

## Soil gas exploration at Rotokawa geothermal field, New Zealand

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### Soil CO<sub>2</sub> as a proxy for heat and mass flow

A significant challenge to geothermal exploration is accurate quantification of the heat and mass flow between deep reservoir(s) and the surface. Here, we use high resolution measurement (10's of m's) of carbon dioxide (CO<sub>2</sub>) flux and heat flow at the land surface to characterise the mass (CO<sub>2</sub> and steam) and heat released from the geothermal reservoir. Statistical and isotopic characterisation of atmospheric, biogenic and hydrothermally sourced CO<sub>2</sub> reduces the level of uncertainty when deriving mass (emissions) and heat flow estimates from high temperature reservoirs. Our results include soil CO<sub>2</sub> flux, soil δ<sup>13</sup>C, and soil temperature (0.1m depth) measurements at the surface of Rotokawa geothermal field (2.5km<sup>2</sup>), in the Taupo Volcanic Zone, New Zealand. Data is modelled and interpolated to predict total CO<sub>2</sub> emissions which are used in conjunction with historic fumarolic discharges to calculate reservoir mass and heat flow. Soil temperature measurements are converted to heat flow units and summed to produce a surface heat flow value.

Initial results indicate a total CO<sub>2</sub> emission rate of 633 ± 16td<sup>-1</sup> which includes 22td<sup>-1</sup> from biogenic and atmospheric sources. The δ<sup>13</sup>C range (-16 and -8‰) is plotted as an isoscape (i.e. isotope value contours) and illustrates spatial variance in magmatic, biogenic and atmospheric CO<sub>2</sub> contribution. The reservoir's steam mass flow of 10,150td<sup>-1</sup> is calculated from the total hydrothermal CO<sub>2</sub> emission (611 ± 16td<sup>-1</sup>) multiplied by the H<sub>2</sub>O:CO<sub>2</sub> molar weight ratio (16.6) characterised for major fumaroles. The equivalent thermal energy of the mass flow of the reservoir is 317 ± 8MW, while the observed surface heat flow through soil is equivalent to 73 ± 5MW. The discrepancy in these two heat flow values is attributed to water vapour condensing (scrubbed) within cool (<160°C) meteoric groundwaters that overlie the high temperature reservoir prior to reaching the surface. In contrast, CO<sub>2</sub> is more conservative and therefore less susceptible to scrubbing by meteoric groundwaters making it a better proxy for heat and mass release from the deep reservoir.

By spatially mapping and comparing the soil flux, temperatures, and δ<sup>13</sup>C, there is more control over the soil permeability/soil gas flux (magnitude) relationship. The connectivity from the deep source through to the shallow subsurface through structural (fault/fracture) control of fluid flow pathways can be constrained with more certainty by identifying the CO<sub>2</sub> source.

This study concludes that the combination of CO<sub>2</sub> flux and δ<sup>13</sup>C can successfully quantify heat flow and predict connectivity to deeper heat sources as well as illustrate shallow spatial variation in permeability.

## The effect of extracellular polysaccharides on the mobility of phosphates bound to iron oxides

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### Introduction

The biogeochemical cycle of P is unique due to its strong tendency to adsorb to environmental particles, such as iron oxides, resulting in the formation of sparingly soluble solid phases. Furthermore, phosphorus does not form volatile compounds in the environment; hence the biogeochemical cycle of phosphorus occurs exclusively in the biosphere. Thus, due to the high stability of phosphates, key processes for biomass production are the transfer of phosphorus from adsorbed, solid, or organically bonded states into bioavailable forms, and these processes occur primarily at primarily at solution interfaces with minerals, microbes, or organic ligands.

The types of environmental perturbations that may result in the release of phosphates from iron oxide surfaces are not well understood. For example, many microorganisms and plants can release extracellular polysaccharides (EPS) into their local environments. EPS is known to adsorb to environmental particles, including iron oxides, and therefore the adsorption of EPS may out-compete the adsorbed phosphate, or even preferentially bind the oxyanion. It was previously thought that organics that form inner sphere complexes with the iron oxides would be able to out-compete the phosphates and remobilize them into solution. However, Lindegren et al. [1] found that strong, multiple H-bond donors and acceptors, in lieu of inner sphere species, out-compete phosphate. Therefore, EPS may be expected to have an effect on phosphate mobility in the subsurface. Currently, there is little information available regarding the ability of EPS to remobilize essential nutrients, such as phosphate, into the environment.

### Experimental

In this study we investigated the remobilization of both inorganic and organophosphate following their adsorption to iron oxides. The inorganic phosphate used was orthophosphate and the organophosphate was the phosphate monoester, glucose phosphate. We examined qualitatively and quantitatively the effect of alginate, which was used as a model for EPS, on the remobilization mechanisms and competition reactions of pre-adsorbed phosphates. This was accomplished by a combination of in-situ infrared spectroscopy and wet-chemical experiments. Data were collected as a function of phosphate and alginate concentrations, pH, and time, and the collective results from these experiments will be presented and the co-adsorption and competitive mechanisms will be discussed. These results are important as they provide constraints on the mobility and, thereby, bioavailability of phosphate in the environment.

[1] Lindegren (2009) *European Journal of Soil Science* **60**, 982-993.