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

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## ABSTRACT

Soil diffuse $CO_2$ flux (also called soil $CO_2$ 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 $CO_2$ originating from deeper layers associated with magmatism. From the geological perspective, in any survey of $CO_2$ flux a key task is the identification of the biogenic component of the total $CO_2$ flux, so this “background” can be accounted for. Conventional approaches for identification of the biogenic $CO_2$ flux component include i) statistical methods, ii) experimental control sampling in non-geothermal areas, and iii) isotopic ($^{13}C$) analysis of soil $CO_2$. In this literature review we compile past estimates of biogenic $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 “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 $CO_2$ 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).

### 1.3 Global Database of Soil Respiration Data (SRDB)

A comprehensive review of $CO_2$ 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 $CO_2$ 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/ORNLDAAC/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 $CO_2$ flux in the Taupo Volcanic Zone (TVZ).

## 2. ESTIMATES OF BIOGENIC $CO_2$ FLUX

### 2.1 Volcanology and geothermal literature

Table 1 provides a summary of studies where the biogenic component of $CO_2$ 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 $CO_2$ flux is the GSA method ($BK_S$ Table 1.), utilized in nearly all studies. Use of a control set of measurements has been applied in about 1/3 of the studies

($BK_C$ 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 $g\cdot m^{-2}\cdot d^{-1}$, 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 $\delta^{13}CO_2$ 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).

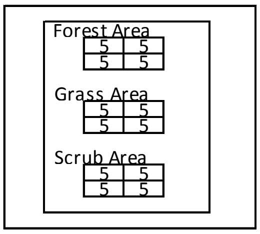

**Figure 1: $CO_2$ flux experimental control design. Each site is marked by a survey peg and is measured five times per day to capture diurnal variability. Survey is repeated in winter, spring, summer and autumn.**

**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 $g\cdot m^{-2}\cdot d^{-1}$, Table 3) is within a single standard deviation of the SRDB temperate mean (7.5 ± 4.2 $g\cdot m^{-2}\cdot d^{-1}$, Table 2). However, the mean of grass control samples (21.0 $g\cdot m^{-2}\cdot d^{-1}$, Table 3) from Taupo is in the top 2% of temperate means from the SRDB. The mean for scrub (low vegetation) (13.3 $g\cdot m^{-2}\cdot d^{-1}$, Table 3) falls within 2 standard deviations of the SRDB temperate mean (7.5 ± 4.2 $g\cdot m^{-2}\cdot d^{-1}$). 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 $\delta^{13}$ (-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 $g\cdot m^{-2}\cdot d^{-1}$) showed an extremely low $\delta^{13}$ 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 $CO_2$ 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 $CO_2$ 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.

$\delta^{13}CO_2$ 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 $CO_2$ flux measurements in the Taupo area.

One anomalous $\delta^{13}$ value (-150 ‰) was measured for a soil $CO_2$ 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.

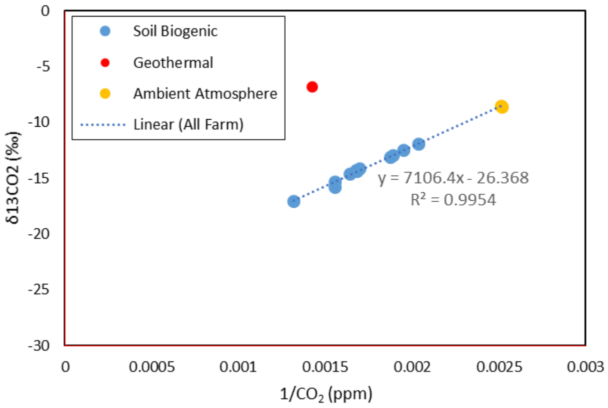

**Figure 3. Keeling plot showing $\delta^{13}C$ for representative $CO_2$ sources in Taupo, New Zealand**

## 4. CONCLUSION

We have compared estimates of biogenic soil $CO_2$ flux from the geothermal, volcanology and soil ecology disciplines (SRDB), and found reasonable agreement. The agreement should provide confidence that biogenic $CO_2$ flux can be quantified and separated from magmatic $CO_2$, particularly where multiple evaluation techniques are applied.

The SRDB provides volcanologists and geothermal scientists with an independent estimate of biogenic $CO_2$ flux. However it is important to note the SRDB only provides data for long-term (seasonal and annual) mean $CO_2$ flux; measurements made during a geothermal survey are typically of short duration (~5 minutes). Accordingly, data from the SRDB is smoothed.

Preliminary $CO_2$ flux and $\delta^{13}CO_2$ 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 $CO_2$ 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 $\delta^{13}C$ value of magmatic soil $CO_2$ samples. However, the high flux of typical geothermal gases found in thermal areas may cause anomalous results, and further testing is needed. Ongoing $\delta^{13}CO_2$ isotopic measurements will be utilised to identify the biogenic component of geothermal flux in the Wairakei-Tauhara area.

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**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 |
| Solfotara, It. | 110 | 23.9 | na | na | 6 |
| Solfotara, 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$^{-1}$ $CO_2$

n = number of measurments

$BK_S$ = statistical method

[1]Notsu et al. (2005)

[2]Harvey et al. (2011)

[3]Lewicki et al.(2003)

[4]Chiodini et al. (2007)

[5]Chiodini et al. (1998)

[6]Cardellini et al. (2003)

[7]Brombach et al. (2001)

[8]Hernandez et al. (2001)

[9]Lan et al. (2007)

[10]Giammanco et al. (2007)

[11]Frondini et al. (2004)

[12]Chiodini et al. (2004)

$BK_C$ = control group

$BK_I$ = isotopic method

[13]Werner et al. (2004)

[14]Bergfeld et al. (2001)

[15]Bergfeld et al. (2006)

[16]Dereinda (2008)

[17]Viveiros et al. (2010)

[18]Hernández et al. (2012)

[19]Rissmann et al. (2012)

[20]Fridriksson et al. (2006)

[21]Werner & Cardellini (2006)

[22]Werner et al. (2000)

[23]Chiodini et al. (2008)

**Table 2: Soil Respiration Database (SRDB) Summary**

| | SRDB | | | Table 1 | |
|---|---|---|---|---|---|
| **Climate** | **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$^{-1}$ $CO_2$

**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** |

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