3 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, Table 3) is within a single standard deviation of the SRDB temperate mean ($7.5 \pm 4.2 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, Table 2). However, the mean of grass control samples ($21.0 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, Table 3) from Taupo is in the top 2% of temperate means from the SRDB. The mean for scrub (low vegetation) ($13.3 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, Table 3) falls within 2 standard deviations of the SRDB temperate mean ($7.5 \pm 4.2 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$). Note only 2 out of the 3 planned repeat diurnal measurements were made due to time constraints.

Isotopic results are presented as a Keeling plot (Figure 3) and confirm the biogenic origin of the soil CO_2 flux at this location. The plot shows a clear mixing line ($R^2=0.995$) between ambient atmospheric CO_2 (-8.5‰) and biogenic soil CO_2 flux (-26.4‰). -26‰ is typical of biogenic soil CO_2 flux (Smith et al. 2003).

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

One other relatively high-flux geothermal sample from Tauhara ($302 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) showed an extremely low $\delta^{13}\text{C}$ value (-150‰).

4. DISCUSSION

Mean biogenic fluxes from the geothermal and volcanology literature (Table 1) are slightly higher than biogenic fluxes from the SRDB (Table 2). Results from both datasets give the same general relationship between mean CO₂ flux and climate; tropical soils are greatest, and temperate soils are lowest.

The SRDB mean fluxes are comparable but slightly lower than values from the geothermal and volcanology literature (Table 1). A possible explanation is that mean “biogenic” fluxes reported by the volcanology literature actually contain a magmatic component of CO₂ flux. This conclusion is supported by several studies from the volcanology literature (Cardellini et al., 2003; Chiodini et al., 2007; Rissmann et al., 2012).

The mean of grass control samples (Table 3) from Taupo is in the top 2% of temperate means from the SRDB (Table 2). Additional sampling under different environmental conditions (time of day, temperature, moisture, wind), and in different grass areas is required to determine why the grass control mean is so high relative to the SRDB mean.

δ¹³CO₂ isotopic results were as expected for biogenic, ambient and geothermal samples. The clear mixing trend (Figure 3) provides confidence that the method will be of use to discriminate between biogenic and geothermal CO₂ flux measurements in the Taupo area.

One anomalous δ¹³ value (-150 ‰) was measured for a soil CO₂ sample collected in an area of steaming ground at Tauhara (Figure 2). This value is probably an artefact of interference between high concentrations of geothermal gases (e.g. methane, sulphur) and the laser-based optical absorption technique.

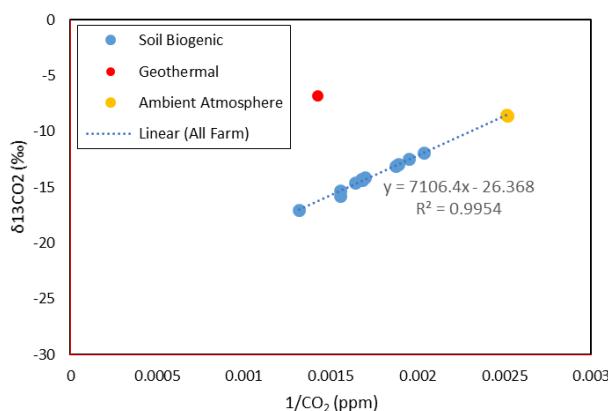


Figure 3. Keeling plot showing δ¹³C for representative CO₂ sources in Taupo, New Zealand

4. CONCLUSION

We have compared estimates of biogenic soil CO₂ flux from the geothermal, volcanology and soil ecology disciplines (SRDB), and found reasonable agreement. The agreement should provide confidence that biogenic CO₂ flux can be quantified and separated from magmatic CO₂, particularly where multiple evaluation techniques are applied.

The SRDB provides volcanologists and geothermal scientists with an independent estimate of biogenic CO₂ flux. However it is important to note the SRDB only provides data

for long-term (seasonal and annual) mean CO₂ flux; measurements made during a geothermal survey are typically of short duration (~5 minutes). Accordingly, data from the SRDB is smoothed.

Preliminary CO₂ flux and δ¹³CO₂ isotopic results from the experimental control design are consistent with previous results from both the geothermal and volcanology literature, and the SRDB. Further control measurements are planned to better constrain biogenic CO₂ flux signature in the Taupo area.

To our knowledge this is the first attempt to utilise a laser-based optical absorption technique (Cavity Ring-Down Spectroscopy, Picarro G2132) for geothermal gas samples in New Zealand. Our results suggest the analyser may be used to evaluate the δ¹³C value of magmatic soil CO₂ samples. However, the high flux of typical geothermal gases found in thermal areas may cause anomalous results, and further testing is needed. Ongoing δ¹³CO₂ isotopic measurements will be utilised to identify the biogenic component of geothermal flux in the Wairakei-Tauhara area.

ACKNOWLEDGEMENTS

We would like to acknowledge and thank GNS for providing financial support to this project. We would also like to thank Contact Energy for providing information and logistical support.

Table 1: Summary of Studies

Study Area	n	BK _S	BK _C	BK _I	Ref
Tropical					
Iwojima, Japan	424	27.9	na	na	¹
San Jacinto, Nic.	609	13.0	na	na	²
Masaya, Nic.	678	na	na	na	³
Tropical Mean		20.5	na	na	
Mediterranean					
Latera, It., 07/03	1089	23.5	15.7	na	⁴
Puzzolaie, It., 7/03	930	13.5	15.7	na	⁴
Latera, It., 10/03	452	4.3	15.7	na	⁴
Vulcano Island, It.	423	0.5	na	na	⁵
Santorini, It.	43	1.6	1.6	na	⁵
Poggio dell'Olivo, It.	196	8.4	na	na	⁶
Solfatara of Poz., It.	414	23.9	na	na	⁶
Nisyros, Greece	650	6.8	na	na	⁷
Nisyros Cald., Gr.	2883	na	15.0	na	⁶
Miyakejim, Jap.	110	32.0	na	na	⁸
Liu-Huang-Ku, Tai.	163	21.0	na	na	⁹
Mt Etna, It.	712	9.2	na	na	¹⁰
Vesuvio, It.	636	7.2	10.9	na	¹¹
Solfatara, It.	110	23.9	na	na	⁶
Solfatara, It.	373	47.0	na	<26	²³
Ishia, It.	336	na	28.7	na	¹²
Mediterranean Mean		15.9	14.8	na	
Temperate					
Yangbajain, Tibet	331	0.3	na	na	⁵
Karapiti, NZ	105	na	na	na	¹³
Dixie Valley, US	166	7.0	na	na	¹⁴
Long Valley, USA	755	6.6	12.0	na	¹⁵
Krafla, Iceland	3095	6.8	na	na	¹⁶
Furnas volcano, Az.	1362	32.0	15.0	17.5	¹⁷
Hengill, Iceland	752	4.3	na	na	¹⁸
Ohaaki, NZ	2663	15.0	na	15.0	¹⁹
Reykjanes, Iceland	352	4.1	na	na	²⁰
Rotorua, NZ	956	na	na	20.0	²¹
Yellowstone, US	410	na	19.0	na	²²
Vesuvio, It.	636	7.2	10.9	na	¹¹
Temperate Mean		9.3	14.2	17.5	
Overall Mean		13.0	14.6	17.5	

All values in g·m⁻²·d⁻¹ CO₂

n = number of measurements

BK_S = statistical method¹Notsu et al. (2005)²Harvey et al. (2011)³Lewicki et al. (2003)⁴Chiodini et al. (2007)⁵Chiodini et al. (1998)⁶Cardellini et al. (2003)⁷Brombach et al. (2001)⁸Hernandez et al. (2001)⁹Lan et al. (2007)¹⁰Giammanco et al. (2007)¹¹Frondini et al. (2004)¹²Chiodini et al. (2004)BK_C = control groupBK_I = isotopic method¹³Werner et al. (2004)¹⁴Bergfeld et al. (2001)¹⁵Bergfeld et al. (2006)¹⁶Dereinda (2008)¹⁷Viveiros et al. (2010)¹⁸Hernández et al. (2012)¹⁹Rissmann et al. (2012)²⁰Fridriksson et al. (2006)²¹Werner & Cardellini (2006)²²Werner et al. (2000)²³Chiodini et al. (2008)**Table 2: Soil Respiration Database (SRDB) Summary**

Climate	SRDB			Table 1	
	μ	n	s.d.	μ	n
Tropical	12.9	353	6.4	20.5	1
Mediterranean	8.2	143	4.4	15.4	15
Temperate	7.5	2373	4.2	13.7	12

All values g·m⁻²·d⁻¹ CO₂**Table 3: Taupo Control Measurements Preliminary Results**

Time	Forest	Grass	Scrub
1100	9.5	21.9	na
1400	13.1	20.0	13.3
mean	11.3	21.0	13.3
Overall mean			15.6

REFERENCES

Bergfeld, D., Goff, F., & Janik, C. J. (2001). Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada; relations between surface phenomena and the geothermal reservoir. *Chemical Geology*, 177(1), 43-66.

Bergfeld, D., Evans, W. C., Howle, J. F., & Farrar, C. D. (2006). Carbon dioxide emissions from vegetation-kill zones around the resurgent dome of Long Valley caldera, eastern California, USA. *Journal of Volcanology and Geothermal Research*, 152(1), 140-156.

Bond-Lamberty, B.P. and A.M. Thomson. 2014. A Global Database of Soil Respiration Data, Version 3.0. Data set. Available on-line [<http://daac.ornl.gov>] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, USA <http://dx.doi.org/10.3334/ORNLDaac/1235>.

Brombach, T., Hunziker, J. C., Chiodini, G., Cardellini, C., & Marini, L. (2001). Soil diffuse degassing and thermal energy fluxes from the southern Iakki plain, Nisyros (Greece). *Geophysical Research Letters*, 28(1), 69-72.

Cao, G., Tang, Y., Mo, W., Wang, Y., Li, Y., & Zhao, X. (2004). Grazing intensity alters soil respiration in an alpine meadow on the Tibetan plateau. *Soil Biology and Biochemistry*, 36(2), 237-243.

Cardellini, C., Chiodini, G., & Frondini, F. (2003). Application of stochastic simulation to CO₂ flux from soil: Mapping and quantification of gas release. *Journal of Geophysical Research: Solid Earth* (1978-2012), 108(B9).

Chiodini, G., Cioni, R., Guidi, M., Raco, B., & Marini, L. (1998). Soil CO₂ flux measurements in volcanic and geothermal areas. *Applied Geochemistry*, 13(5), 543-552.

Chiodini, G., Avino, R., Brombach, T., Caliro, S., Cardellini, C., De Vita, S., Ventura, G. (2004). Fumarolic and diffuse soil degassing west of Mount Epomeo, Ischia, Italy. *Journal of Volcanology and Geothermal Research*, 133(1), 291-309.

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.

Dereinda, F. H. (2008). CO₂ emissions from the Krafla geothermal area, Iceland. UNU Reports 2008 Number 15.

Frank, A. B., Sims, P. L., Bradford, J. A., Mielnick, P. C., Dugas, W. A., & Mayeux, H. S. (2000). Carbon dioxide fluxes over three Great Plains grasslands. *The Potential of US Grazing Lands to Sequester Carbon and Mitigate the Greenhouse Effect* (eds Follett RF, Kimble JM, Lal R), 167-188.

Fridriksson, T., Kristjansson, R., Armannsson, H., Margretardottir, E., Olafsdottir, S., Chiodini, G. (2006). CO₂ 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.

Frondini, F., Chiodini, G., Caliro, S., Cardellini, C., Granieri, D., & Ventura, G. (2004). Diffuse CO₂ degassing at Vesuvio, Italy. *Bulletin of volcanology*, 66(7), 642-651.

Giammanco, S., Sims, K. W., & Neri, M. (2007). Measurements of 220Rn and 222Rn and CO₂ emissions in soil and fumarole gases on Mt. Etna volcano (Italy): Implications for gas transport and shallow ground fracture. *Geochemistry, Geophysics, Geosystems*, 8(10).

Harvey, M. C., White, P. J., MacKenzie, K. M., & Lovelock, B. G. (2011). Results from a soil CO₂ flux and shallow temperature survey at the San Jacinto-Tizate geothermal power project, Nicaragua.

Hernández, P. A., Salazar, J. M., Shimoike, Y., Mori, T., Notsu, K., & Pérez, N. (2001). Diffuse emission of CO₂ from Miyakejima volcano, Japan. *Chemical Geology*, 177(1), 175-185.

Hernández, P. A., N. M. Pérez, T. Fridriksson, J. Egbert, E. Ilyinskaya, A. Thárhallsson, G. Ívarsson, G. Gíslason, I. Gunnarsson, and B. Jónsson (2012), Diffuse volcanic degassing and thermal energy release from Hengill volcanic system, Iceland, *Bulletin of Volcanology*, 74, 2435-2448.

Lan, T. F., Yang, T. F., Lee, H. F., Chen, Y. G., Chen, C. H., Song, S. R., & Tsao, S. (2007). Compositions and flux of soil gas in Liu-Huang-Ku hydrothermal area, northern Taiwan. *Journal of Volcanology and Geothermal Research*, 165(1), 32-45.

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.

Lewicki, J., Connor, C., St-Amand, K., Stix, J., & Spinner, W. (2003). Self-potential, soil CO₂ flux, and temperature on Masaya volcano, Nicaragua. *Geophysical Research Letters*, 30(15)

Mazot, A., Smid, E. R., Schwendenmann, L., Delgado-Granados, H., & Lindsay, J. (2013). Soil CO₂ flux baseline in an urban monogenetic volcanic field: the Auckland Volcanic Field, New Zealand. *Bulletin of volcanology*, 75(11), 1-9.

Notsu, K., Sugiyama, K., Hosoe, M., Uemura, A., Shimoike, Y., Tsunomori, F., ... & Hernández, P. A. (2005). Diffuse CO₂ from Iwojima volcano, Izu-Ogasawara arc, Japan. *Journal of volcanology and geothermal research*, 139(3), 147-161.

Ostapenko, S. V. and Romero, F. (1995) Levantamiento de gases del subsuelo y temperaturas superficiales en el campo geotermico San Jacinto-Tizate. *Geotermia* 11, 145-154.

Rissmann, C., B. Christenson, C. Werner, M. Leybourne, J. Cole, and D. Gravley (2012), Surface heat flow and CO₂ emissions within the Ohaaki hydrothermal field, Taupo Volcanic Zone, New Zealand, *Appl. Geochem.*, 27, 223-239.

Sinclair, A. J., Selection of threshold values in geochemical data using probability graphs, *J. Geochem. Explor.*, 3, 129– 149, 1974.

Sinclair Knight Merz (2008) Geoscientific study and review of the San Jacinto Geothermal System. Client Report.

Smith K. A., Ball, B., Conen, F., Dobbie, K.E., Massheder, J., Rey, A. (2003) Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur J Soil Sci* 54:779–791.doi:10.1046/j.1365-2389.2003.00567.x.

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).

Werner, C., Brantley, S. L., & Boomer, K. (2000). CO₂ emissions related to the Yellowstone volcanic system: 2. Statistical sampling, total degassing, and transport mechanisms. *Journal of Geophysical Research: Solid Earth (1978–2012)*, 105(B5), 10831-10846.

Werner, C., Hochstein, M. P., & Bromley, C. (2004). CO₂ fluxes of steaming ground at Karapiti (Wairakei, NZ). In *The 26th New Zealand Geothermal Workshop/GEO3, Taupo, New Zealand*.

Werner, C., & Cardellini, C. (2006). Comparison of carbon dioxide emissions with fluid upflow, chemistry, and geologic structures at the Rotorua geothermal system, New Zealand. *Geothermics*, 35(3), 221-238.