

# CO<sub>2</sub> discharge from Lake Rotoiti, New Zealand

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## ABSTRACT

Twenty percent of the surface area of Okataina Caldera is covered with lakes. Lake Rotoiti located at the northwest edge of Okataina Caldera, hosts numerous underwater hydrothermal vents. Western Lake Rotoiti has relatively shallow waters (10-40m) and is closely associated with Tikitere and Taheke geothermal fields. Plumes of gas and bubbling warm water can be observed in the lake resulting in a 10-20 MW geothermal heat flux of Central Basin located at the centre part of Lake Rotoiti. In this study, we present the results of a lake survey that focuses on surface CO<sub>2</sub> emission using the floating accumulation chamber method and sequential Gaussian simulation for processing the data. In addition, dissolved gas composition and surface CO<sub>2</sub> flux measurement give us a better understanding of the degassing pathways and mechanism of the geothermal fluids in Lake Rotoiti. The result of this lake survey benefits from the comparison of natural greenhouse gas output of Rotoiti to other volcanic lakes in Okataina Caldera and in New Zealand.

## 1. INTRODUCTION

The chemistry of volcanic lake can reflect magma degassing in the hydrothermal system (Mazot & Bernard, 2015). CO<sub>2</sub> is the most abundant volcanic gas species after H<sub>2</sub>O. The degassing process can be observed as plume in the water column, or as bubbling, steaming area on the lake surface. In New Zealand, detail CO<sub>2</sub> flux data has been published for individual geothermal systems distributed around the calderas (Tarawera, Hughes et al., 2019; Lake Rotomahan, Mazot et al., 2014). By using a combination of accumulation measurement to assess the CO<sub>2</sub> flux and gas geochemistry, we aim to understand the breathing of a volcanic caldera system. The quantification of the gas flux from the water-atmosphere interface provide insights of fluid transport and regional CO<sub>2</sub> output (Mazot et al., 2014), and is vital to assess the gas emission of the active Okataina caldera. In this study, we report the CO<sub>2</sub> flux from the Lake Rotoiti using the floating accumulation chamber method (Pérez et al., 2011). Together with water chemistry through the water column and gas composition of bubbles, the results provide better understanding of the relationship between Lake Rotoiti, geothermal system and the caldera boundary.

## 2. GEOLOGICAL SETTINGS

Lake Rotoiti spans across three geothermal systems: Tikitere, Taheke, and Lake Rotoiti (Fig.1). It is part of the Horohoro volcanic complex located in the northwest part of the Okataina Volcanic Centre (OVC), the most recently

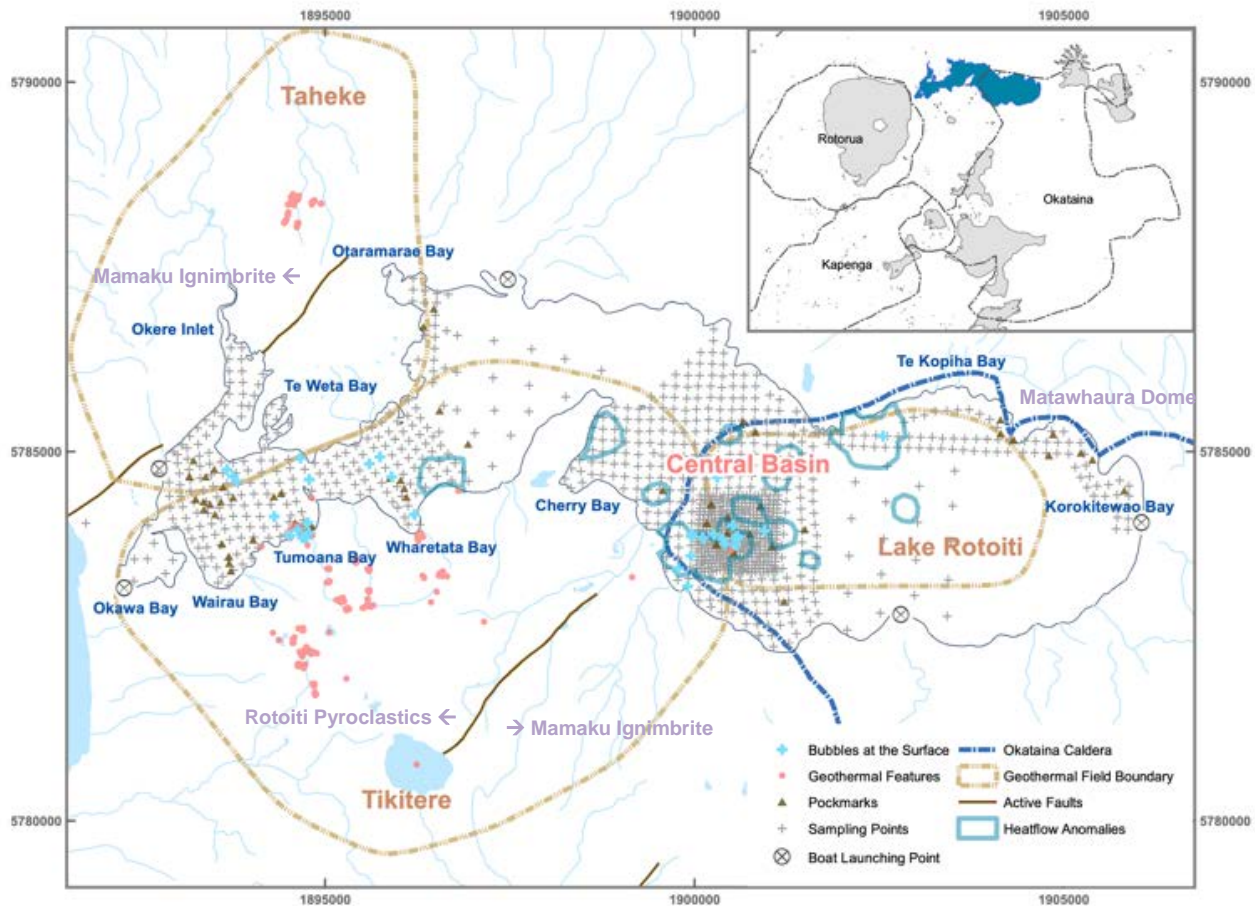
active of the eight major rhyolite eruptive centre in the Taupo Volcanic Zone, North Island, New Zealand (Nairn, 2002). The latest large caldera volcanic event occurred ~ 25 ka with the Rotoiti eruptions followed by rhyolitic pyroclastic and lava eruptions from multiple vents in the northern part of Horohoro caldera, and Okareka embayment. After the Te Rere eruption episode, the outflow from the Rotorua catchment formed Lake Rotoiti (Hodgson & Nairn, 2004). The northern rim of the Horohoro Caldera on the northeast edge of Lake Rotoiti shows a strongly scalloped scarp developed in the pre-caldera Matawhaura Okataina rhyolite lavas (Pérez et al., 2011). In the eastern part of Lake Rotoiti, the Central Basin is located just inside the Horohoro caldera rim (Fig. 1). It is close to the inferred northeastern extension of a fault that forms the southeastern boundary of the Tikitere Graben (Calheam, 1973). Earlier heat flow assessment of the Central Basin revealed high sediment temperature and heat flows (Stewart & de Ronde, 2015). Widespread gas plumes are discharging from the lake floor of Central Basin where water depth reach over 100m and bubble can be observed at the surface. In contrast, the eastern part of Lake Rotoiti has relatively shallow water depth (<50m). Hot spring on land and warm water extend to the lake at Tumoana Bay, Puketitoti Point, and Wharetata Bay (Fig. 1). Steaming water surface and sinters can also be observe near the shore.

## 3. SAMPLING METHOD

In August 2020, 1119 points for CO<sub>2</sub> flux measurement were taken to cover most of the lake area. Two water columns and 2 bubble samples were collected in the Central Basin and Tumoana Bay (Fig 1,2). The work was planned to be conducted during winter when the lake was not stratified.

### 3.1 Flux Measurement

The CO<sub>2</sub> flux measurement is divided into 3 different types of gridding based on the resolution of high CO<sub>2</sub> flux area: 50m, 150, and 500m (Fig. 1). Most 50m grids were conducted in the Central Basin within the 1km<sup>2</sup> area where high heat flow anomalies were identified (Stewart & de Ronde, 2015). The 150m-grid covered the geothermal fields boundaries, the river input and where pockmarks were recorded (Pickrill, 1993). A 500m-grid was performed where low CO<sub>2</sub> flux was expected. Gas flux measurements of CO<sub>2</sub> and H<sub>2</sub>S were realized using an accumulation chamber (Chiodini, et al., 1998). We used the West System LICOR LI-820 infrared gas analyzer for CO<sub>2</sub> and TOX05 H<sub>2</sub>S gas analyzer is used for H<sub>2</sub>S. Ambient air pressure and temperature are measured during the flux survey for correlation of data. Water temperature and wind speed were also taken to constrain the variation of time and spacing. The flux is calculated following the equation:



**Figure 1: Location and sampling grids of 1119 CO<sub>2</sub> flux measurements on Lake Rotoiti during August 2020. Two set of water sampled through the water column were taken at the bubbling areas (Central Basin and Tumoana Bay).**

$$F_c = F_r \cdot (P/10) / (101.3) \cdot ((298)/(T+273)) \cdot D_f$$

$$D_f = k \cdot V/A$$

(  $F_c$ : Calculated Flux (g/m<sup>2</sup>/d)  $F_r$ : Raw Flux(ppm/s)  $P$ : Ambient air pressure (mbar)  $T$ : Ambient air temperature (°C)  $D_f$ : Dimension factor  $k$ : Coefficient converting ppm/s to g/day  $V$ : Total volume combining the chamber volume and the dead volume for the system (m<sup>3</sup>)  $A$ : Area covered by the chamber (m<sup>2</sup>) )

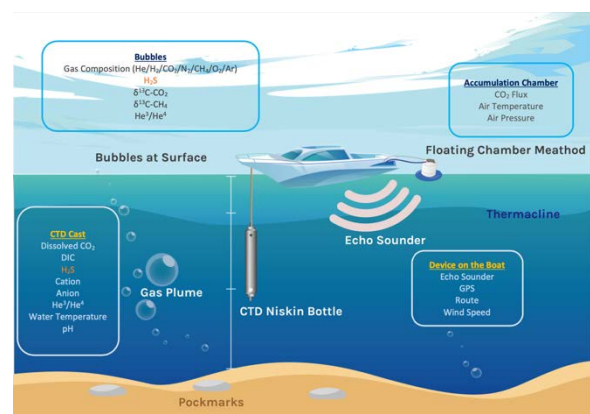
### 3.2 Water Column Sampling

Water samples were collected using Niskin-type sampler along vertical profiles between the lake floor and lake surface at two bubbling sites. In the Central Basin, water samples from 4 depths were taken: 0m, 5m, 20m, 75m. At Tumoana Bay, water samples from 2 depths were taken: 0m, 8m.

CO<sub>2</sub> flux measurements at the surface were done before collecting the water column samples. The dissolved CO<sub>2</sub> in the water of each depth were analyzed with headspace syringe method with a Vaisala GMP251 carbon dioxide probe (Maussen, 2018).

Samples for sulfide was realised by adding filtered water to bottles with 0.5ml of 1M Zinc acetate and 0.2ml of 6N NaOH added. Bottles for anion water chemistry were rinsed three times before filling. Samples were filtered through 0.45μm syringe filters on site. Anions in water samples were

analyzed by a DIONEX ICX 5000 Ion Chromatography at the New Zealand Geothermal Analytical Laboratory at GNS Science Wairakei Research Centre (NZGAL). Bottles for cation samples were acidified with nitrate acid and filled with filtered water sample. ICP-OES (Inductive Coupled Plasma – Optical Emission Spectroscopy) is used to determine cationic species in aqueous samples. Dilution of the water will be done in laboratory-based on the estimation of concentration of cationic species (GNS Science, 2019).



**Figure 2: Sampling method for surface CO<sub>2</sub> flux, bubbles, water column and physical parameters for data correction and calculation.**

### 3.3 Bubble sampling

Utilising pre-evacuated, low permeability glass bottle with two evacuated stopcocks at both ends, gas bubbles were collected by a funnel connected with a plastic tubing using water replacement technique (Lee et al., 2005). Gas analysis are conducted using a Shimadzu-2014 GC at the NZGAL. The same bubble sampling method is also used with the copper tubes for helium analysis.

## 4. RESULTS AND DISCUSSION

### 4.1 CO<sub>2</sub> Flux Mapping

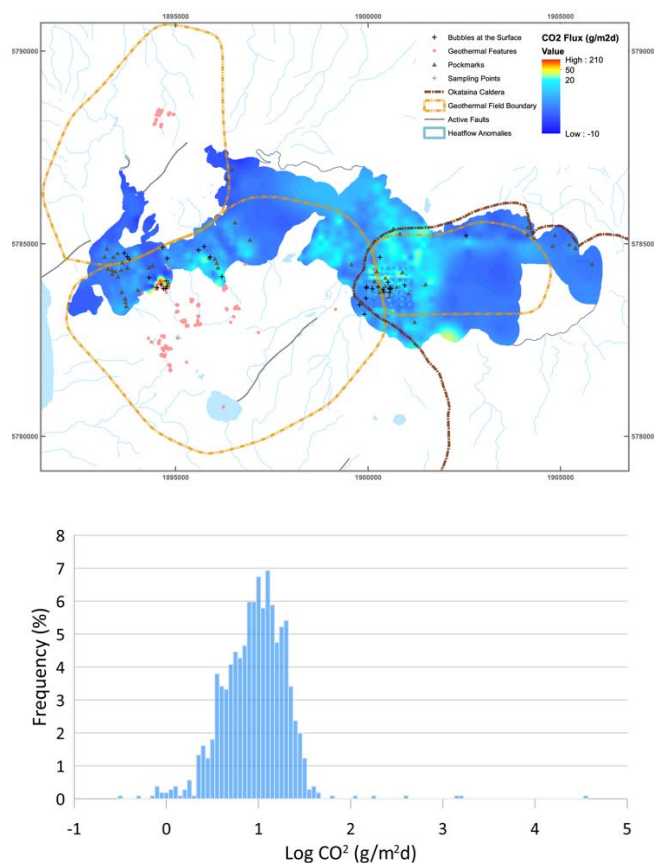
The CO<sub>2</sub> flux of Lake Rotoiti ranged from minimum -4.44 g/m<sup>2</sup>/d at Te Karaka Bay to maximum 33881 g/m<sup>2</sup>/d at Tumoana Bay. The Kriging method is a useful tool to estimate the gas flux at unsampled locations using a limited number of in-situ measurements (Chiles & Delfiner, 1999). The Kriging method considers the spatial variance between pairs of points and the values to give different weight for existing points; it is one of the most common used interpolation methods when creating a flux map. Graphical statistical analysis (GSA) of the CO<sub>2</sub> flux data allows differentiation of data populations that correspond to different ranges of flux values (Cardellini, et al., 2003; Chiodini et al., 1998). Dividing the flux data into populations not only help interpolation of flux data within different range, but also is the basis of defining background values in geothermal fields (Bloomberg et al., 2014; Harvey, et al., 2015; Rissmann et al., 2012; Sheppard & Wild, 2002).

#### 4.1.1 East Lake Rotiti

Preliminary results of the CO<sub>2</sub> flux map for Lake Rotoiti is showed in Fig. 4. Wide area of CO<sub>2</sub> flux greater than 20 g/m<sup>2</sup>/d trending from southeast Central Basin to Ngapuka Bay and Puketapu Point of the north coast where no pockmarks and bubbles were recorded. The highest CO<sub>2</sub> flux measured in the region is 43.04 g/m<sup>2</sup>/d. At the time of writing, the source and composition of the gas have not been analysed yet. At the Northeast lake margin from Te Kopiha Bay to Korokitewao Bay, pockmarks are distributing along the Caldera rim (Pickrill, 1993). Bubbling areas were observed during the survey. However, low CO<sub>2</sub> flux may suggest that the hydrothermal gases may not be dominated by CO<sub>2</sub>. Another area with slightly high CO<sub>2</sub> flux locates at Cherry Bay, west of the Central Basin.

#### 4.1.2 West Lake Rotiti

From the CO<sub>2</sub> flux results, outflows from Tikitere geothermal system seems to enter Tumoana Bay, Puketitoe Point, and Wharetata Bay, where the water depth are shallower than 15 m. High CO<sub>2</sub> flux, bubbling area, steaming surface were distributed from Tumoana Bay, following the lakeshore towards Te Rei Bay. The highest CO<sub>2</sub> flux measured was 33,881 g/m<sup>2</sup>/d. In the area northeast of Tumoana Bay, no CO<sub>2</sub> anomalies were observed around the Wairau Bay area despite widespread pockmarks and bubbles observed at the surface. This suggests that the growth (photosynthesis) of algae at the lake floor would likely be the product of a biotic uptake of CO<sub>2</sub>, resulting in negative CO<sub>2</sub> flux (-4.44 g/m<sup>2</sup>/d) at the northwest part of the lake (Okere Inlet, Te Weta Bay, and Otaramarae Bay), which turns the lake into a sink for atmospheric CO<sub>2</sub> (Domysheva et al., 2013).

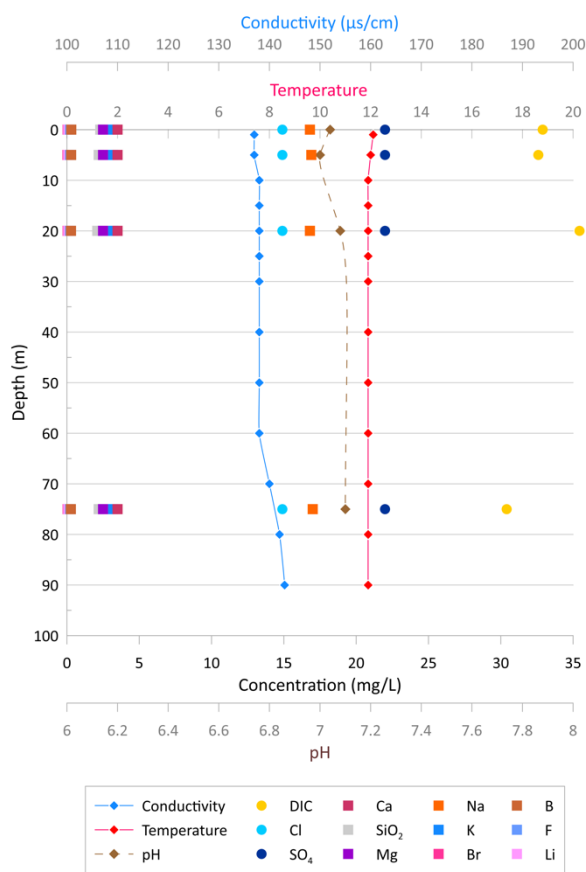


**Figure 4: CO<sub>2</sub> flux map and histogram (in g/m<sup>2</sup>/d) of 1119 flux measurements during Aug 2020 using Kriging method. Blue triangles mark the pockmarks and red circles mark the geothermal features. Bubbles at the lake surface are marked as black cross.**

### 4.2 Bubbles and depth water profiles

Preliminary results from the water column above the Central Basin is showed in Figure 5. This may reduce the effect of a thermocline which could stop uprising CO<sub>2</sub> from passing through all the water column. From the temperature, conductivity and ionic composition results, parameters besides pH and dissolved CO<sub>2</sub> (DIC in Figure 5) are consistent between the different water depths. This indicates that fluids can migrate upward without barrier. The cause of relatively low CO<sub>2</sub> flux at Central Basin is thus unlikely to be due dissolution of CO<sub>2</sub> in the water column. Thick water column can absorb gas coming from depth, and the low water temperature during winter will increase the solubility of CO<sub>2</sub>, thus stop CO<sub>2</sub> emitting to the surface (Diamond & Akinfiev, 2003). The dissolve CO<sub>2</sub> results (Fig.5, yellow circle) is relatively low compared to other volcanic lakes (Mazot et al., 2014), and showed similar trend as the pH (Fig. 5, brown diamond).





**Figure 5: Preliminary results from the water column sampling above the Central Basin in Lake Rotoiti. The conductivity and temperature were taken at 13 different depths.**

## 5. CONCLUDING REMARKS

- (1) CO<sub>2</sub> flux measurement at the water air surface showed the special distribution of CO<sub>2</sub> degassing with possible caldera structure or geothermal boundaries.
- (2) High CO<sub>2</sub> flux result (33.881 g/m<sup>2</sup>/d) were observed at Tumoana Bay, Puketitoti Point, and Wharetata Bay.
- (3) Relatively low CO<sub>2</sub> flux anomalies (43.4 g/m<sup>2</sup>/d) were measured at the eastern part of Lake Rotoiti (Central Basin, Punawhakareia Bay, and the area between Cherry Bay and Ngapuka Bay/Puketapu Point).
- (4) Negative flux (-4.44 g/m<sup>2</sup>/d) was observed at Okere Inlet, Te Weta Bay, and Otaramarae Bay

## ACKNOWLEDGEMENTS

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