

# Water Resources Research®

## RESEARCH ARTICLE

10.1029/2026WR044239

### Key Points:

- A lumped-parameter physics model tracks CO<sub>2</sub> content and emissions from geothermal reservoirs
- Metered plant emissions overcount anthropogenic climate impact when surface emissions changes are ignored
- Long-term CO<sub>2</sub> storage security requires either mineralization or reinjection that delays reservoir returns

### Supporting Information:

Supporting Information may be found in the online version of this article.

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### Citation:

Dempsey, D. (2026). A physics-based, lumped-parameter model for attributing natural and anthropogenic CO<sub>2</sub> emissions from producing geothermal systems. *Water Resources Research*, 62, e2026WR044239. <https://doi.org/10.1029/2026WR044239>

Received 30 MAR 2026

Accepted 2 SEP 2026

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## A Physics-Based, Lumped-Parameter Model for Attributing Natural and Anthropogenic CO<sub>2</sub> Emissions From Producing Geothermal Systems

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**Abstract** Although geothermal energy is a low-carbon resource, some powerplants can coproduce and release CO<sub>2</sub>, which is then subject to emissions monitoring and sometimes financial penalty. Accurate attribution of these emissions is difficult because exploitation of the reservoir alters hydrological flows that in turn modify surface CO<sub>2</sub> fluxes. Hence, emissions metered through the powerplant do not represent the true anthropogenic impact. This study develops a lumped-parameter model of a geothermal reservoir that tracks pressure evolution, dissolved CO<sub>2</sub> and emissions through the powerplant and the Earth's surface. Closed-form analytical solutions are obtained for reservoir degassing, outflow reversal, delayed reinjection returns and mineralization reactions, and these are calibrated against emissions data from the Rotokawa and Ngā Tamariki geothermal fields in New Zealand. The interplay of characteristic timescales for pressure equilibration, CO<sub>2</sub> loss, reservoir residence, breakthrough delay and mineralization are shown to control whether a field's emissions decline, stabilize or rebound over decades. Calibrated models indicate that plant-metered emissions at Rotokawa overcount the true anthropogenic impact by 17–45 kt yr<sup>-1</sup>, because production suppresses surface emissions that are not credited to the operator. CO<sub>2</sub> storage in geothermal reservoirs is shown to be fundamentally different from conventional carbon capture and storage, as it is a flow-through system in which dissolved CO<sub>2</sub> only resides temporarily. Long-term sequestration requires either mineralization or reinjection at sufficient distance to delay returns. Field-specific models and repeat CO<sub>2</sub> flux surveys are needed to constrain these effects and support emissions accounting based on true anthropogenic impact.

**Plain Language Summary** Geothermal power plants are known to release carbon dioxide (CO<sub>2</sub>) that is naturally contained in underground water. Sometimes, governments track and penalize these emissions by measuring CO<sub>2</sub> leaving the power plant. However, when water is pumped from a geothermal system it reduces the underground pressures such that less CO<sub>2</sub> flows naturally out through the ground surface. Here, a mathematical model is introduced to track CO<sub>2</sub> through a geothermal reservoir, including the emissions from the power plant, natural ones at the surface and dissolved storage underground. Tested against real data from two New Zealand geothermal fields, it is shown that plant-based monitoring on its own significantly overestimates emissions caused by humans. Also, storing captured CO<sub>2</sub> back underground in geothermal systems is not the same as conventional carbon storage because the CO<sub>2</sub> eventually flows back out unless it reacts with rocks or is injected far enough away to delay its return to the reservoir. This suggests that more accurate emissions accounting for geothermal energy requires measuring both plant and surface emissions together.

## 1. Introduction

Most geothermal power plants have low carbon emissions compared to fossil fuel alternatives (Aksoy et al., 2015; Ármannsson et al., 2005; McLean et al., 2024). At some plants however, non-condensable gases (NCGs) like CO<sub>2</sub> and H<sub>2</sub>S are coproduced and released to the atmosphere. These emissions are monitored and reported via national inventories to the United Nations Framework Convention on Climate Change, and financially penalized in some jurisdictions, for example, through the surrender of purchased units under New Zealand's Emissions Trading Scheme. Thus, emissions from geothermal power production can be subject to both political and financial pressure, and hence the accurate measurement of emissions ensures such pressure is appropriately sized.

A full picture of a geothermal system's emissions profile can be difficult to establish as it should ideally disaggregate operational versus lifecycle emissions (McLean & Richardson, 2021), power plant emissions versus those released through the Earth's surface (e.g., Ármannsson et al., 2005; M. O'Sullivan et al., 2021; Sbrana et al., 2021), and changes in emissions over time including the pre-development baseline, the new equilibrium

once power plant operations have stabilized, and any natural or anthropogenic transients (Ármannsson et al., 2005; M. O'Sullivan et al., 2021). While direct monitoring of soil emissions or outgassing features is preferred (Bloomberg et al., 2014; Sbrana et al., 2021; Taussi et al., 2023; Óladóttir & Friðriksson, 2015), it may only be practical to estimate or model certain parts of the emission profile (M. O'Sullivan et al., 2021), especially the pre-development state.

This study builds on the 0-dimensional lumped parameter (tank) framework for modeling geothermal systems, introduced by Fradkin et al. (1981) and adapted for CO<sub>2</sub> tracking by Hosgor et al. (2016). It introduces new descriptions of depletion-induced upflow, reversal of outflow, delayed injection returns, CO<sub>2</sub> degassing from depressurization and boiling, and fluid-rock reactions. These extensions are what distinguish the present model from that of Hosgor et al. (2016), which tracks dissolved CO<sub>2</sub> under production, reinjection and recharge but does not resolve degassing, outflow reversal, delayed returns, or mineralization, and does not partition emissions between the plant and the surface. The resulting closed-form analytical solutions are then calibrated to emissions data from Rotokawa and Ngā Tamariki geothermal fields, which support power generation in the Taupo Volcanic Zone (TVZ) of New Zealand's central North Island (Bibby et al., 1995). These models are used to explain probable mechanisms behind declining emissions at these fields and predict at what level these might stabilize. Furthermore, likely changes in surface emissions are estimated and their implications for emissions accounting frameworks discussed.

As a final note, this study reports measured and modeled CO<sub>2</sub> emissions in units of kt yr<sup>-1</sup> (thousand tonnes per year), which is the natural scale for these processes and also accords with emissions reporting conventions.

### 1.1. Production and Reinjection of NCGs From Geothermal Power Plants

In a geothermal reservoir, CO<sub>2</sub> will exist either as a dissolved component in the liquid pore fluid or as a co-mingled gas in a two-phase or gas zone (Figure 1). Production of liquid or gas from the reservoir brings a mixture of H<sub>2</sub>O and CO<sub>2</sub> into the well, alongside other NCGs and dissolved components. Preferential partitioning leads to high CO<sub>2</sub> concentrations in the gas phase (Grant, 1977; M. J. O'Sullivan et al., 1985) and the early-time phenomenon of “degassing” where this component is quickly stripped from the reservoir. Further degassing of CO<sub>2</sub> dissolved in the liquid component can occur as pressure drops through the aboveground pipework. It is common to discharge the exsolved CO<sub>2</sub> and other NCGs such as H<sub>2</sub>S and CH<sub>4</sub> to atmosphere. A binary generating system may capture and return a larger fraction of these gases (e.g., dissolved in the condensate) and so reduce, though not necessarily eliminate, atmospheric discharge.

In 2017, reported CO<sub>2</sub> emissions from 12 NZ power stations totaled 600 kt yr<sup>-1</sup>, although this number has reduced over time as reservoir CO<sub>2</sub> concentrations decline and as NCG capture and reinjection is increasingly adopted (McLean et al., 2024). In Turkey, Aksoy et al. (2015) has collated emissions factors for a subset of power stations, and these collectively account for at least 3,000 kt yr<sup>-1</sup>. This is likely a low estimate with the outsized emissions footprint largely attributed to the high gas content of Turkish geothermal systems that tend to be hosted in carbonate reservoirs. These have emission factors that span a wide range 400–1,300 g kWh<sup>-1</sup> (Akin et al., 2020; Aksoy et al., 2015), albeit observed to be declining over the operating life of the fields (Akin et al., 2020). Emissions reported from Icelandic power stations have risen steadily over the last few decades, from about 150 kt yr<sup>-1</sup> at the turn of the century, to more than 200 kt yr<sup>-1</sup> in 2024 (Environment and Energy Agency of Iceland, 2026). Note that reported plant emissions are typically quoted to an accuracy of about 1 kt yr<sup>-1</sup> and uncertainties beyond this are not commonly disclosed.

Plant emissions are often observed to decline during the operational life of the station (Akin et al., 2020; Friðriksson et al., 2017; McLean et al., 2024). This may occur because depressurization drives exsolution and removal of CO<sub>2</sub> that was dissolved in the liquid reservoir, or because the reservoir is diluted due to encroachment of relatively CO<sub>2</sub>-depleted peripheral waters or reinjection returns. Further reductions in power plant emissions are expected as NCG reinjection operations continue to proliferate (Ghafar et al., 2022; Snæbjörnsdóttir et al., 2020).

CO<sub>2</sub> capture and reinjection of dissolved phase CO<sub>2</sub> has been piloted and deployed in Iceland since 2012 (Gíslason et al., 2018), and in New Zealand since 2021 (Ghafar et al., 2022). Injection of supercritical liquid CO<sub>2</sub> has also been piloted in Umurlu, Turkey and Hijiori, Japan, as well as captured H<sub>2</sub>S in Coso, California and Puna,

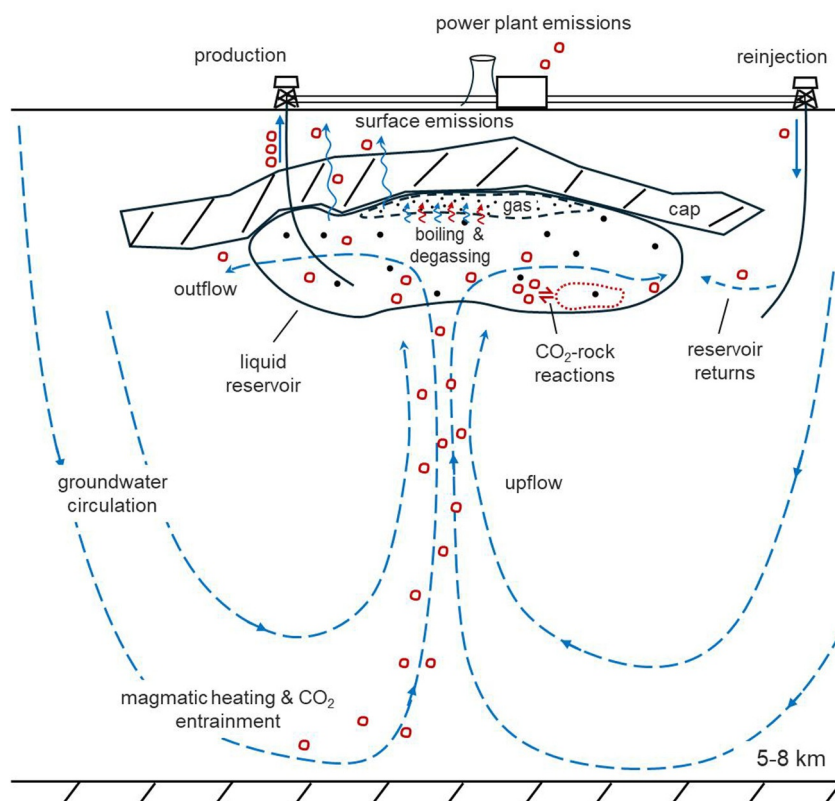


**Figure 1.** A conceptual schematic of a convective, liquid-dominated geothermal system of the type found in the Taupo Volcanic Zone, showing the deep magmatic heat and  $\text{CO}_2$  source, buoyant upflow, the liquid reservoir beneath a leaky caprock with an overlying two-phase gas zone, lateral outflow to aquifers, surface emissions, and a power plant that produces and reinjects fluid. The diagram is illustrative and is not a depiction of either case-study field (Rotokawa or Ngā Tamariki) in particular.

Hawai'i (Carmichael & Zarrouk, 2023). Geothermal systems and their adjacent recharge zones have also been suggested as storage sites for  $\text{CO}_2$  produced by other industries, including net-negative bioenergy sources (Titus et al., 2023). Managing breakthrough of the injected  $\text{CO}_2$  to production regions becomes a key consideration in such systems, although von Hirtz (2016) reports that 20 years of NCG reinjection at Puna has yet to result in breakthrough at production wells.

Water-rock interaction has implications for  $\text{CO}_2$  storage security while impacts on porosity and permeability could affect reservoir performance. For sufficiently reactive rocks, injected  $\text{CO}_2$  may react to form stable carbonate minerals like calcite, dolomite or magnesite. Snæbjörnsdóttir et al. (2020) report that, at Carbfix in Iceland, 65% of  $\text{CO}_2$  injected into basalt is mineralized within 2 months, corresponding to a half-life of 39.6 days. An injection experiment into an Oman peridotite reported 88% mineralization of  $\text{CO}_2$  within 45 days (Matter et al., 2025), corresponding to a 14.7 day half-life. However, in less reactive formations that commonly occur in New Zealand systems, mineralization reactions may be negligible (Altar et al., 2024) or even be dominated by calcite dissolution (Siahaan et al., 2024).

## 1.2. Changes in Geothermal Surface Emissions in Response to Power Production

Geothermal systems have a natural propensity to flux  $\text{CO}_2$  derived from magmatic sources or from thermal decomposition of carbonates (Ármannsson et al., 2005; Giggenbach, 1995; Hoefs, 2009; Seward & Kerrick, 1996). However, these natural fluxes can be disturbed by pressure and phase changes in the geothermal reservoir caused by fluid extraction through wells (Allis, 1981; Óladóttir & Friðriksson, 2015). This process, while widely recognized (Ármannsson et al., 2005; Bertani & Thain, 2002; M. O'Sullivan et al., 2021; Sbrana et al., 2021), is difficult to measure or estimate in a consistent manner. As such, anthropogenic changes in

geothermal surface emissions are not generally considered when calculating emissions factors or reporting plant emissions in global inventories (Fridriksson et al., 2016).

CO<sub>2</sub> is transported through geothermal systems and is released at the surface through a mix of both diffuse soil degassing and focused venting. For instance, at the Karapiti area of the Wairakei geothermal field, Werner et al. (2004) measured 7 t d<sup>-1</sup> (0.08 kg s<sup>-1</sup>) of diffuse fluxing through steaming ground versus 16 t d<sup>-1</sup> (0.19 kg s<sup>-1</sup>) focused through fumaroles (total 23 t d<sup>-1</sup> or 8.4 kt yr<sup>-1</sup>). The thermal surface features are not entirely natural having developed above and in response to a steam-dominated two-phase region of the exploited Wairakei reservoir (Allis, 1981). Thus, surface CO<sub>2</sub> emissions measured today may not be the same as the pre-development baseline.

Rissmann et al. (2012) studied diffuse CO<sub>2</sub> soil fluxes at Ohaaki and showed that surface emissions remain high (40.5 kt yr<sup>-1</sup> in 2006–2008 cf. 215 kt yr<sup>-1</sup> power plant emissions in 2011; McLean et al., 2024) after 20 years of production, although, as frequently is the case, a measured pre-development baseline is not available to judge whether it is different from its natural condition. Seward and Kerrick (1996) introduced a method to estimate CO<sub>2</sub> emissions based on CO<sub>2</sub> content of the liquid reservoir and heat flow through the geothermal system. Their method estimated 31.2 kt yr<sup>-1</sup> through the Ohaaki system (about 30% less than contemporary soil measurements) and 400 kt yr<sup>-1</sup> total for all New Zealand fields.

Bloomberg et al. (2014) and Yang et al. (2024) have both conducted CO<sub>2</sub> flux measurements at Rotokawa geothermal system (New Zealand). Yang et al. (2024) derived unified CO<sub>2</sub> emissions estimates of 141.2 kt yr<sup>-1</sup> in 2012 and 127.4 kt yr<sup>-1</sup> in 2021, substantially higher than the 20.2 kt yr<sup>-1</sup> estimated by Seward and Kerrick (1996). A large power plant (Ngā Awa Pūrua) was commissioned in 2011 that has likely driven reductions in reservoir CO<sub>2</sub> content that in turn may be reflected in reduced surface emissions. Although the reported emissions reduction between 2012 and 2021 supports this model, confidence intervals for the two estimates do overlap considerably making it difficult to be conclusive. Nevertheless, Yang et al. (2024) place the monetary value of this induced emissions reduction, in avoided emissions charges, on the order of 2.6 M \$NZ.

Óladóttir and Friðriksson (2015) analyzed 9 years of soil CO<sub>2</sub> flux data at Reykjanes geothermal area in Iceland and noted a substantial increase in emissions from 13.5 t d<sup>-1</sup> (0.16 kg s<sup>-1</sup>; 4.9 kt yr<sup>-1</sup>) in 2004 to 51.4 t d<sup>-1</sup> (0.60 kg s<sup>-1</sup>; 18.8 kt yr<sup>-1</sup>) in 2013. As this coincided with startup of a power plant in 2006, as well as an increase in surface heat flux accompanying development of a shallow boiling zone, it seems likely CO<sub>2</sub> surface fluxes were accelerated by the plant. Changes in CO<sub>2</sub> surface emissions in Iceland can also arise from natural drivers such as magmatism associated with the Krafla fires (Ármannsson et al., 2005). Werner et al. (2004) noted poor correlation between CO<sub>2</sub> and H<sub>2</sub>O flux in their survey, which suggests that changes in steam release or surface heat flow may not always be a good proxy for corresponding changes in CO<sub>2</sub> flux (as they do appear to be at Reykjanes, Iceland; Óladóttir & Friðriksson, 2015).

Taussi et al. (2023) measured CO<sub>2</sub> fluxes at the Larderello geothermal field in Italy, notably dividing their measurements into Central region close to production where average fluxes were lower (145 t d<sup>-1</sup> km<sup>-2</sup>), and Peripheral regions that were further away and, although cooler, had higher fluxes (508 t d<sup>-1</sup> km<sup>-2</sup>). They offer the possible explanation that this reflects a suppression of surface emissions from production, although this characterization depends in part on reconstructions of historic emissions that suggested pre-development fluxes were higher. The suggestion is further complicated by disparate isotopic compositions for Central and Peripheral regions that suggest separate CO<sub>2</sub> sources may be operating and could account for the flux differences.

Sbrana et al. (2021) measured CO<sub>2</sub> fluxes across several power producing and pristine regions of the Amiata geothermal field. They identified that regions with power plants had diffuse surface emissions that were lower than pristine regions by an amount similar to CO<sub>2</sub> from power production (about 50% in this case). Hence, they hypothesized that geothermal production suppresses surface emissions and further suggest that capture and reinjection of NCGs in geothermal power plants may not always achieve environmental goals if those captured NCGs simply restore the otherwise suppressed surface emissions.

### 1.3. Modeling Geothermal Systems and Their CO<sub>2</sub> Emissions

Changes in surface and power plant emissions can be matched and extrapolated using computer models (e.g., Kaya & Zarrouk, 2017; M. O'Sullivan et al., 2021). Geothermal modeling paradigms have largely moved

away from earlier lumped parameter ODEs (also called tank models, e.g., Axelsson, 1989; Fradkin et al., 1981; Sarak et al., 2005; Whiting & Ramey, 1969), toward the use of finely discretized simulators that capture heat and mass transfer physics on detailed geological structures and wellfield operations. For modeling geothermal CO<sub>2</sub> fluxes, there are relatively few simple models (Atkinson et al., 1980; Hosgor et al., 2016) that can be applied to estimate changes in power plant and surface emissions over time.

Early modeling studies of CO<sub>2</sub>-rich geothermal fields focused on the role of the CO<sub>2</sub> component in shifting the thermodynamic behavior of the reservoir. At Ohaaki, a high concentration of CO<sub>2</sub> causes boiling to 2 km depth under pre-development conditions. Both lumped parameter (Grant, 1977) and column models (M. J. O'Sullivan et al., 1985) emphasized the rapid initial pressure drop from CO<sub>2</sub> escaping the bores ("degassing") and the role of relative permeability. These early lumped representations traded spatial detail for analytical tractability, which meant that exact or near-exact solutions could be obtained. This meant that the dominant controls on pressure and phase behavior could be investigated, albeit at the cost of averaging said processes across the reservoir.

Subsequent models of Ohaaki have progressed toward higher spatial and temporal resolution (J. O'Sullivan et al., 2025; M. O'Sullivan et al., 2021), with a focus on improved geological modeling and history matching. These models are necessarily numerical in their solutions, but physical intuition has nevertheless been obtained through calibrated case studies and sensitivity analysis. As a result, M. O'Sullivan et al. (2021) suggest the pre-development CO<sub>2</sub> flux at Ohaaki to be approximately 140 kt yr<sup>-1</sup> substantially higher than the 30 kt yr<sup>-1</sup> estimated by Seward and Kerrick (1996). They further resolve discrete episodes of degassing associated with early production testing, a steady decline in surface emissions as the field is produced, and a multi-decade recovery to back to the pre-development equilibrium if the power plant was closed. The decline in surface emissions during production highlights the value of a holistic understanding of the field for emissions accounting. A feature of the M. O'Sullivan et al. (2021) model is that CO<sub>2</sub> mass input at the base of the model occurs at a fixed rate.

Recent modeling studies have turned toward the role of CO<sub>2</sub> reinjection in geothermal fields. Kaya and Zarrouk (2017) modeled reinjection of CO<sub>2</sub> and other gases into a generic geothermal reservoir and showed that a variety of impacts on the production are possible depending on injection strategy. Swanepoel et al. (2024) extended this to include injection of additional CO<sub>2</sub> beyond that captured from the field for negative emissions applications. They found a steady increase in CO<sub>2</sub> returning to the production wells. Recent advances have also included coupled reactions between dissolved CO<sub>2</sub> and reservoir minerals (Siahaan et al., 2024).

Analytical and semi-analytical lumped-parameter approaches have continued to provide insight into CO<sub>2</sub> inventories and system-level response. Hosgor et al. (2016) developed a lumped-parameter model that tracks the amount of dissolved CO<sub>2</sub> in a reservoir in response to production, reinjection, and recharge. Their formulation yielded closed-form solutions for CO<sub>2</sub> evolution under a range of reinjection scenarios, recovering the exponential decline in CO<sub>2</sub> concentration observed in New Zealand geothermal systems (McLean et al., 2024).

#### 1.4. Contribution of This Study

Three related issues emerge from this review of the literature. First, NCGs co-produced from geothermal reservoirs are increasingly captured and reinjected rather than discharged, and plant emissions tend to decline over the operating life of a field as the reservoir is depleted and diluted (Section 1.1). Second, production also perturbs the naturally discharging flux to the surface of CO<sub>2</sub>, through pressure and phase changes, with the size and sign of this change being difficult to measure and typically omitted from emissions accounting (Section 1.2). Third, while detailed numerical simulators can reproduce these behaviors, there remain few simple models able to track CO<sub>2</sub> across both the plant and the surface over time (Section 1.3).

The model developed in this study addresses these issues by providing closed-form solutions that couple reservoir pressure, dissolved CO<sub>2</sub> concentration, and plant and surface emissions, and by calibrating them to the declining emissions records of two New Zealand fields. Because current inventory practice applies empirical, data-driven emissions factors that do not represent these production-induced changes in natural surface flux, a physics-based description of the coupled reservoir and surface response is needed to attribute emissions correctly.

## 2. Methodology

This section develops a 0-dimensional lumped parameter (tank) formulation of a geothermal reservoir. The reservoir is conceptualized as a subpart of a larger convecting geothermal system that also comprises an upflow,

connected aquifers, a caprock and an overlying power station that extracts and returns water (Figure 1). Parameterizations are introduced for mass conservation, CO<sub>2</sub> solubility, Darcy flow, production and reinjection, boiling and mineralization, and surface flux losses. These physics are assembled under a single ordinary differential equation system that, when solved, outputs trajectories of reservoir pressure, dissolved CO<sub>2</sub> concentration, plant and surface emissions, and mineralized storage.

Although a tank model does not have the full spatial resolution of geothermal reservoir simulations, it nevertheless retains the relevant physics, namely Darcy-driven mass transfer between the reservoir and its surroundings, thermodynamic control of CO<sub>2</sub> solubility, and conservation of mass. However, the schematic has been styled on the convective, liquid-dominated systems that tend to abound in New Zealand and, although similar physics constrain geothermal systems in other geologic settings, modifications may be required if this model is to be applied more widely.

## 2.1. Reservoir Definition

The liquid reservoir is modeled as a cylindrical region of porous rock with upper surface area  $S$  [m<sup>2</sup>], vertical height  $H$  [m], volume  $V = SH$  [m<sup>3</sup>], and constant porosity  $\phi$  [–]. The mass of liquid water in the pore volume is  $M = V\rho\phi$ , where  $\rho$  [kg m<sup>–3</sup>] is the liquid density at the appropriate reservoir conditions.

Mass flow into and out of the reservoir,  $q$  [kg s<sup>–1</sup>], is assumed to be governed by Darcy's law and therefore proportional to the pressure difference between the reservoir and an external source or sink

$$q = \frac{k\rho A}{\mu} \frac{P - P_j}{L}, \quad (1)$$

where  $k$  is permeability [m<sup>2</sup>],  $\mu$  is viscosity [Pa s],  $A$  is the area across which the flow occurs [m<sup>2</sup>],  $P$  is hydrodynamic pressure of the reservoir [Pa] defined with respect to a liquid hydrostatic baseline, that is,  $P = 0$  corresponds to an aquifer at cold hydrostatic pressure,  $P_j$  is the external reference pressure, and  $L$  [m] is some characteristic distance across which the pressure drop occurs. Note, in this convention mass rates are negative if entering the reservoir and positive if leaving.

It is convenient to use a lumped version of Equation 1

$$q_i = K_i(P - P_j), \quad (2)$$

with  $K_i$  [m s] is a reservoir recharge coefficient that combines values of  $k$ ,  $\rho$ ,  $A$ ,  $\mu$  and  $L$  particular to the flow of interest.

The three flows considered here are: (a) an upflow that enters the reservoir from beneath, driven by buoyancy  $P_{up}$ , (b) a lateral outflow to connected aquifers at hydrostatic pressure ( $P_{aq} = 0$ ), and (c) a vertical outflow through a leaky caprock to the surface where  $P_{cap} = 0$ . Note, the outflow may reverse direction if pressure in the reservoir drops sufficiently.

Prior to pumping, the liquid reservoir is at initial pressure,  $P_0$ , and in a steady state ( $dP/dt = 0$ ), which requires all mass flows to balance:

$$-K_{up}(P_{up} - P_0) + K_{aq}P_0 + K_{cap}P_0 = 0, \quad (3)$$

from which initial reservoir pressure can be expressed as

$$P_0 = \frac{K_{up}}{K} P_{up}, \quad K = K_{up} + K_{out}, \quad (4)$$

where  $K$  is a total recharge coefficient for the reservoir that lumps the two outflows together ( $K_{out} = K_{cap} + K_{aq}$ ). These can be later disaggregated if it is useful to do so.

The lumped coefficients  $K_i$ ,  $M$ , and derived timescales  $t_p$  and others introduced later are reservoir-averaged quantities. Spatial variations in porosity  $\phi$  and permeability  $k$ , together with the flow geometry ( $A$ ,  $L$ ), are subsumed into the single recharge coefficient  $K_i$  of Equation 2 and into the stored liquid mass  $M = V\rho\phi$ . Variations in fluid density and viscosity with temperature, pressure, and dissolved-gas content are likewise folded into  $K_i$  (through  $\rho$  and  $\mu$  in Equation 1) and into  $M$ , and are not tracked explicitly. This choice trades spatial detail and some thermodynamic nuance for analytical tractability following the lumped tradition of Fradkin et al. (1981) and Sarak et al. (2005) with the effective coefficients determined by calibration to field data (Section 3.3). In a strongly heterogeneous reservoir this averaging means the model describes only the aggregate response and cannot resolve behavior at individual wells or locations. Changes in temperature due to reinjection could modify density and viscosity, and hence cause  $K$  to change over time, although additional modeling suggests this effect is second order (see Supporting Information S1).

The dependence of these coefficients on time could be made explicit by accounting for evolving pressure or temperature of the reservoir fluid. Density varies with pressure and temperature via compressibility and thermal expansivity properties, while porosity varies with pore pressure through the pore (rock) compressibility. Because  $M = V\rho\phi$  and  $K \propto k\rho/\mu$  (Equation 1), both in principle could be time dependent,  $M = M(t)$  and  $K = K(t)$ , as the reservoir depressurizes and cools. These effects have been partially modeled in the Supporting Information S1 and are likely to be second order when averaged over the reservoir. However, the effects could be locally important such as in the vicinity of wells in which case full-fidelity reservoirs simulations should be used.

## 2.2. Reservoir Production, Mass Conservation, and Pressure Evolution

When production occurs from the liquid reservoir, its pressure will decrease over time. Here, the reservoir is assumed to be extracted from at a constant pumping rate,  $q_0$ , with a fraction of the produced mass reinjected for pressure support (the remaining mass is discharged elsewhere). If the reinjection rate is  $(1 - f_q)q_0$  then net extraction is  $f_q q_0$  with  $f_q = 1$  corresponding to zero reinjection and  $f_q = 0$  full reinjection. Under a net extraction condition ( $f_q > 0$ ), pressure in the reservoir is expected to decline, and the upflow and outflows to adjust per Equation 2.

Following Fradkin et al. (1981), pressure evolution in the reservoir is approximated by a tank model with a linear response term

$$\frac{dP}{dt} = \underbrace{-a_p f_q q_0}_{\text{pumping}} - \underbrace{b_p (P - P_0)}_{\text{linear response}}, \quad (5)$$

where, for a reservoir overlaid by a two-phase boiling region, pressure changes reflect an instantaneously dropping liquid level (instant drainage),

$$a_p = \frac{g}{S\phi}, \quad b_p = \frac{Kg}{S\phi}, \quad (6)$$

where  $g$  is the acceleration due to gravity [ $\text{m s}^{-2}$ ]. As  $b_p$  has units of inverse time, the formulation can be re-expressed in terms of a characteristic time  $t_p$  that quantifies how rapidly system pressure responds to extraction. Furthermore, the ratio of  $a_p$  and  $b_p$  can be used to approximate  $K$ . As  $K$  and  $t_p$  are a physically interpretable pair, they can be inferred by calibration to production drawdown data, for example, Fradkin et al. (1981) estimated  $a_p = 3.1 \times 10^{-6} \text{ m}^{-1} \text{ s}^{-2}$ ,  $b_p = 3.0 \times 10^{-9} \text{ s}^{-1}$ , equivalent to  $t_p = 10 \text{ yr}$  and  $K \approx 10^{-3} \text{ m s}$  for Wairakei.

$$K = \frac{b_p}{a_p}, \quad t_p = \frac{1}{b_p}. \quad (7)$$

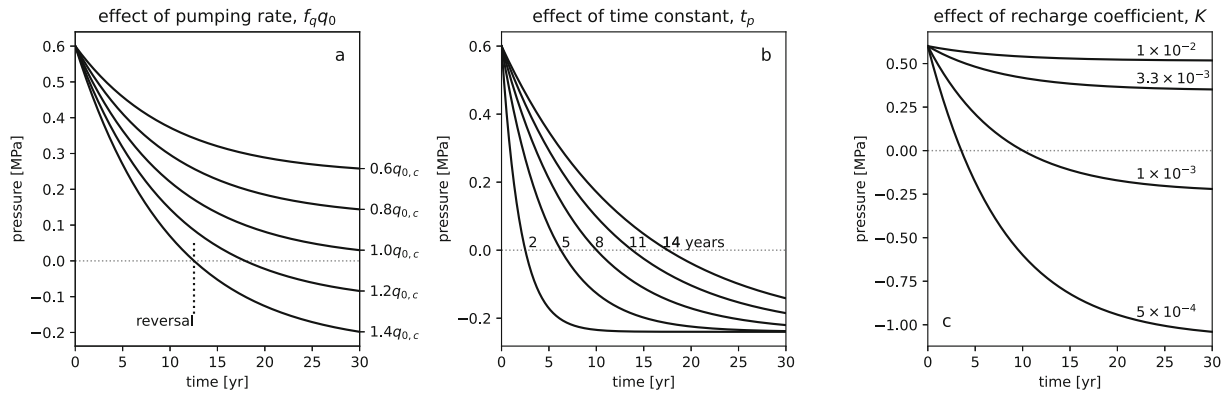


**Figure 2.** Relative pressure of a reservoir responding to continued pumping ( $K_{up} = K_{out} = 10^{-3}$  m s,  $P_{up} = 1.2$  MPa,  $P_0 = 0.6$  MPa). (a) Effect of pumping rate  $f_q q_0$  expressed as a fraction of the critical rate  $q_{0,c}$ , with  $t_p = 10$  yr. Pumping rates exceeding  $q_{0,c}$  cause reversal of the outflow. (b) Effect of pressure equilibration timescale  $t_p$  (2–14 years), with  $f_q q_0 = 1.4 q_{0,c}$ . (c) Effect of recharge coefficient  $K$  ( $5 \times 10^{-4}$  to  $10^{-2}$  m s) at fixed effective pumping rate.

Equation 5 has the exponential solution (Figure 2)

$$P = P_0 - \frac{f_q q_0}{K} (1 - e^{-t/t_p}) = P_0 - (P_0 - P_\infty) (1 - e^{-t/t_p}), \quad (8)$$

where the new steady pressure limit is  $P_\infty = P_0 - f_q q_0 / K$ .

Mass flows into and out of the reservoir also now have an exponential character, with  $q_{up}$  and  $q_{out}$  obtained by combining Equations 2, 4, and 8:

$$q_{up} = -\frac{K_{up}}{K} (P_{up} K_{out} + f_q q_0 (1 - e^{-t/t_p})) \quad (9)$$

$$q_{out} = \frac{K_{out}}{K} (P_{up} K_{up} - f_q q_0 (1 - e^{-t/t_p})). \quad (10)$$

The second term in Equation 9 is an induced upflow,  $\Delta q_{up}$ , which has the limit  $\Delta q_{up} \rightarrow -K_{up} f_q q_0 / K$ , reflecting additional hot upflow drawn into the reservoir as the reservoir's pressure declines.

In a similar fashion, if net extraction is large enough, then the reservoir outflow will reverse, occurring when the two terms in Equation 10 balance each other. The critical pumping rate to trigger a reversal is

$$q_{0,c} = K P_0 = K_{up} P_{up}, \quad (11)$$

and the reversal itself occurs at a time  $t_r$  given by

$$t_r = t_p \ln \left( \frac{f_q q_0}{f_q q_0 - q_{0,c}} \right) \quad (12)$$

### 2.2.1. Reservoir Residence Time

A useful characterization of the geothermal system is its residence time, defined as the ratio of fluid mass stored in the reservoir to the mass throughput rate,

$$t_{res} = \frac{M}{|q_{up}|}. \quad (13)$$

This quantity measures the characteristic time that a fluid parcel, and any dissolved species such as  $\text{CO}_2$ , resides in the reservoir before exiting via the outflow or extraction wells.

In the pre-development state, the upflow and outflow rates balance ( $|q_{up,0}| = q_{out,0}$ ), where these natural-state values follow from Equations 9 and 10 evaluated before production ( $f_q q_0 = 0$ ), and the residence time is

$$t_{res,0} = \frac{M}{|q_{up,0}|} = \frac{MK}{K_{up}K_{out}P_{up}}. \quad (14)$$

After extraction begins, the reservoir depressurizes and additional upflow is drawn into the reservoir (Equation 9). At the new steady state, the upflow magnitude is

$$|q_{up,\infty}| = \frac{K_{up}}{K} (K_{out}P_{up} + f_q q_0) = |q_{up,0}| + \frac{K_{up}}{K} f_q q_0, \quad (15)$$

which always exceeds the natural upflow because the induced upflow term  $K_{up}f_q q_0/K$  is strictly positive. Consequently, the post-development residence time

$$t_{res,\infty} = \frac{M}{|q_{up,\infty}|} < t_{res,0}, \quad (16)$$

is always shorter than the pre-development value. Physically, extraction accelerates the throughput of deep fluid and CO<sub>2</sub> through the reservoir.

### 2.3. Governing Equation for CO<sub>2</sub> Mass Balance and Concentration

This study's analysis principally deals with CO<sub>2</sub> that is dissolved in the reservoir fluid. The mass of CO<sub>2</sub> in the reservoir,  $M_{CO_2}$ , is thus characterized by its concentration  $C$  [kg CO<sub>2</sub> kg<sup>-1</sup> H<sub>2</sub>O], here expressed as a mass fraction,  $C = M_{CO_2}/M$ . Note, this study does not track additional NCGs beyond CO<sub>2</sub>, such as the smaller mole fractions of H<sub>2</sub>S and CH<sub>4</sub> sometimes reported. These are assumed not to materially alter the CO<sub>2</sub> mass balance or its solubility-controlled partitioning, an assumption supported by the high CO<sub>2</sub> fraction of dissolved gas in the New Zealand reservoirs considered here (Ghafari et al., 2022).

Under steady, pre-development conditions, CO<sub>2</sub> enters the reservoir via the upflow at a concentration  $C_0$ . The reservoir and outflows are at the same concentration.

A mass-balance of CO<sub>2</sub> in the liquid part of the reservoir is

$$M \frac{dC}{dt} = \underbrace{-q_{up}(t)C_{up}}_{\text{upflow}} - \underbrace{q_0 C(t)}_{\text{extract}} + \underbrace{(1-f_c)q_0 C(t-\tau)}_{\text{(delayed) reinjection}} - \underbrace{q_{out} C'(t)}_{\text{outflow/reversal}} - \underbrace{\kappa(C(t) - C_r)}_{\text{chemical reactions}} - \underbrace{Q_{dg}(\dot{P}(t))}_{\text{degas}}, \quad (17)$$

where the time dependence of relevant terms has been made explicit for clarity. This expression captures the following reservoir processes:

1. Changes in upflow or outflow under the evolving pressure regime. If the reservoir is outflowing, then CO<sub>2</sub> exits at the reservoir concentration,  $C' = C(t)$ . If there is an outflow reversal, then  $C' = C_{out}$ , which would typically be set to zero. Flow rates  $q_{up}$  and  $q_{out}$  are exponential functions of time given by Equations 9 and 10.
2. Removal of CO<sub>2</sub> from the reservoir via extraction at  $q_0$ , but allowing that some portion of this CO<sub>2</sub> may be directly returned to the subsurface via reinjection, and later arrive at the reservoir after time  $\tau$ . The effective rate of removal of CO<sub>2</sub> from the reservoir is parameterized by  $f_c$ . Similar to  $f_q$ , a value of  $f_c = 1$  corresponds to no capture and reinjection of produced CO<sub>2</sub> whereas  $f_c = 0$  corresponds to full reinjection of captured CO<sub>2</sub> directly into the reservoir. In practice, only a proportion of the reinjected CO<sub>2</sub> returns to the producing reservoir, a partial-return case that is examined later through the return fraction  $\eta$  (Section 4.3). Furthermore, this return may be smeared over a finite time, owing to dispersion of the injected volume on its passage back to

- the reservoir. Although such effects are readily treated in tracer-recovery models, they have not been considered here.
3. A first-order chemical reaction that buffers dissolved CO<sub>2</sub> through a precipitation-dissolution reaction. The reaction rate depends on disequilibrium relative to a reference concentration  $C_r$ , which can be set to zero for mineralization only, or non-zero for reversible reactions. A possible choice is that the equilibrium concentration is the initial concentration, that is,  $C_r = C_0$ , reflecting a reservoir liquid in equilibrium with the host rock. The constant  $\kappa$  [kg s<sup>-1</sup>] moderates the rate of reaction and may depend on kinetics, surface area or other factors. This formulation does not account for exhaustion of the reservoir's buffering capacity or the effects of temperature and pH on reaction rate.
  4. A degassing term  $Q_{dg}$  [kg CO<sub>2</sub> s<sup>-1</sup>] that tracks the loss of CO<sub>2</sub> mass into a gas phase through pressure driven reduction of CO<sub>2</sub> solubility. If reservoir storage of CO<sub>2</sub> becomes saturated, limited by the solubility  $C_s(P)$ , then excess CO<sub>2</sub> carried into the reservoir by the upflow is partitioned with  $C_{up} = C_s(P)$  entering the reservoir and the balance contributing to steady degassing. For simplicity, its time dependence is ignored and  $C_{up} = C_s(P_\infty) = C_{s,\infty}$ .

### 2.3.1. Saturation Effects

The maximum possible concentration of CO<sub>2</sub> in the liquid phase is determined by its solubility  $C_s$ . The solubility in turn depends on temperature, and pressure, the latter exercising an approximately linear effect

$$C_s = \left. \frac{dC_s}{dP} \right|_T (P - P_{s,ref}) + C_{s,ref}, \quad (18)$$

where  $P_{s,ref} = 1.5$  MPa,  $C_{s,ref} = 0.01$  are the reference pressure and concentration about which the solubility is linearized. Because the solubility is close to linear in pressure over the range of interest, the choice of reference point is arbitrary and any point within the validity window given below yields the same approximation. The linear slope parameter  $dC_s/dP$  [wt% MPa<sup>-1</sup>] is a quadratic function of temperature (see Appendix A). Equation 18 is correct to about 1% for  $P$  between 5 and 15 MPa and  $T$  between 150 and 280°C. Solubility here is evaluated from the pure-water model of Duan and Sun (2003) (Appendix A), with the gas phase taken to be pure CO<sub>2</sub> and salinity effects neglected. This is a reasonable approximation for the high-pressure, liquid-dominated reservoirs considered here, but it will overestimate solubility where steam or other NCGs occupy a substantial fraction of the gas-phase pressure. This shortcoming might be addressed by developing a second coupled ODE to better describe the gas-phase, which is identified as follow-up work.

Thus, for a liquid reservoir that is CO<sub>2</sub>-saturated ( $C = C_s$ ), depressurization will induce an amount of degassing and CO<sub>2</sub> loss in proportion to the reduction in solubility

$$Q_{dg}(t) = M \left. \frac{dC_s}{dP} \right|_T \frac{dP}{dt} = \frac{f_q q_0 M}{K t_P} \left. \frac{dC_s}{dP} \right|_T e^{-t/t_P}, \quad (19)$$

and hence the degassing rate is exponential and principally controlled by net extraction.

### 2.3.2. Boiling Effects

For reservoirs close to the boiling-point-for-depth curve, depressurization may lead to boiling. As the two-phase reservoir boils, it cools and follows the saturation curve,  $T_{sat}(P)$ . Thus, degassing must account for both temperature and pressure changes as solubility moves along this curve  $C_s(P, T_{sat}(P))$ . The degassing rate becomes:

$$Q = \frac{f_q q_0 \rho g}{H} \underbrace{\left( \frac{\partial C_s}{\partial P} + \frac{\partial C_s}{\partial T} \frac{\partial T_{sat}}{\partial P} \right)}_{\text{derivative along saturation curve}} \Big|_T e^{-t/t_P}, \quad (20)$$

which is similar to Equation 19 apart from the derivative term. Fortunately, this derivative is approximately constant for pressures less than 11 MPa. The solubility is retrograde above 12 MPa (see Appendix A).

In addition to degassing, CO<sub>2</sub> exits alongside the boiled liquid component and commingles with steam in the overlying gas cap (Grant, 1977; M. J. O'Sullivan et al., 1985). Increased gas outflow rates reflecting viscosity or buoyancy changes have not been considered.

#### 2.4. Geothermal Emissions Accounting

The total CO<sub>2</sub> emission rate from a geothermal system is the sum of both surface emissions, which may potentially be modified from their natural level,  $Q_{\text{surf},0}$ , and plant emissions.

$$Q_{\text{total}} = Q_{\text{surf},0} + \Delta Q_{\text{surf}} + Q_{\text{plant}}. \quad (21)$$

Here  $Q_{\text{surf},0}$  denotes the natural (pre-development) surface emission rate, that is, the baseline flux that would occur in the absence of production, while  $\Delta Q_{\text{surf}}$  is the production-induced change in surface emission, which may be positive (e.g., enhanced by degassing or induced upflow) or negative (e.g., suppressed as outflow declines). Their sum  $Q_{\text{surf},0} + \Delta Q_{\text{surf}} = Q_{\text{surf}}$  is the actual post-development surface emission modeled in Equation 23.

Emissions attributable to an anthropogenic activity, namely development of the geothermal system for power production, are defined (after M. O'Sullivan et al., 2021).

$$Q_{\text{anthropogenic}} = Q_{\text{total}} - Q_{\text{surf},0} = Q_{\text{plant}} + \Delta Q_{\text{surf}}(Q_{\text{plant}}). \quad (22)$$

In this model, surface emissions comprise the sum of outflow and degassing

$$Q_{\text{surf}}(t) = q_{\text{out}}(t) C(t) + Q_{\text{dg}}(t), \quad (23)$$

where the outflow term  $q_{\text{out}}(t) C(t)$  is the product of the mass flow rate leaving through the caprock and connected aquifers and the reservoir CO<sub>2</sub> concentration, and the degassing term (Equation 19) accounts for CO<sub>2</sub> exsolved due to depressurization-induced solubility reduction. Note that if a proportion of the degassed CO<sub>2</sub> is considered to be permanently stored as a buoyant gas beneath the caprock, or if some dissolved CO<sub>2</sub> exiting via the outflow remains permanently stored in shallow aquifers, then a proportional reduction to these emissions terms should be applied.

Plant emissions are defined as the portion of extracted CO<sub>2</sub> that is not captured and hence assumed to be released to the atmosphere

$$Q_{\text{plant}}(t) = f_C q_0 C(t). \quad (24)$$

From Equation 23, it is clear that changes in surface emissions can arise from either a change in the outflow rate  $q_{\text{out}}$  or a change in reservoir concentration  $C$ . The former is governed by the pressure response of the system (Equation 10), while the latter evolves according to the CO<sub>2</sub> mass balance (Equation 17).

During early-time when extraction is driving reservoir depressurization, surface emissions could be suppressed through a reduction of  $q_{\text{out}}$  or alternatively increased due to degassing,  $Q_{\text{dg}}$ . Additionally,  $C$  may increase or decrease depending on the balance of CO<sub>2</sub> extraction, reinjection returns, chemical reactions, and induced upflow of fresh CO<sub>2</sub>-bearing fluid. Thus, even if the outflow rate is reduced over the long-term, a compensating increase in CO<sub>2</sub> concentration could maintain or elevate surface emissions. These mechanisms allow the model to represent a production-driven acceleration of surface CO<sub>2</sub> flux of the kind inferred at Reykjanes (Section 1.2). Depressurization drives boiling-driven degassing,  $Q_{\text{dg}}$ , whose duration is expected to coincide with the pressure decline and hence with the pressure-equilibration timescale  $t_p$ .

#### 2.5. Solutions to the Governing Equation

Various solutions can be obtained for Equation 17 under suitable approximations.

### 2.5.1. Instantaneous ReInjection Returns ( $\tau = 0$ )

The  $\text{CO}_2$  balance is considerably simplified when the  $C(t - \tau)$  term is eliminated. This arises in three cases: (a) no  $\text{CO}_2$  is reinjected into the reservoir ( $f_c = 1$ ), (b)  $\text{CO}_2$  is reinjected far enough away that it never returns to the reservoir ( $\tau = \infty$ , equivalent to  $f_c = 1$ ), and (c)  $\text{CO}_2$  is immediately captured and reinjected directly into the reservoir ( $\tau = 0$ ).

A general form of the  $\text{CO}_2$  balance covering the above three cases is

$$\frac{dC}{dt} = \alpha - \beta C - \gamma C e^{-t/t_p} - \delta e^{-t/t_p}, \quad (25)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are constants defined as:

$$\begin{aligned} \alpha &= \frac{C_0}{M} \left( \kappa \frac{C_r}{C_0} + \frac{C_{s,\infty}}{C_0} \frac{K_{\text{up}}}{K} (P_{\text{up}} K_{\text{out}} + f_q q_0) \right) = \frac{C_0}{t_\alpha} \\ \beta &= \frac{1}{M} \left( f_c q_0 + \kappa + \frac{K_{\text{out}}}{K} (K_{\text{up}} P_{\text{up}} - f_q q_0) \right) = \frac{1}{t_\beta} \\ \gamma &= \frac{f_q q_0}{M} \frac{K_{\text{out}}}{K} = \frac{1}{t_q} \frac{K_{\text{out}}}{K} \\ \delta &= \frac{1}{t_q} \left( \frac{K_{\text{up}}}{K} C_{s,\infty} + \frac{M}{K t_p} \frac{dC_s}{dP} \right), \end{aligned} \quad (26)$$

where three new time scales have been introduced:

1. Loss of  $\text{CO}_2$  from the reservoir over time  $t_\beta$ , which is sensitive to the effective  $\text{CO}_2$  extraction ( $f_c$ ), chemical reactions ( $\kappa$ ) and outflows ( $K_{\text{out}}$ ).
2. Restoration of  $\text{CO}_2$  over time  $t_\alpha$ , which is sensitive to chemical reactions ( $\kappa$ ) and the degassing upflow ( $K_{\text{out}}$ ).
3. A reservoir flushing time  $t_q$  that measures how long it takes to replace the reservoir pore fluid mass ( $M$ ) at the effective extraction rate ( $f_q q_0$ ).

Note, if the reservoir is not initially saturated and does not reach saturation during depressurization, then degassing can be neglected and the second term inside the brackets for  $\delta$  is dropped.

A solution to Equation 25 satisfying the initial condition  $C(t = 0) = C_0$  is

$$C' = \exp(-bt' + ce^{-t'}) (C'_0 e^{-c} + a(c)^b I(t'; b, c)), \quad (27)$$

where

$$\begin{aligned} I(t; b, c) &= \int_{ce^{-t}}^c s^{-b-1} e^{-s} ds \\ C' &= C + \delta/\gamma, \quad t' = t/t_p \\ a &= (\alpha + \beta\delta/\gamma)t_p, \quad b = t_p/t_\beta, \quad c = \gamma t_p. \end{aligned} \quad (28)$$

The integral  $I(t; \cdot)$  involves gamma functions that must be evaluated numerically. However, the solution has an exponential-like character that can be approximated as

$$C = \underbrace{C_\infty}_{\text{new eq}^m \text{ conc.}} + \underbrace{\Delta C_\beta e^{-t/t_\beta}}_{\text{"fast" reservoir with CO}_2 \text{ bottlenecks}} + \underbrace{\Delta C_P e^{-t/t_p}}_{\text{"slow" reservoir conc in quasi eq}^m}, \quad (29)$$

where the system's new steady state  $C_\infty$  trades off  $\text{CO}_2$  loss and restoration times, with the additional constants

$$\begin{aligned} C_{\infty} &= \frac{\alpha}{\beta}, \quad \Delta C = C_0 - C_{\infty} \\ \dot{C}_0 &= \alpha - (\beta + \gamma) C_0 - \delta \\ \Delta C_P &= \frac{t_P}{t_P - t_{\beta}} \Delta C + \frac{t_{\beta} t_P}{t_P - t_{\beta}} \dot{C}_0 \\ \Delta C_{\beta} &= -\frac{t_{\beta}}{t_P - t_{\beta}} \Delta C - \frac{t_{\beta} t_P}{t_P - t_{\beta}} \dot{C}_0. \end{aligned} \quad (30)$$

A second exponential form is obtained in the event of an outflow reversal that draws freshwater into the reservoir ( $C_{\text{out}} = 0$ ). In this case, a piecewise solution is obtained:  $C(t)$  is given by Equation 27 prior to the reversal ( $t < t_r$ ), obtaining the intermediate concentration  $C_1$  at  $t = t_r$ . Thereafter, Equation 25 is modified so that  $\gamma = 0$ , and  $\beta' = (f_c q_0 + \kappa)/M = 1/t'_{\beta}$ , with initial condition  $C(t = t_r) = C_1$ . The solution has the same structure as Equation 29 but with modified expressions for  $C_{\infty}$ ,  $\Delta C_{\beta}$  and  $\Delta C_P$ , and  $t'_{\beta}$  replacing  $t_{\beta}$ .

$$\begin{aligned} C_{\infty} &= \frac{\alpha}{\beta}, \\ \Delta C_P &= -\frac{\delta}{\beta' - 1/t_P}, \\ \Delta C_{\beta} &= (C_1 - C_{\infty} - \Delta C_P e^{-t_r/t_P}) e^{t_r/t_{\beta'}}. \end{aligned} \quad (31)$$

### 2.5.2. Delayed Reinjection Returns ( $\tau \neq 0$ )

The impact of delayed reinjection returns can be analytically resolved only when pressure is approximately steady. This occurs when  $\tau$  is very small or very large compared to  $t_P$ , corresponding to  $P = P_0$  or  $P = P_{\infty}$ . In both cases, mass fluxes are approximately constant and the appropriate replacement is made  $q_i = q_{i,0}$  or  $q_{i,\infty}$  where  $i = [\text{up}, \text{out}]$  in Equation 17.

The  $\text{CO}_2$  mass balance is now written

$$\begin{aligned} M \frac{dC}{dt} &= \underbrace{-q_{\text{up},\infty} C_0}_{\text{upflow}} - \underbrace{q_0 C(t)}_{\text{extract}} + \underbrace{(1 - f_c) q_0 C(t - \tau)}_{\text{(delayed)reinjection}} \\ &\quad - \underbrace{q_{\text{out},\infty} C'(t)}_{\text{outflow/reversal}} - \underbrace{\kappa(C(t) - C_r)}_{\text{chemical reactions}}, \end{aligned} \quad (32)$$

or in the simpler form of a delay differential equation

$$\frac{dC}{dt} = \alpha - \beta_0 C(t) + \beta_{\tau} C(t - \tau), \quad (33)$$

where constants  $\beta_0$  and  $\beta_{\tau}$  describe immediate removing and delayed concentrating responses of the reservoir.

$$\begin{aligned} \alpha &= \frac{C_0}{M} \left( \kappa \frac{C_r}{C_0} + \frac{K_{\text{up}}}{K} (P_{\text{up}} K_{\text{out}} + f_c q_0) \right) = \frac{C_0}{t_{\alpha}}, \\ \beta_0 &= \frac{1}{M} \left( q_0 + \kappa + \frac{K_{\text{out}}}{K} (q_{0,c} - f_c q_0) \right) = \frac{1}{t_{\beta}}, \\ \beta_{\tau} &= \frac{1}{M} (1 - f_c) q_0. \end{aligned} \quad (34)$$

Note that when  $\tau = 0$ , then  $\beta_0 - \beta_{\tau} = \beta$  recovering the earlier form of Equation 25. In the event of a reversal that draws in water with  $C_{\text{out}} = 0$ , the modified coefficient is used  $\beta_0 = (q_0 + \kappa)/M$ .

To solve the equation, a supplementary function is required to describe concentration in the period  $[-\tau, 0]$ , which in this case is chosen to be  $C(t) = 0$ , denoting no return of reservoir fluids.

The solution to Equation 33 is expressed in an exponential basis

$$\begin{aligned} C &= C_{\infty}^{(\tau)} + \sum_{k=1}^N A_k e^{-\lambda_k t} \\ \lambda_k &= \beta_0 - \frac{1}{\tau} W_k(\beta_{\tau} \tau e^{\beta_0 \tau}) \\ C_{\infty}^{(\tau)} &= \frac{\alpha}{\beta_0 - \beta_{\tau}}, \quad C_{\infty}^{(0)} = \frac{\alpha}{\beta_0} \\ A_k &= \frac{C_0 - \alpha/\lambda_k}{1 + \beta_{\tau} \tau e^{\lambda_k \tau}}, \end{aligned} \quad (35)$$

where  $W_k(\cdot)$  is the  $k$ th branch of the Lambert-W function.

At early time when  $t < \tau$  there are no returns from the reservoir, in which case the solution is exponentially declining for the case that  $\beta_{\tau} = 0$ .

At late time, the highest frequency values of  $\lambda_k$  decay away and the solution is dominated by the slowest decaying term  $\lambda_1$ . The approximate closed form solution becomes

$$C(t) = \begin{cases} C_{\infty}^{(0)} + (C_0 - C_{\infty}^{(0)}) e^{-\beta_0 t}, & t < \tau, \\ C_{\infty}^{(\tau)} + \frac{C_0 - \alpha/\lambda_1}{1 + \beta_{\tau} \tau e^{\lambda_1 \tau}} e^{-\lambda_1 t}, & t \gg \tau. \end{cases} \quad (36)$$

The solution sometimes overshoots on the initial dilution pathway, with the return restoring the system to a higher equilibrium concentration. Overshoot occurs when the term

$$C_0 - \frac{\alpha}{\lambda_1} < 0 \quad \text{or} \quad \lambda_1 < \frac{1}{t_a}. \quad (37)$$

### 2.5.3. Verification of the Closed-Form Solutions

Detailed verification of these solutions is included in Supporting Information S1 with only a summary presented here. First, the incomplete-gamma and Lambert-W solutions are verified against an independent forward-Euler integration of the governing equations, agreeing to a relative error below  $10^{-3}$ . Second, in the limiting case of no degassing, no reactions and no delay, the balance reduces to  $dC/dt = \alpha - \beta C$  and recovers the lumped-parameter form of Hosgor et al. (2016). Third, a single-block simulation in the reservoir simulator FEHM (Zyvoloski, 2007), carrying a full water and  $\text{CO}_2$  equation of state, reproduces the pressure, concentration and flux behavior of the closed-form solutions and matches the degassing rate on depressurization. Finally, a further non-isothermal FEHM case indicates that cold reinjection does not significantly shift model predictions under sustained cooling.

## 2.6. Equilibrium States

The solutions developed above describe trajectories that approach new steady states for reservoir concentration and emissions at long time. These equilibria can be obtained either in the  $t \rightarrow \infty$  limit of the explicit solutions (Equations 8, 29, and 35), or by setting  $dP/dt = dC/dt = 0$  directly in the governing equations (Equations 5 and 25) and discarding the exponential transients.

### 2.6.1. Steady-State Concentration

At long time, pressure-driven exponential terms in Equation 25 decay away and the ODE reduces to  $0 = \alpha - \beta C_{\infty}$ , giving

$$C_{\infty} = \frac{\alpha}{\beta}, \quad (38)$$

which is also the constant offset in the approximate solution Equation 29.

For a non-reactive reservoir ( $\kappa = 0$ ), substituting the definitions of  $\alpha$  and  $\beta$  from Equation 26 yields the expanded form

$$C_{\infty} = C_{s,\infty} \left( 1 + q_0 K \frac{f_c - f_q}{K_{\text{out}} q_{0,c} + f_q q_0 K_{\text{up}}} \right)^{-1}, \quad (39)$$

where  $C_{s,\infty} = C_0$  for an undersaturated reservoir and  $C_{s,\infty} = C_s(P_{\infty}) \leq C_0$  when solubility is limiting the amount of dissolved  $\text{CO}_2$ . When fluid and  $\text{CO}_2$  reinjection are balanced ( $f_c = f_q$ ), concentration changes reflect pressure-solubility effects only ( $C_{\infty} = C_{s,\infty}$ ). Imbalanced reinjection drives the reservoir to a diluted ( $f_c > f_q$ ) or concentrated ( $f_c < f_q$ ) state, although the concentrating scenario should strictly only apply for undersaturated systems, otherwise excess  $\text{CO}_2$  would be expected to immediately exsolve. For a reactive reservoir,  $\kappa$  appears in both  $\alpha$  and  $\beta$  of Equation 38, tending  $C_{\infty}$  toward  $C_r$  as mineralization dominates. If the outflow reverses,  $\beta$  is modified per Equation 31.

For delayed reinjection returns ( $\tau > 0$ ), the equivalent result from Equation 35 is

$$C_{\infty}^{(\tau)} = \frac{\alpha}{\beta_0 - \beta_{\tau}}, \quad (40)$$

which always exceeds the immediate-return equilibrium  $C_{\infty}^{(0)} = \alpha/\beta_0$  for any non-zero  $\beta_{\tau}$ .

### 2.6.2. Surface and Plant Emissions

At steady state, the outflow rate is  $q_{\text{out},\infty} = K_{\text{out}}(K_{\text{up}}P_{\text{up}} - f_q q_0)/K$  (positive for  $f_q q_0 < q_{0,c}$ , zero after reversal) and the upflow rate magnitude is  $|q_{\text{up},\infty}| = K_{\text{up}}(K_{\text{out}}P_{\text{up}} + f_q q_0)/K$ . Substituting into Equations 23 and 24 gives

$$Q_{\text{surf},\infty} = q_{\text{out},\infty} C_{\infty} + Q_{\text{dg},\infty}, \quad (41)$$

$$Q_{\text{pp},\infty} = f_c q_0 C_{\infty}, \quad (42)$$

where the residual steady-state degassing is

$$Q_{\text{dg},\infty} = |q_{\text{up},\infty}| \max(0, C_0 - C_{s,\infty}). \quad (43)$$

This term captures the  $\text{CO}_2$  fraction of the upflow that exceeds solubility at the new reservoir pressure and hence degasses rather than dissolving.

An equivalent and compact expression for  $Q_{\text{surf},\infty}$  follows directly from a steady-state  $\text{CO}_2$  mass balance: input via the upflow must equal output through the surface and the plant. For a non-reactive reservoir this gives

$$Q_{\text{surf},\infty} = |q_{\text{up},\infty}| C_0 - Q_{\text{pp},\infty} = \underbrace{\frac{K_{\text{up}} K_{\text{out}}}{K} P_{\text{up}} C_0}_{\text{pre-development surface emissions}} + \underbrace{\frac{K_{\text{up}}}{K} f_q q_0 C_0}_{\text{induced upflow}} - \underbrace{f_c q_0 C_{\infty}}_{\text{plant}}. \quad (44)$$

The first term is precisely the pre-development surface emission rate

$$Q_{\text{surf},0} = q_{\text{out},0} C_0 = \frac{K_{\text{up}} K_{\text{out}}}{K} P_{\text{up}} C_0, \quad (45)$$

and Equation 44 shows that post-development surface emissions are elevated by the induced upflow and reduced by any  $\text{CO}_2$  diverted to the plant. The total  $Q_{\text{surf},\infty} + Q_{\text{pp},\infty} = |q_{\text{up},\infty}|C_0$ , which always exceeds  $Q_{\text{surf},0}$  because the induced upflow term is strictly positive.

### 3. Results

This section presents model findings in three stages. First, representative parameter ranges for New Zealand geothermal systems are established (Section 3.1, Table 2). Second, a sequence of illustrative scenarios isolates the physical mechanisms that drive changes in emissions, including degassing in  $\text{CO}_2$  saturated fields, dilution in undersaturated fields, mineralization, outflow reversal, and the delayed return of reinjected  $\text{CO}_2$  (Section 3.2). Third, the model is calibrated to the measured emissions records of the Rotokawa and Ngā Tamariki fields (Section 3.3), yielding the field-specific parameters used in the Discussion.

#### 3.1. Parameter Ranges for New Zealand Geothermal Systems

Reservoir liquid mass,  $M$ , controls the responsiveness of concentration changes, with larger masses taking comparatively longer to shift (Equation 26). For parameter orders representative of New Zealand geothermal fields ( $S \sim 10 \text{ km}^2$ ,  $H \sim 100\text{--}1,000 \text{ m}$ ,  $\rho \sim 10^3 \text{ kg m}^{-3}$ ,  $\phi \sim 0.1$ , with field areas after Bibby et al. (1995)), the liquid mass  $M$  is of the order of  $10^{11}\text{--}10^{12} \text{ kg}$ . However, it is reasonable to expect order of magnitude variation in this parameter arising from reservoir compartmentalization or in fracture-dominated systems with low porosity.

Initial overpressure (relative to hydrostatic) controls the strength of upflow into the reservoir and when extraction could lead to an outflow reversal. Grant and Bixley (2011) suggest typical pressure conditions in New Zealand geothermal reservoirs are about 10% higher than hydrostatic. Taking an illustrative reservoir at 600 m, where the cold-hydrostatic baseline is a round  $\sim 6 \text{ MPa}$ , this corresponds to  $P_0 \sim 0.6 \text{ MPa}$ . This depth is chosen only to fix a representative baseline for the illustrative scenarios that follow (Figures 3–6). The deeper, hotter production zones of the case-study fields reported later (Section 3.3) have parameters drawn from field reports. Once a target  $P_0$  is specified,  $P_{\text{up}}$  is computed from (Equation 4) on the basis of the split between  $K_{\text{up}}$  and  $K_{\text{out}}$ , with  $P_{\text{up}} = 1.2 \text{ MPa}$  for the simple case of  $K_{\text{up}} \approx K_{\text{out}}$  tested first here. Unequal values are considered later for fields with suitable emissions data to determine their values through calibration.

Reservoir recharge coefficients,  $K_i$ , control how rapidly and by how much the reservoir pressure responds to extraction (Equation 7). Fradkin et al. (1981) describe an improved version of Equation 5 that accounts for non-instantaneous drop of the reservoir liquid level. Applying this model to production data from Wairakei, they inferred  $a_p = 3.1 \times 10^{-6} \text{ m}^{-1} \text{ s}^{-2}$  and  $b_p = 3.0 \times 10^{-9} \text{ s}^{-1}$ , corresponding to a reservoir response time of  $t_p$  of 10 years and  $K \approx 10^{-3} \text{ m s}$ . These values give a pre-exploitation mass throughput estimate of  $300 \text{ kg s}^{-1}$  (Equation 9), which is a similar order to the  $400 \text{ kg s}^{-1}$  estimated by Allis (1981). Later, models are developed for Rotokawa and Ngā Tamariki that use  $t_p \sim 1$  year based on reported pressure declines, and find through calibration  $K \approx 0.55 \times 10^{-4} \text{ m s}$  for Rotokawa and  $K \approx 1 \times 10^{-5} \text{ m s}$  for Ngā Tamariki.

Reservoir dissolved  $\text{CO}_2$  concentrations for New Zealand geothermal systems have been summarized by Giggenbach (1995) and Seward and Kerrick (1996). While the different fields exhibit a range of concentrations, it is useful to separate high concentration reservoirs, such as the shallow wells at Ohaaki with initial concentrations exceeding 3 wt% at 6 MPa (M. J. O'Sullivan et al., 1985), from comparatively more dilute waters such as at Wairakei ( $<0.2 \text{ wt\%}$ ).

Although the Giggenbach (1995) and Seward and Kerrick (1996) compilations date from the 1990s, they characterize the pre-development reservoir  $\text{CO}_2$  inventory and remain the most complete field-wide data sets for the Taupo Volcanic Zone. This is a useful baseline for the initial concentration  $C_0$ , which production subsequently depletes. Their magnitudes are corroborated by the field-specific concentrations inferred here by calibration ( $C_0 = 0.78 \text{ wt\%}$  at Rotokawa,  $0.46 \text{ wt\%}$  at Ngā Tamariki; Section 3.3), although targeted resampling of individual reservoirs would refine these values.

**Table 1**  
*Nomenclature Used in This Study*

| Symbol              | Definition                              | Units                         | Equations   |
|---------------------|-----------------------------------------|-------------------------------|-------------|
| $a_P$               | Pressure ODE pumping coefficient        | $\text{m}^{-1} \text{s}^{-2}$ | Equation 5  |
| $b_P$               | Pressure ODE recharge coefficient       | $\text{s}^{-1}$               | Equation 5  |
| $c_i$               | Solubility fit coefficients             | Various                       |             |
| $f_C$               | CO <sub>2</sub> capture efficiency      | —                             | Equation 17 |
| $f_q$               | Net extraction fraction                 | —                             | Equation 5  |
| $g$                 | Acceleration due to gravity             | $\text{m s}^{-2}$             |             |
| $k$                 | Permeability                            | $\text{m}^2$                  | Equation 1  |
| $q$                 | Mass flow rate                          | $\text{kg s}^{-1}$            | Equation 1  |
| $q_0$               | Extraction rate                         | $\text{kg s}^{-1}$            | Equation 5  |
| $q_{0,c}$           | Critical extraction rate for reversal   | $\text{kg s}^{-1}$            |             |
| $q_{\text{out}}$    | Outflow rate to surface/aquifers        | $\text{kg s}^{-1}$            | Equation 10 |
| $q_{\text{up}}$     | Upflow rate from depth                  | $\text{kg s}^{-1}$            | Equation 9  |
| $t$                 | Time                                    | s                             |             |
| $t_P$               | Pressure equilibration timescale        | yr                            | Equation 8  |
| $t_q$               | Reservoir flushing timescale            | yr                            | Equation 26 |
| $t_{\text{res}}$    | Reservoir residence time                | yr                            | Equation 13 |
| $t_r$               | Outflow reversal time                   | yr                            |             |
| $t_\alpha$          | CO <sub>2</sub> restoration timescale   | yr                            | Equation 26 |
| $t_\beta$           | CO <sub>2</sub> loss timescale          | yr                            | Equation 26 |
| $A$                 | Cross-sectional flow area               | $\text{m}^2$                  | Equation 1  |
| $C$                 | Dissolved CO <sub>2</sub> concentration | wt%                           | Equation 17 |
| $C_0$               | Initial reservoir concentration         | wt%                           |             |
| $C_r$               | Equilibrium concentration for reactions | wt%                           | Equation 17 |
| $C_s$               | CO <sub>2</sub> solubility in liquid    | wt%                           | Equation 18 |
| $C_\infty$          | Steady-state concentration              | wt%                           | Equation 29 |
| $H$                 | Reservoir vertical height               | m                             |             |
| $K$                 | Total recharge coefficient              | m s                           | Equation 4  |
| $K_{\text{aq}}$     | Aquifer recharge coefficient            | m s                           |             |
| $K_{\text{cap}}$    | Caprock recharge coefficient            | m s                           |             |
| $K_{\text{out}}$    | Combined outflow coefficient            | m s                           | Equation 4  |
| $K_{\text{up}}$     | Upflow recharge coefficient             | m s                           | Equation 4  |
| $L$                 | Characteristic flow distance            | m                             | Equation 1  |
| $M$                 | Reservoir liquid mass                   | kg                            |             |
| $P$                 | Reservoir pressure (rel. hydrostatic)   | Pa                            | Equation 2  |
| $P_0$               | Initial reservoir pressure              | MPa                           | Equation 4  |
| $P_{\text{up}}$     | Upflow driving pressure                 | MPa                           | Equation 4  |
| $P_\infty$          | Steady-state pressure                   | MPa                           | Equation 8  |
| $Q_{\text{dg}}$     | Degassing emissions rate                | kt yr <sup>-1</sup>           | Equation 19 |
| $Q_{\text{surf}}$   | Surface emission rate                   | kt yr <sup>-1</sup>           | Equation 23 |
| $Q_{\text{surf},0}$ | Pre-development surface emission rate   | kt yr <sup>-1</sup>           | Equation 45 |
| $Q_{\text{plant}}$  | Power plant emissions rate              | kt yr <sup>-1</sup>           |             |
| $Q_{\text{total}}$  | Total emissions rate                    | kt yr <sup>-1</sup>           |             |
| $S$                 | Reservoir upper surface area            | $\text{km}^2$                 |             |

**Table 1**  
*Continued*

| Symbol                     | Definition                                        | Units               | Equations   |
|----------------------------|---------------------------------------------------|---------------------|-------------|
| $T$                        | Temperature                                       | °C                  |             |
| $V$                        | Reservoir volume                                  | m <sup>3</sup>      |             |
| $\alpha$                   | CO <sub>2</sub> source coefficient                | s <sup>-1</sup>     | Equation 26 |
| $\beta$                    | CO <sub>2</sub> decay coefficient                 | s <sup>-1</sup>     | Equation 26 |
| $\gamma$                   | CO <sub>2</sub> -pressure coupling coefficient    | s <sup>-1</sup>     | Equation 26 |
| $\delta$                   | CO <sub>2</sub> -pressure coupling source         | s <sup>-1</sup>     | Equation 26 |
| $\kappa$                   | Mineralization rate constant                      | kg s <sup>-1</sup>  | Equation 17 |
| $t_\kappa$                 | Mineralization timescale $M/\kappa$               | yr                  |             |
| $\lambda_1$                | Dominant DDE characteristic root                  | s <sup>-1</sup>     | Equation 35 |
| $\mu$                      | Dynamic viscosity                                 | Pa s                | Equation 1  |
| $\eta$                     | Return fraction of reinjected CO <sub>2</sub>     | —                   |             |
| $\rho$                     | Liquid density                                    | kg m <sup>-3</sup>  |             |
| $\tau$                     | Reinjection breakthrough delay                    | yr                  | Equation 33 |
| $\phi$                     | Porosity                                          | —                   |             |
| $\beta_0$                  | DDE immediate removal coefficient                 | s <sup>-1</sup>     | Equation 33 |
| $\beta_\tau$               | DDE delayed return coefficient                    | s <sup>-1</sup>     | Equation 33 |
| $C_{\text{up}}$            | CO <sub>2</sub> concentration of upflow           | wt%                 | Equation 17 |
| $C_{\text{out}}$           | CO <sub>2</sub> concentration of reversed inflow  | wt%                 | Equation 17 |
| $\Delta P$                 | Pressure drawdown                                 | MPa                 |             |
| $f_K$                      | Upflow fraction $K_{\text{up}}/K$                 | —                   |             |
| $Q_{\text{anthropogenic}}$ | Anthropogenic emissions rate                      | kt yr <sup>-1</sup> |             |
| $Q_{\text{overcount}}$     | Overcount of plant versus anthropogenic emissions | kt yr <sup>-1</sup> | Equation 46 |
| $t_{\text{CO}_2}$          | Time CO <sub>2</sub> reinjection begins           | yr                  |             |

### 3.2. General CO<sub>2</sub> Emissions Trends

The results presented in this section are intended to be illustrative of the physical mechanisms that may combine to drive emissions changes in geothermal fields over years to decades. To highlight particular features, certain parameter selections have been made. More extensive parameter sweeps are included in the Supporting Information S1, while field-specific parameter choices are presented in Section 3.3.

#### 3.2.1. CO<sub>2</sub> Saturated Fields

Figure 3 shows the CO<sub>2</sub> content and emissions trajectory of a non-reactive ( $\kappa = 0$ ), high-gas field of typical size, throughput and responsiveness ( $M = 10^{11}$  kg,  $K = 10^{-4}$  m s,  $t_p = 10$  years). The field is subject to fluid extraction at 150% of  $q_{0,c}$  but with 60% fluid reinjection ( $f_q = 0.4$ ) to prevent an outflow reversal. The field has initial CO<sub>2</sub> content of 3.5 wt%, pre-development emissions of 33 kt yr<sup>-1</sup>, with production driving pressure depletion (relative to hydrostatic) from 0.6 to 0.24 MPa. Production is held at a constant net rate for a period of 200 years for illustrative purposes, which is much longer than the envisaged lifetime of 30–50 years.

For the case of zero emissions capture and injection ( $f_c = 1$ ), CO<sub>2</sub> concentration in the reservoir declines steadily at a characteristic time,  $t_\beta$  of 31 years. Dilution is driven by the reinjection of CO<sub>2</sub> depleted fluid. The diluting effect is lessened in the case of 50% emissions capture and injection ( $f_c = 0.5$ ), with the characteristic time lengthening to 56 years.

From an emissions perspective, the pressure decline from production drives degassing of up to 18 kt yr<sup>-1</sup> for the first two decades. A similar response is observed in the model of M. O'Sullivan et al. (2021) coincident with the start of production from the Ohaaki reservoir.

**Table 2**  
Representative Values and Basis for the Key Model Parameters

| Parameter          | Representative value/range                               | Units                  | Source/basis                                                                        |
|--------------------|----------------------------------------------------------|------------------------|-------------------------------------------------------------------------------------|
| $S$                | $\sim 10$                                                | $\text{km}^2$          | Bibby et al. (1995)                                                                 |
| $H$                | 100–1000                                                 | m                      | Illustrative (NZ fields)                                                            |
| $\phi$             | $\sim 0.1$                                               | –                      | Illustrative (NZ fields)                                                            |
| $\rho$             | $\sim 10^3$                                              | $\text{kg m}^{-3}$     | Illustrative                                                                        |
| $M$                | $10^{11}$ – $10^{12}$                                    | kg                     | Illustrative (NZ range)                                                             |
|                    | $1.2 \times 10^{11}$ (RK),<br>$1.5 \times 10^{11}$ (NT)  | kg                     | Calibrated                                                                          |
| $P_0$              | $\sim 0.6$ ( $\sim 10\%$ over hydrostatic)               | MPa                    | Grant and Bixley (2011)                                                             |
| $P_{\text{up}}$    | 1.2 (for $K_{\text{up}} \approx K_{\text{out}}$ )        | MPa                    | Equation 4                                                                          |
| $K$                | $\sim 10^{-3}$ (Wairakei)                                | m s                    | Fradkin et al. (1981)                                                               |
|                    | $0.55 \times 10^{-4}$ (RK),<br>$1.0 \times 10^{-5}$ (NT) | m s                    | Calibrated                                                                          |
| $t_P$              | 10 (Wairakei); 1 (RK, NT)                                | yr                     | Fradkin et al. (1981); calibrated                                                   |
| $C_0$              | $> 3$ (Ohaaki, shallow),<br>$< 0.2$ (Wairakei)           | wt%                    | M. J. O'Sullivan et al. (1985), Giggenbach (1995),<br>and Seward and Kerrick (1996) |
|                    | 0.78 (RK), 0.46 (NT)                                     | wt%                    | Calibrated                                                                          |
| $f_q$              | 0–1; 0.26 (RK), 0.018 (NT)                               | –                      | Illustrative; calibrated                                                            |
| $f_C$              | $\leq 1$ ; 1 (RK), 0.85 (NT)                             | –                      | Illustrative; Ghafar et al. (2022) (NT)                                             |
| $\Delta P$         | 2.5 (RK), 0.2 (NT)                                       | MPa                    | Quinao et al. (2013) and Potter et al. (2020)                                       |
| $t_k = M/\kappa$   | 2 months (basalt), $\sim 5$ yr, $\gg$ decades (silicic)  | yr                     | Snæbjörnsdóttir et al. (2020); illustrative; Altar et al. (2024)                    |
| $\tau$             | 0–30                                                     | yr                     | Illustrative                                                                        |
| $P_{s,\text{ref}}$ | 1.5                                                      | MPa                    | Reference state, Equation 18                                                        |
| $C_{s,\text{ref}}$ | 0.01                                                     | –                      | Reference state, Equation 18                                                        |
| $dC_s/dP$          | $T$ -dependent (Appendix A)                              | $\text{wt\% MPa}^{-1}$ | Duan and Sun (2003)                                                                 |

Note. Symbols and units are defined in Table 1. RK denotes Rotokawa and NT Ngā Tamariki.

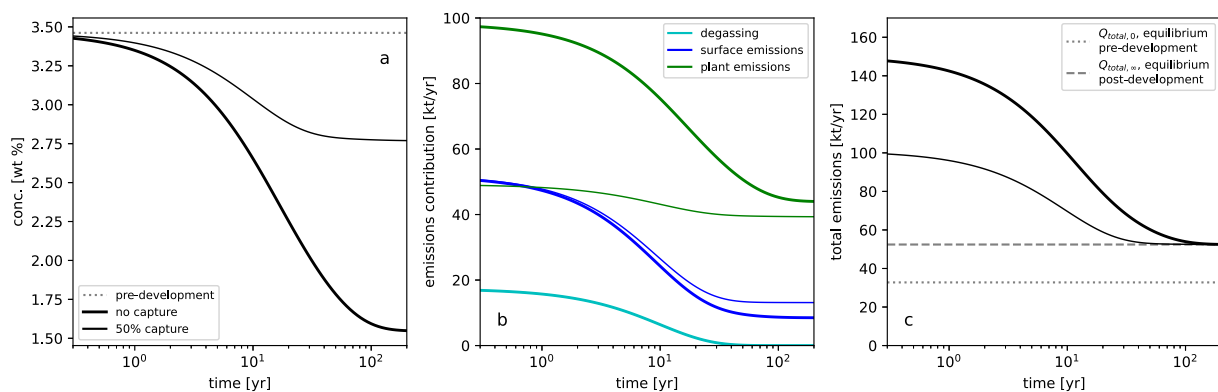


**Figure 3.** A high-gas, solubility-constrained field with  $K = 10^{-4}$  m s and 60% fluid reinjection. Two  $\text{CO}_2$  capture scenarios are distinguished by line weight: zero capture (bold solid,  $f_C = 1$ ) and 50% capture and injection (thin solid,  $f_C = 0.5$ ). (a) Reservoir  $\text{CO}_2$  concentration, with the pre-development level shown as a gray dotted line. (b) Disaggregated emissions, where color denotes the pathway, degassing (cyan), surface (blue) and plant (green), and line weight denotes the capture scenario as in (a). (c) Total (plant plus surface) emissions; the gray dotted line is the pre-development equilibrium  $Q_{\text{total},0}$  and the gray dashed line is the post-development equilibrium  $Q_{\text{total},\infty}$ .

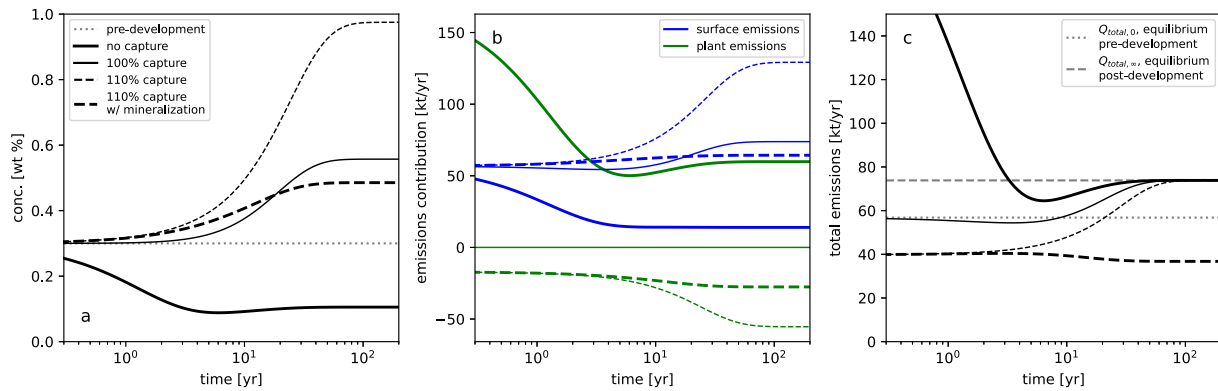


**Figure 4.** A low-gas field ( $K_{up} = K_{out} = 10^{-3}$  m s). Four cases are distinguished by line weight and style: no capture (bold solid, black), 100% capture of produced  $CO_2$  (thin solid, black), 110% capture (thin dashed, black), and 110% capture with mineralization (bold dashed, black;  $C_r = C_0$ ). (a) Reservoir  $CO_2$  concentration, with the pre-development level shown as a gray dotted line. (b) Disaggregated emissions, where color denotes the pathway, surface (blue) and plant (green), and line weight and style denote the case as in (a). (c) Total (plant plus surface) emissions; the gray dotted line is the pre-development equilibrium  $Q_{total,0}$  and the gray dashed line is the post-development equilibrium  $Q_{total,\infty}$ .

Surface emissions are higher than pre-development at early time (Figure 3c), primarily due to the degassing. Later, they drop below the pre-development level as outflows diminish and reservoir concentration drops. Plant emissions are mostly higher than field emissions, ranging near parity (early on, for the case of 50%  $CO_2$  capture and injection) to more than a factor of 5 at late time (Figure 3b).

Total emissions from the field, summing contributions from the plant and through the surface, always exceeds the pre-development baseline. They are especially elevated in early decades (from degassing), and then trend down to a new equilibrium. This new equilibrium exceeds the pre-development baseline by an amount equal to the  $CO_2$  content of the induced upflow.

### 3.2.2. Undersaturated Fields

The contrasting end-member to the solubility-constrained field is the low-gas system (Figure 4). This field is closer in character to Wairakei, having a higher mass throughput ( $K = 10^{-3}$  m s) but lower initial  $CO_2$  concentration (0.3 wt%). Fluid is extracted at 150% of  $q_{0,c}$  with 80% then reinjected; the high recharge ( $K = 10^{-3}$  m s) places this case at the high-throughput, Wairakei-like end of the range in Section 3.1, an order of magnitude above the high-gas case of Figure 3, and the relatively high reinjection fraction is chosen so that the outflow does not reverse (contrast the 20% reinjection case of Figure 5). Three  $CO_2$  capture scenarios were considered as

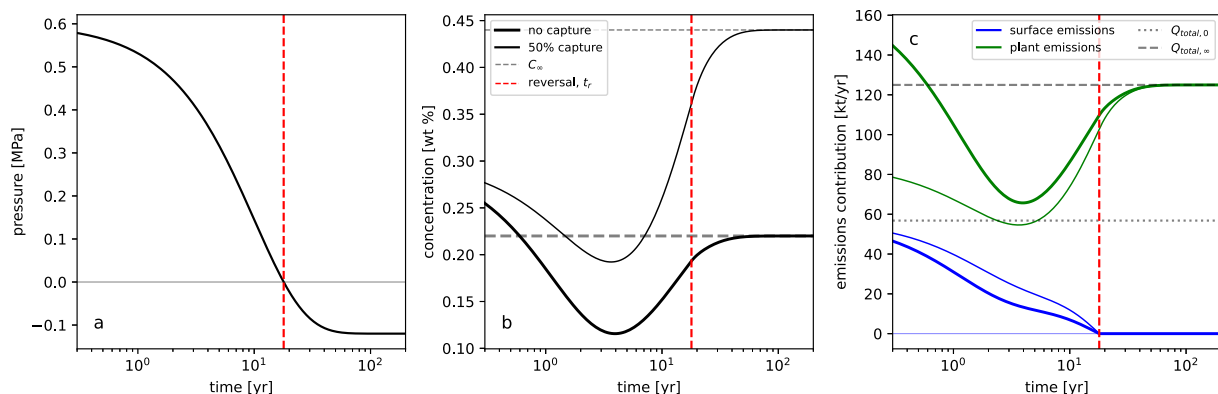


**Figure 5.** Evolution of  $CO_2$  content and emissions in a low-gas field ( $K_{up} = K_{out} = 10^{-3}$  m s) prior to and after a reversal of outflow. Two cases are distinguished by line weight: no capture (bold solid, black) and 50% capture (thin solid, black). In all panels the red dashed vertical line marks the reversal time  $t_r$ . (a) Reservoir pressure. (b) Reservoir  $CO_2$  concentration; the gray dashed line is the post-reversal equilibrium concentration  $C_{\infty}$ . (c) Surface (blue) and plant (green) emissions, with line weight denoting the capture case as in (b); the gray dotted line is the pre-development equilibrium of total emissions  $Q_{total,0}$  and the gray dashed line is the post-development equilibrium  $Q_{total,\infty}$ .

illustrative end-members spanning the under-injecting ( $f_c > f_q$ ), balanced ( $f_c = f_q$ ) and over-injecting regimes of Equation 39: no capture, 100% capture, and 110% capture. In the latter, an additional 10% of CO<sub>2</sub>, sourced elsewhere, is injected into the reservoir for storage (e.g., Titus et al., 2025). These parameter choices are illustrative only, selected to show the different categories of response that may arise rather than to represent a specific field.

Without CO<sub>2</sub> capture, the field follows a quite rapid diluting trend, reflecting the high rates of reinjection. When CO<sub>2</sub> capture exceeds the reinjection fraction ( $f_c > f_q$ ), a relatively concentrated fluid is now injected into the reservoir, resulting in a concentrating trajectory. In this case, CO<sub>2</sub> content approximately doubles to 0.55 wt% for the case of 100% CO<sub>2</sub> capture, and about 1.0 wt% when a further 10% is injected (110% capture,  $f_c = -0.1$ ).

For the 110% capture scenario, although plant emissions are increasingly negative over time (Figure 4b), the concentrating of CO<sub>2</sub> in the reservoir increases the natural field emissions in equal proportion. The net impact on total emissions is eventually the same for all scenarios (Figure 4c), although the lower capture scenarios had higher emissions at early times. This result highlights the advice of Titus et al. (2025) that if carbon removal is to be undertaken in geothermal systems, particular care must be taken that re-entry of injected CO<sub>2</sub> into the reservoir be minimized as much as possible.

### 3.2.3. Mineralization Reactions

For illustration purposes, the possibility was considered that mineralization reactions within the reservoir might partially suppress elevated CO<sub>2</sub> concentrations back to their equilibrium level. The quite rapid mineralization that occurs with basalts at CarbFix should use a reaction time constant of  $M/\kappa = 2$  months (Snæbjörnsdóttir et al., 2020). For illustration here, a reaction time constant of 5 years (30-times slower than Carbfix) was used, with  $C_r = C_0$ , applied to the negative emissions scenario. This intermediate value is chosen to bracket the plausible range: it is far slower than the ~2-month basalt rate at Carbfix (Snæbjörnsdóttir et al., 2020) but faster than the decades-to-centuries timescales expected in the comparatively unreactive silicic and rhyolitic reservoirs typical of New Zealand (Altar et al., 2024; Siahaan et al., 2024), and is large enough that its buffering effect is visible over the modeled period.

The principal effect of mineralization reactions is to reduce CO<sub>2</sub> concentration in the reservoir, which stabilizes at about half the value it would have reached if no reactions were present. This in turn reduces the field emissions and ensures overall total emissions remain below even the initial pre-development baseline for this field. Mineralization reactions are clearly a key process for secure, long-term carbon storage in negative emissions operations.

### 3.2.4. Reversal of Outflow

For geothermal operations characterized by high rates of extraction and relatively low fractions of reinjection, pressure in the reservoir can drop below the threshold at which the outflow reverses. The example considered here is a variant of the low-gas system from the previous subsection except that reinjection is limited to just 20% of extraction. This results in an outflow reversal after ~18 years that brings fresh water ( $C_{\text{out}} = 0$ ) into the reservoir (Figure 5).

Three transients are present in the CO<sub>2</sub> content and emissions trajectory of this model. At early time, CO<sub>2</sub> decline is dominated by reinjection of relatively CO<sub>2</sub> depleted water to the reservoir. The decline arrests and is eventually reversed as pressure depletion brings additional CO<sub>2</sub> through induced upflow. Finally, this ascending trend is itself limited following the outflow reversal as fresh water starts to enter the reservoir. In the absence of degassing, surface emissions drop to zero once the reversal occurs, however total emissions via the plant remain elevated compared to the pre-development baseline.

### 3.2.5. Delayed Return of Rejected CO<sub>2</sub>

Reinjection of captured CO<sub>2</sub> at sufficient distance from the production area will result in a delay in its return. Figure 6 illustrates how reservoir inertia and degree of capture influence CO<sub>2</sub> content trends. In all cases, the early-time is characterized by a diluting trend that follows the no capture solution. Following the breakthrough

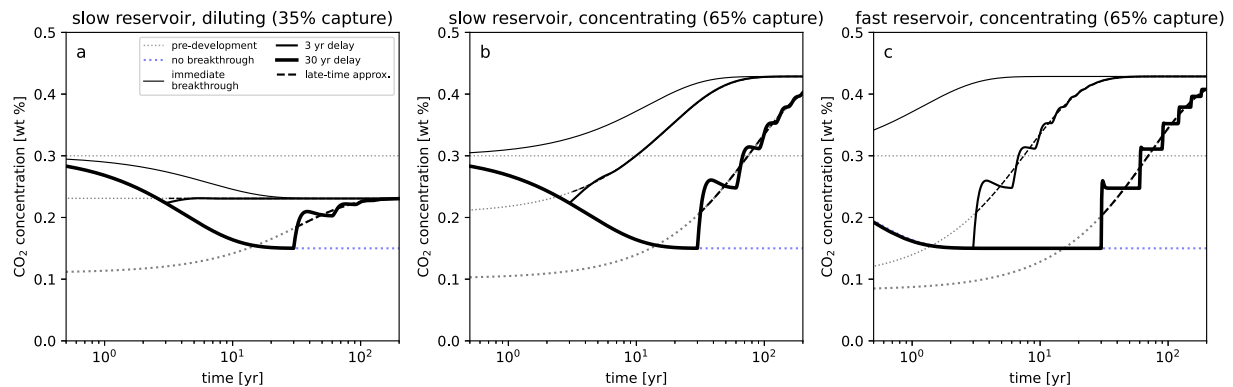


**Figure 6.** Effect of a delay in reinjection returns on reservoir  $\text{CO}_2$  content. (a) A less responsive reservoir ( $K = 10^{-4}$  m s) and 35%  $\text{CO}_2$  capture, (b) the same reservoir with 65% capture, and (c) a more responsive reservoir with  $K = 10^{-3}$  m s and 65% capture. Within each panel, progressively larger breakthrough delays of 0 (immediate; thin solid), 3 (medium solid) and 30 years (bold solid) are denoted by increasing line weight. Post-breakthrough late-time approximate solutions (Equation 36) are shown as dashed black lines. For reference, the gray dotted line is the pre-development concentration and the blue dotted line is the no-breakthrough (never-returning) solution.

time,  $\tau$ , the diluting trend is reversed, and  $\text{CO}_2$  content starts to increase, potentially exceeding the pre-development baseline depending on the amount of  $\text{CO}_2$  capture.

Reservoir responsiveness, here characterized by recharge coefficient  $K$ , controls some aspects of the post-breakthrough trajectory. “Fast” reservoirs that respond more rapidly to  $\text{CO}_2$  arrival, present as a series of stepped increases in  $\text{CO}_2$  content (Figure 6c), however this requires multiple terms of the exponential basis in Equation 35 to be evaluated. In practice, mixing and dispersion effects are unlikely to permit such sharp arrivals and, as such, the approximate solution Equation 36 is likely to provide an adequate representation, even more so in less responsive reservoirs (Figure 6b).

### 3.3. Calibrated Models for Rotokawa and Ngā Tamariki

Models were calibrated for Ngā Tamariki and Rotokawa geothermal fields by Bayesian inference. The emcee ensemble Markov chain Monte Carlo (MCMC) sampler (Foreman-Mackey et al., 2013) was used, with 10 walkers, 3,000 burn-in steps, and 8,000 production steps thinned by a factor of five, yielding 16,000 posterior samples per field. In both cases, initial dissolved  $\text{CO}_2$  concentration  $C_0$  and reservoir liquid mass  $M$  (log-uniform on  $[5 \times 10^{10}, 10^{12}]$  kg) were free parameters, as was the upflow fraction  $f_K = K_{\text{up}}/K$  ( $f_K$  is not meaningfully identified by plant-emissions data alone and its posteriors are presented separately in the Supporting Information S1). The two fields had different parameterizations for the remaining degrees of freedom, as described in the field subsections below. Figures 7 and 8 show 100-member posterior ensemble trajectories alongside observed plant emissions and marginal histograms of calibrated parameters and derived quantities.

The likelihood scores each candidate model by the Gaussian misfit between its predicted annual plant emissions and the reported values. The standard deviation  $\sigma$  reflects a judgment of model error embodied in the expected year-to-year variability of emissions that a lumped model is unable to resolve, and is set large enough to admit a reasonable spread of models passing through the scatter in the emissions record. The larger value at Rotokawa ( $\sigma = 8 \text{ kt yr}^{-1}$  vs.  $4 \text{ kt yr}^{-1}$  at Ngā Tamariki) reflects its larger absolute emissions and more variable record. The priors were chosen to be weakly informative where field constraints are scarce and informative where they are not. The log-uniform priors on  $M$  and  $f_q$  span the plausible orders of magnitude of TVZ reservoir mass and net extraction fraction without favoring a particular value, the Gaussian prior  $q_{\text{up}} \sim \mathcal{N}(39, 5^2) \text{ kg s}^{-1}$  at Ngā Tamariki is centered on the natural-upflow estimate of Seward and Kerrick (1996), and the uniform prior  $f_q \in [0.2, 1.0]$  at Rotokawa encodes the  $\sim 78\%$  fluid reinjection (Quinao et al., 2013) as a lower bound on net extraction, and the broad prior on  $f_K$  reflects that plant-emissions data cannot identify the upflow fraction independently (Supporting Information S1).

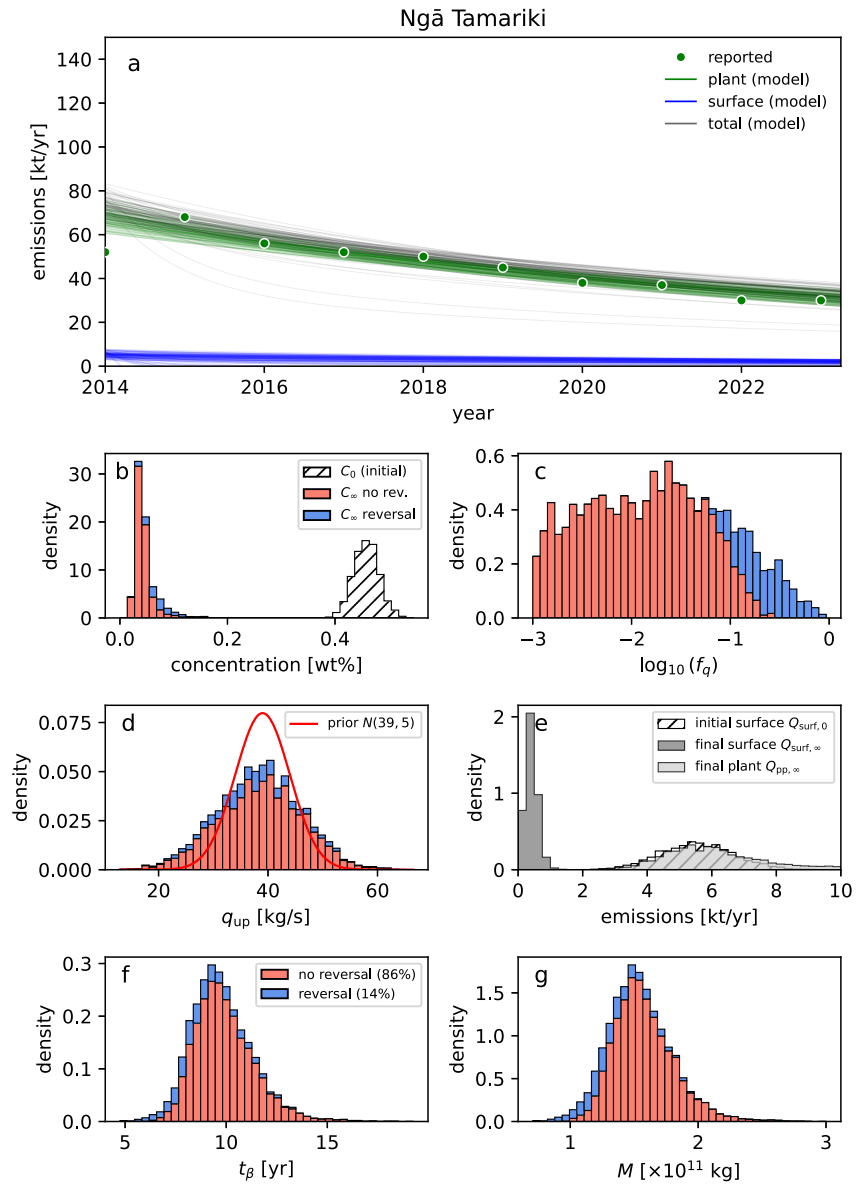


**Figure 7.** Calibrated model results for Ngā Tamariki. (a) 100-member posterior ensemble of plant (green), surface (blue), and total (black) emission trajectories against reported plant emissions (circles). (b) Marginal histograms of initial dissolved  $\text{CO}_2$  concentration  $C_0$  (hatched) and equilibrium value  $C_\infty$  (shaded; pink: no outflow reversal, blue: outflow reversal). (c) Net extraction fraction  $f_q$  (sampled in  $\log_{10}$  space). (d) Natural upflow  $q_{\text{up}}$  [ $\text{kg s}^{-1}$ ] with prior  $\mathcal{N}(39, 5^2)$  overlaid (red curve). (e) Initial surface emissions  $Q_{\text{surf},0}$  (hatched), final surface  $Q_{\text{surf},\infty}$  (medium gray), and final plant  $Q_{\text{pp},\infty}$  (light gray). (f)  $\text{CO}_2$  loss timescale  $t_\beta$ . (g) Reservoir liquid mass  $M$ . The upflow fraction  $f_K$  is shown in Supporting Information S1.

### 3.3.1. Ngā Tamariki

At Ngā Tamariki, an 83 MWe binary power station was commissioned in 2013 with a resource consent for up to  $60,000 \text{ t d}^{-1}$  ( $694 \text{ kg s}^{-1}$ ) of geothermal fluid (Ghafar et al., 2022). The four generating units collectively extract approximately  $2,000 \text{ t h}^{-1}$  ( $556 \text{ kg s}^{-1}$ ), with nominally 100% fluid reinjection. The reservoir is  $280\text{--}290^\circ\text{C}$  with dissolved gas content below 0.3 wt%, of which approximately 95% is  $\text{CO}_2$  (Ghafar et al., 2022). About 15% of produced NCGs are dissolved in the binary system condensate and returned to the subsurface naturally. This is represented in the model by setting  $f_c = 0.85$  (Ghafar et al., 2022). Reservoir pressure drawdown is reported to have equilibrated within about 18 months of the start of production (Potter et al., 2020). This was captured by setting the pressure timescale to  $t_p = 1 \text{ yr}$ . The model extraction rate was fixed at  $48,000 \text{ t d}^{-1}$  ( $556 \text{ kg s}^{-1}$ ; the

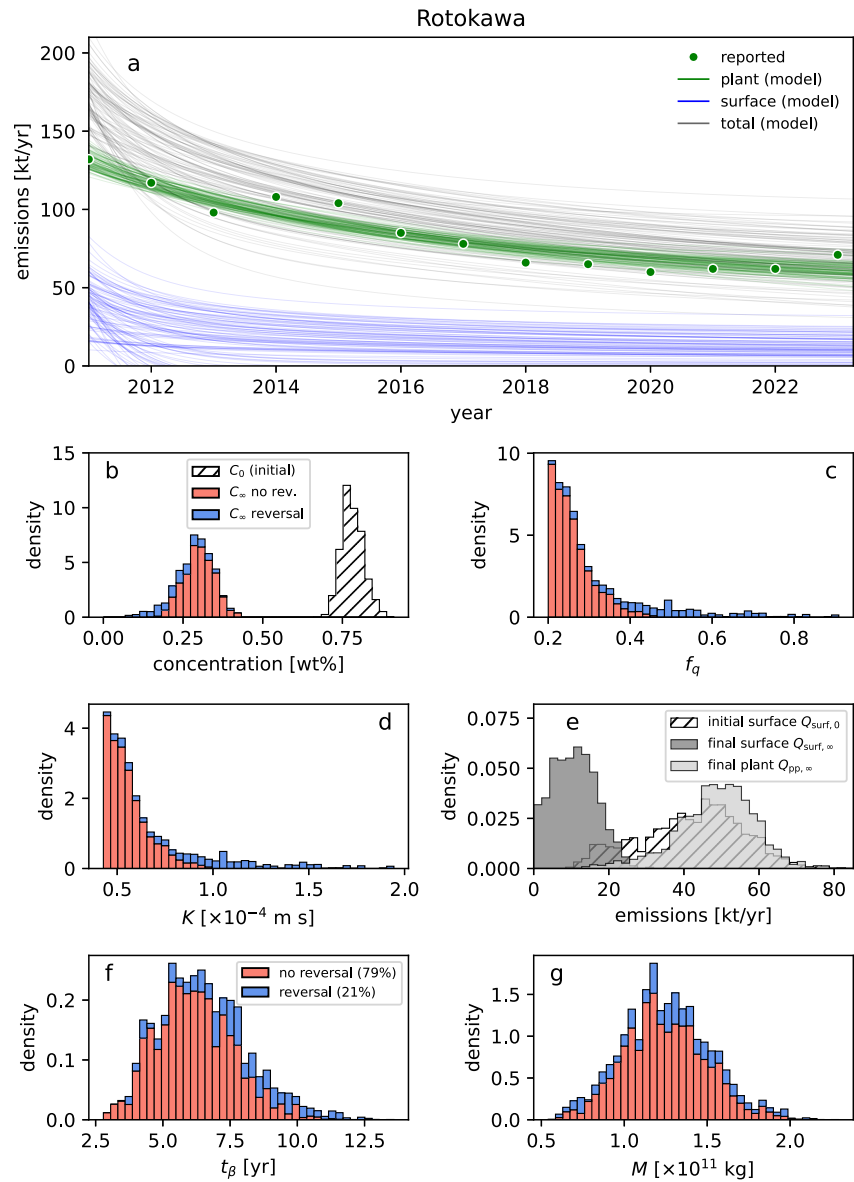


**Figure 8.** Calibrated model results for Rotokawa - Ngā Awa Pūrua. (a) 100-member posterior ensemble of plant (green), surface (blue), and total (black) emission trajectories against reported plant emissions (circles). (b) Marginal histograms of initial dissolved concentration (hatched) and equilibrium value (shaded; pink: no outflow reversal, blue: outflow reversal). (c) Net extraction fraction (sampled in space). (d) Recharge coefficient. (e) Initial surface emissions (hatched), final surface (medium gray), and final plant (light gray). (f) Loss timescale. (g) Reservoir liquid mass. The upflow fraction is shown in Supporting Information S1.

reported actual throughput (Ghafar et al., 2022)) and the pressure drawdown at  $\Delta P = 0.2$  MPa (Potter et al., 2020).

Rather than inferring  $K$  from the pressure constraint alone,  $K$  was constrained using estimates of the pre-development natural upflow. In the pre-development state,  $q_{up,0} = f_K(1 - f_K)KP_{up}$ , and a Gaussian prior  $q_{up} \sim \mathcal{N}(39, 5^2)$  kg s<sup>-1</sup> was placed on the natural upflow based on values reported by Seward and Kerrick (1996). The net extraction fraction  $f_q$  was sampled in log<sub>10</sub> space with a uniform prior over log<sub>10</sub> ( $f_q$ )  $\in [-3, 0]$ . A Gaussian likelihood with  $\sigma = 4$  kt yr<sup>-1</sup> was used to score models based on their similarity to plant emissions data from McLean et al. (2024), covering 2015–2023 and excluding the partial-year 2014 during which the plant was starting up.

Posterior estimates give reservoir averaged  $C_0 = 0.46$  wt% (10–90th percentile: 0.43–0.49 wt%), a natural upflow  $q_{up} = 38.5$  kg s<sup>−1</sup> (28–48 kg s<sup>−1</sup>, close to the prior), and a recharge coefficient  $K \approx 1.0 \times 10^{-5}$  m s (0.73–1.8  $\times 10^{-5}$  m s). The net extraction fraction  $f_q = 0.018$  (0.002–0.16) is broadly distributed, reflecting weak sensitivity of the concentration decline to small residual extraction under near-complete reinjection. The inferred reservoir mass is  $M = 1.5 \times 10^{11}$  kg (1.2–1.9  $\times 10^{11}$  kg), which is on the low end of the range expected for TVZ geothermal systems (10<sup>11</sup>–10<sup>12</sup> kg), suggesting extraction accesses only a part of the full reservoir height or a low-porosity fracture network. The associated CO<sub>2</sub> loss timescale is  $t_\beta \approx 9.6$  yr (8.0–11.7 years). Approximately 14% of posterior samples had an outflow reversal. At the new equilibrium, the dissolved concentration falls to  $C_\infty \approx 0.041$  wt% (0.030–0.073 wt%), with steady-state plant emissions of approximately 6 kt yr<sup>−1</sup> (4–11 kt yr<sup>−1</sup>) and surface emissions of approximately 0.4 kt yr<sup>−1</sup> (essentially zero for the reversal fraction). Pre-development surface emissions are estimated at 5.5 kt yr<sup>−1</sup> (4.1–7.0 kt yr<sup>−1</sup>; Figure 7).

The median inferred natural upflow of 38.5 kg s<sup>−1</sup> and reservoir mass of  $1.5 \times 10^{11}$  kg give a pre-development residence time  $t_{res,0} \approx 123$  yr (Equation 14). Under production, the induced upflow raises total throughput to approximately 44 kg s<sup>−1</sup>, shortening the residence time to  $t_{res,\infty} \approx 109$  yr ( $t_{res,\infty}/t_{res,0} \approx 0.89$ ). The relatively modest reduction reflects the small net extraction fraction ( $f_q = 0.018$ ) under near-complete reinjection, which only weakly perturbs the natural circulation.

### 3.3.2. Rotokawa - Ngā Awa Pūrua

The Rotokawa field has produced geothermal power since 1997, initially at 24 MW via a combined-cycle plant, which expanded to 34 MWe by 2003. The 138 MWe Ngā Awa Pūrua (NAP) flash plant was commissioned in 2010 (Quinao et al., 2013), increasing total fluid extraction from 645 t h<sup>−1</sup> (179 kg s<sup>−1</sup>) to 2,570 t h<sup>−1</sup> (714 kg s<sup>−1</sup>), with approximately 78% reinjected (Quinao et al., 2013). Pressure drawdown across the production area reached 2.5–3.0 MPa, inducing boiling in parts of the field, and the rate of drawdown stabilized 16–18 months after commissioning (Quinao et al., 2013). Reservoir temperatures in the production area are approximately 320–330°C (Quinao et al., 2013). No CO<sub>2</sub> capture was in place during the calibration period (2011–2021), so  $f_C = 1$ . Model extraction and pressure drawdown were fixed at 1,925 t h<sup>−1</sup> (535 kg s<sup>−1</sup>) and 2.5 MPa, respectively.  $K$  was inferred from the pressure constraint  $K = f_q q_0 / \Delta P$ , with  $f_q$  given a uniform prior on [0.2, 1.0] consistent with the field's ~78% fluid reinjection (Quinao et al., 2013), which implies a minimum net extraction fraction of 0.2. A Gaussian likelihood was again used to score the models with  $\sigma = 8$  kt yr<sup>−1</sup>.

Posterior estimates give  $C_0 = 0.78$  wt% (10–90th percentile: 0.74–0.83 wt%),  $f_q = 0.26$  (0.21–0.47), and  $K \approx 0.55 \times 10^{-4}$  m s (0.45–1.0  $\times 10^{-4}$  m s). Reservoir mass  $M = 1.2 \times 10^{11}$  kg (0.9–1.6  $\times 10^{11}$  kg), which, like Ngā Tamariki, is on the low end of the expected range. The corresponding CO<sub>2</sub> loss timescale is  $t_\beta \approx 6.3$  yr (4.4–8.7 years). About 21% of the posterior samples show an outflow reversal, reflecting the high extraction rate relative to the inferred recharge. These samples predict near-zero surface emissions (from the reservoir) and are shown in blue in the histogram panels (Figure 8). For non-reversal samples, at the new equilibrium the dissolved concentration falls to  $C_\infty \approx 0.30$  wt% (0.23–0.36 wt%), with steady-state surface emissions of 3–19 kt yr<sup>−1</sup> and plant emissions of approximately 49 kt yr<sup>−1</sup> (36–59 kt yr<sup>−1</sup>). Pre-development surface emissions are estimated at 44 kt yr<sup>−1</sup> (22–59 kt yr<sup>−1</sup>; Figure 8). This is well below the 126–161 kt yr<sup>−1</sup> measured by surface CO<sub>2</sub> flux surveys (Bloomberg et al., 2014; Yang et al., 2024). The discrepancy likely reflects CO<sub>2</sub> pathways not captured by this single-reservoir lumped model that describes only a producing subsection of the entire system.

For the median Rotokawa model (with  $f_K = K_{up}/K = 0.5$ ), the natural upflow of ~250 kg s<sup>−1</sup> yields a pre-development residence time  $t_{res,0} \approx 15$  yr, considerably shorter than at Ngā Tamariki due to the order-of-magnitude larger recharge coefficient. Under production, the induced upflow raises throughput to ~320 kg s<sup>−1</sup>, reducing the residence time to  $t_{res,\infty} \approx 12$  yr ( $t_{res,\infty}/t_{res,0} \approx 0.78$ ).

## 4. Discussion

The prior results present a number of implications relevant to CO<sub>2</sub> storage in geothermal fields. First, several characteristic timescales govern the emissions response and their relative ordering determines which processes dominate (Section 4.1). Second, the overcount of anthropogenic emissions arising from plant-only metering is quantified, both as a rate and as a cumulative cost (Section 4.2). Third, the distinct behavior of CO<sub>2</sub> reinjection

**Table 3**  
*Characteristic Timescales of the Lumped-Parameter CO<sub>2</sub> Model*

| Timescale  | Definition               | Control     | Calibrated values                            |
|------------|--------------------------|-------------|----------------------------------------------|
| $t_p$      | $S\phi/(Kg)$             | Reservoir   | 1–10 years                                   |
| $t_\beta$  | $1/\beta$                | Both        | 6.3 years (RK), 9.6 years (NT)               |
| $t_\alpha$ | $C_0/\alpha$             | Both        | –                                            |
| $t_{res}$  | $M/ q_{up} $             | Both        | 15 years (RK), 123 years (NT)                |
| $t_q$      | $M/(f_q q_0)$            | Operational | –                                            |
| $\tau$     | Injection-production lag | Operational | 0–30 years                                   |
| $t_\kappa$ | $M/\kappa$               | Reservoir   | 2 months (basalt), $\gg 100$ years (silicic) |

with delayed breakthrough is considered (Section 4.3). Finally, the implications of these mechanisms for long-term CO<sub>2</sub> storage in a flow-through geothermal reservoir are discussed (Section 4.4).

#### 4.1. Timescales

The CO<sub>2</sub> emissions response of a geothermal system is governed by the interplay of several characteristic timescales. Some are intrinsic properties of the reservoir, others are set by operational decisions, and several depend on both. Table 3 summarizes the six timescales that arise in the model, their definitions, and the degree to which they are amenable to operational control.

Exponential responses of pressure and CO<sub>2</sub> content in geothermal reservoirs can be characterized by their associated timescales. The pressure equilibration time  $t_p$  is an intrinsic reservoir property set by hydraulic conductivity, surface area and porosity, with values of order 1–10 yr for the fields considered here. The CO<sub>2</sub> loss time  $t_\beta = 1/\beta$  and restoration time  $t_\alpha = C_0/\alpha$  characterize how rapidly CO<sub>2</sub> is removed from and replenished in the reservoir. Both depend on reservoir properties such as outflow conductivity and natural upflow, and operational parameters like extraction rate, capture fraction and mineralization. The exponential decline in plant emissions documented across New Zealand geothermal fields (McLean et al., 2024) and Turkish fields (Akin et al., 2020) is consistent with the  $t_\beta$ -controlled decay predicted by this model. Hosgor et al. (2016) recovered this exponential character in an earlier lumped-parameter formulation, whereas this study extends that framework to resolve the interplay of  $t_\beta$  with other timescales.

The reservoir residence time  $t_{res} = M/|q_{up}|$  measures how long fluid and dissolved CO<sub>2</sub> reside in the reservoir before exiting. This is primarily a reservoir property but shortens under production as extraction draws additional deep upflow (Section 2.2.1). Under pre-development conditions, Rotokawa has  $t_{res,0} \approx 15$  yr while Ngā Tamariki has  $t_{res,0} \approx 123$  yr, reflecting a ten-fold difference in natural throughput rates. Under production, these shorten to approximately 12 and 105 years, respectively. The flushing time  $t_q = M/(f_q q_0)$  and breakthrough delay  $\tau$  are mainly operational:  $t_q$  is set by net extraction rate and controls the pace of fluid overturning and CO<sub>2</sub> extraction from the reservoir, while  $\tau$  depends on injection well placement and reservoir flow paths. Finally, the mineralization timescale  $t_\kappa = M/\kappa$  is a reservoir property that varies by orders of magnitude with lithology, from  $\sim 2$  months in reactive basalts (Snæbjörnsdóttir et al., 2020) to multiple decades or centuries in mildly reactive silicic formations (Altar et al., 2024).

The relative ordering of these timescales determines which physical processes dominate the emissions trajectory. Four key comparisons are discussed below.

##### 4.1.1. Pressure Equilibration Versus CO<sub>2</sub> Loss ( $t_p$ Relative to $t_\beta$ )

When pressure equilibration is rapid ( $t_p \ll t_\beta$ ), the degassing pulse driven by pressure decline is short-lived relative to the concentration response. This early-time degassing is the same phenomenon described by Grant (1977) and modeled by M. O’Sullivan et al. (2021) in gas-dominated fields such as Broadlands-Ohaaki. This transient damps out within a few  $t_p$  and the subsequent evolution of reservoir concentration is controlled almost entirely by the slower loss timescale  $t_\beta$ . In this limit the two-exponential solution (Equation 29) effectively

reduces to a single decaying exponential, and emissions trajectories are smooth and near-monotone after the first few years.

When pressure equilibration is slow ( $t_P \gg t_\beta$ ), the pressure-driven  $\text{CO}_2$  source changes gradually throughout the field lifetime. Reservoir concentration tracks the slowly-varying pressure quasi-statically, so emissions depend more on the rate of pressure decline rather than on the eventual steady-state pressure.

#### 4.1.2. Breakthrough Delay Versus $\text{CO}_2$ Loss ( $\tau$ Relative to $t_\beta$ )

When the breakthrough delay is short ( $\tau \lesssim t_\beta$ ), the DDE correction to concentration dynamics is modest. Reinjecting fluid returns quickly relative to the concentration response, and the system converges smoothly to the delayed-case equilibrium  $C_\infty^{(\tau)} = \alpha/(\beta - \gamma)$  without significant overshoot. The higher steady-state concentration relative to the no-delay case is approached gradually.

When the breakthrough delay is long ( $\tau \gg t_\beta$ ), the reservoir concentration first approaches the apparent no-delay equilibrium  $C_\infty^{(0)} = \alpha/\beta$ , as if no recirculation were occurring. At time  $t \approx \tau$  the presumably high concentration reinjected fluid returns to the reservoir and begins perturbing the reservoir. An example of a long-delay system is described by von Hirtz (2016) where 20 years of NCG reinjection at Puna, Hawai'i, has yet to produce breakthrough.

The delayed arrival of high- $\text{CO}_2$  reinjected water can cause a secondary rise in emissions. The initial apparent decline may suggest a false equilibrium that is lower than that eventually realized. This poses challenges for monitoring that measures and extrapolates short-term trends. For NCG capture programmes, emissions trajectories measured before  $t = \tau$  are likely to be insufficient for regulatory processes concerned with long-term carbon storage.

#### 4.1.3. Mineralization Versus Return and Residence Times ( $t_k$ Relative to $t_{\text{res}}$ and $\tau$ )

The ratio  $t_k/(\tau + t_{\text{res}})$  determines whether injected  $\text{CO}_2$  is permanently sequestered through water-rock reactions before it returns to and transits the reservoir. When  $t_k \ll \tau + t_{\text{res}}$ , mineralization converts dissolved  $\text{CO}_2$  to stable carbonates faster than it can exit from the subsurface. This is the condition for effective permanent storage. At Carbfix, where  $t_k \approx 2$  months (Snæbjörnsdóttir et al., 2020), this condition is effectively satisfied against most plausible  $t_{\text{res}}$  excepting short-circuit scenarios between injection and production wells.

In less reactive formations typical of New Zealand geothermal systems, where  $t_k$  may be decades to centuries (Altar et al., 2024), mineralization competes poorly with throughput and most dissolved  $\text{CO}_2$  passes through the reservoir unreacted. In such systems, the reservoir functions as a temporary dissolved-phase store rather than a mineralization trap, and  $\text{CO}_2$  retention depends entirely on the residence time and operational strategy (Section 4.4). Where residence and mineralization times are comparable, placing injection wells further from the reservoir may be an effective method to reduce  $t_k/(\tau + t_{\text{res}})$  and maximize mineral trapping.

## 4.2. Overcounting of Emissions

The current emissions pricing scheme in New Zealand (the Emissions Trading Scheme—ETS) charges geothermal operators for  $\text{CO}_2$  emissions derived from produced geothermal fluids that are subsequently discharged to the atmosphere, that is, the plant emissions  $Q_{\text{pp}}$ . While straightforward to measure, this quantity does not always accurately represent the anthropogenic impact of geothermal production on a field's total  $\text{CO}_2$  emissions (M. O'Sullivan et al., 2021). These anthropogenic changes in geothermal surface emissions are not generally considered when calculating emissions factors for global inventories (Fridriksson et al., 2016). To address this gap, an overcount definition is developed that provides a physically-motivated quantification of the effect.

The overcount is defined as the difference between plant emissions and the true anthropogenic emissions:

$$Q_{\text{overcount}} = Q_{\text{pp}} - Q_{\text{anthropogenic}} = Q_{\text{pp}} - (Q_{\text{total}} - Q_{\text{surf},0}), \quad (46)$$

where  $Q_{\text{total}} = Q_{\text{pp}} + Q_{\text{surf}}$  is the total emissions from the field and  $Q_{\text{surf},0}$  is the pre-development surface emission rate (Equation 45). A positive overcount indicates that plant emissions exceed the true anthropogenic impact and that the operator is being charged for emissions that would have occurred naturally. A negative overcount implies that plant emissions undercount the true impact, for instance when production-induced changes to surface fluxes are not accounted for.

At the post-development steady state, the overcount can be evaluated analytically. Using the steady-state mass balance (Equation 44), total emissions are  $Q_{\text{total},\infty} = Q_{\text{surf},0} + (K_{\text{up}}/K)f_q q_0 C_0$ , giving

$$Q_{\text{overcount},\infty} = f_c q_0 C_{\infty} - \frac{K_{\text{up}}}{K} f_q q_0 C_0. \quad (47)$$

This expression highlights two competing effects. The first term represents plant emissions at the new equilibrium concentration, while the second represents the induced upflow of deep  $\text{CO}_2$ -bearing fluid that elevates surface emissions above their natural level. In the limit of zero  $\text{CO}_2$  reinjection ( $f_c = 1$ ), the overcount depends on the balance between plant emissions at the diluted equilibrium concentration and the induced upflow. In the opposite limit of complete  $\text{CO}_2$  reinjection ( $f_c = 0$ ), plant emissions vanish but surface emissions exceed  $Q_{\text{surf},0}$  due to induced upflow, giving a negative overcount. This implies that although the operator pays nothing, they are nevertheless increasing total field emissions.

Integrating the overcount over a period of production gives the cumulative mass of  $\text{CO}_2$  for which an operator is over- or under-charged,

$$G(t) = \int_0^t Q_{\text{overcount}}(t') dt' = \int_0^t [Q_{\text{surf},0} - Q_{\text{surf}}(t')] dt', \quad (48)$$

where the second equality follows because  $Q_{\text{overcount}} = Q_{\text{pp}} - (Q_{\text{total}} - Q_{\text{surf},0})$  and  $Q_{\text{total}} = Q_{\text{pp}} + Q_{\text{surf}}$ , so the cumulative overcount is the time-integrated suppression of surface emissions below their pre-development baseline. For a non-reactive field, solving Equation 48 with the closed-form outflow (Equation 10) and concentration (Equation 29) yields a first term that grows linearly with time at the steady-state rate  $Q_{\text{overcount},\infty}$  (Equation 47), plus early transients that decay within a few characteristic times. Evaluating Equation 48 over the calibrated posterior ensembles, the cumulative overcount at Rotokawa over the 2011–2023 period for which the field has been charged is 0.37 Mt $\text{CO}_2$  (10–90th percentile 0.15–0.60 Mt), approximately one third of the  $\sim 1.1$  Mt of plant emissions charged under the ETS over the same interval. Projected forward, it reaches 1.7 Mt at 50 years and 3.5 Mt at 100 years of production. At Ngā Tamariki the cumulative overcount is an order of magnitude smaller (0.036 Mt over 2015–2023, 0.48 Mt at 100 years), because its pre-development surface emissions are much lower (about 5.5 kt  $\text{yr}^{-1}$  against 44 kt  $\text{yr}^{-1}$  at Rotokawa), leaving far less natural surface flux available to be suppressed.

Figure 9 shows the overcount trajectories and steady-state distributions for the calibrated Rotokawa and Ngā Tamariki models. At Rotokawa (Figure 9a), the overcount is large and positive, typically 17–45 kt  $\text{yr}^{-1}$ , indicating that plant emissions substantially overestimate the anthropogenic contribution. This reflects the field's relatively high  $f_c = 1$  (no  $\text{CO}_2$  capture) and moderate concentration decline. At Ngā Tamariki (Figure 9b), the overcount is much smaller and trends toward zero over time. This is because the field has a relatively small throughput ( $K \approx 1.0 \times 10^{-5}$  m s) compared to the extraction rate, which results in substantial suppression of the surface emissions that are largely substituted by plant emissions.

The practical implication is that plant-based emissions accounting, while easier to implement than field-wide surface flux measurements, is likely introducing a systematic bias whose sign and magnitude depends on field and plant-specific characteristics. This has been recognized by Bertani and Thain (2002) and M. O'Sullivan et al. (2021), the latter who modeled an emissions balance for operation of the Ohaaki geothermal field, although they did not explicitly quantify the overcount. For Rotokawa, a modeled overcount between 30 and 40 kt  $\text{yr}^{-1}$  corresponds to an annual expense of 1.5–2.0 M \$NZ at a contemporary ETS emission price of 50 \$NZ/t. This is 5–6 times higher than the overpayment estimated by Yang et al. (2024) based on changes in surface emissions at the field.

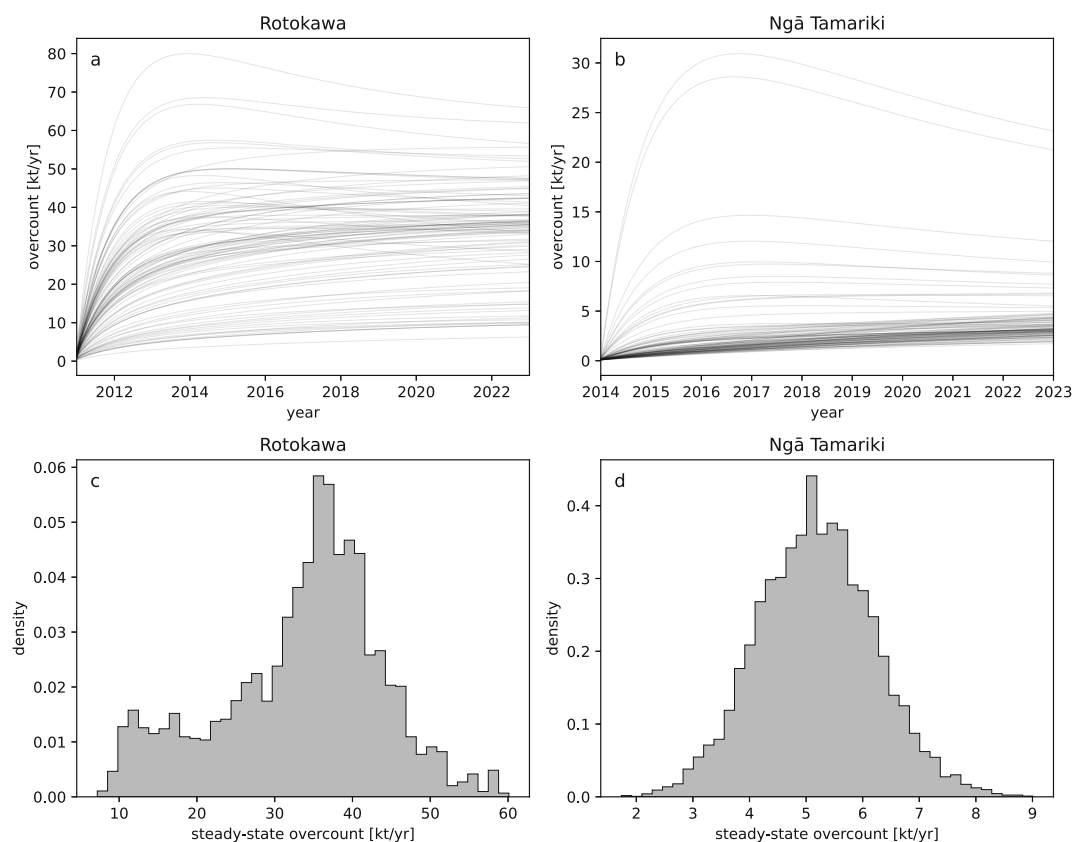


**Figure 9.** Overcount of emissions for the calibrated models. (a, b) Time series of overcount for 100-member posterior ensembles at Rotokawa and Ngā Tamariki, respectively. (c, d) Histograms of steady-state overcount  $Q_{\text{Overcount},\infty}$  across the full posterior.

Sbrana et al. (2021) have gone further, proposing that at locations like Mt. Amiata, surface emissions are suppressed in proportion with plant emissions and, since the net anthropogenic impact is small, such fields should be exempt from emissions charges. This is approximately the case for the median Ngā Tamariki model, but only in the equilibrium limit. Following some decades of the field diluting to low concentration, plant emissions of  $6 \text{ kt yr}^{-1}$  approximately balance the  $5.5 \text{ kt yr}^{-1}$  of pre-development surface emissions that are eventually suppressed to  $0.5 \text{ kt yr}^{-1}$ . In the interim, however, plant emissions are substantially higher than the modeled pre-development level, and the overcount is comparatively small, generally  $<5 \text{ kt yr}^{-1}$ .

These simplified models, although capable of matching and explaining emissions trends and inferring unobserved surface or unobservable baseline emissions, are likely not sufficient on their own to support changes to regulation or field-specific corrections to emissions charges. The advances needed to bridge this gap—including field-specific numerical models, repeat surface  $\text{CO}_2$  flux surveys, and continuous monitoring—are discussed further in Section 5.

### 4.3. $\text{CO}_2$ Reinjection and Delayed Breakthrough

This section considers the impact of 100%  $\text{CO}_2$  reinjection at a producing geothermal field. In these scenarios, pressure equilibration is assumed to occur quickly during initial production, that is,  $t_p \ll t_\beta$ , which is consistent with the calibrated models in Section 3.3. Subsequently, 100%  $\text{CO}_2$  reinjection is implemented at time  $t_{\text{CO}_2}$ , at which time plant emissions drop to zero ( $r_C^{\text{new}} = 0$ ). A fraction  $\eta$  of the stored  $\text{CO}_2$  eventually is assumed to return to the reservoir after a breakthrough delay  $\tau$ , while the remainder  $(1 - \eta)$  is assumed permanently sequestered through mineralization or other trapping mechanisms.

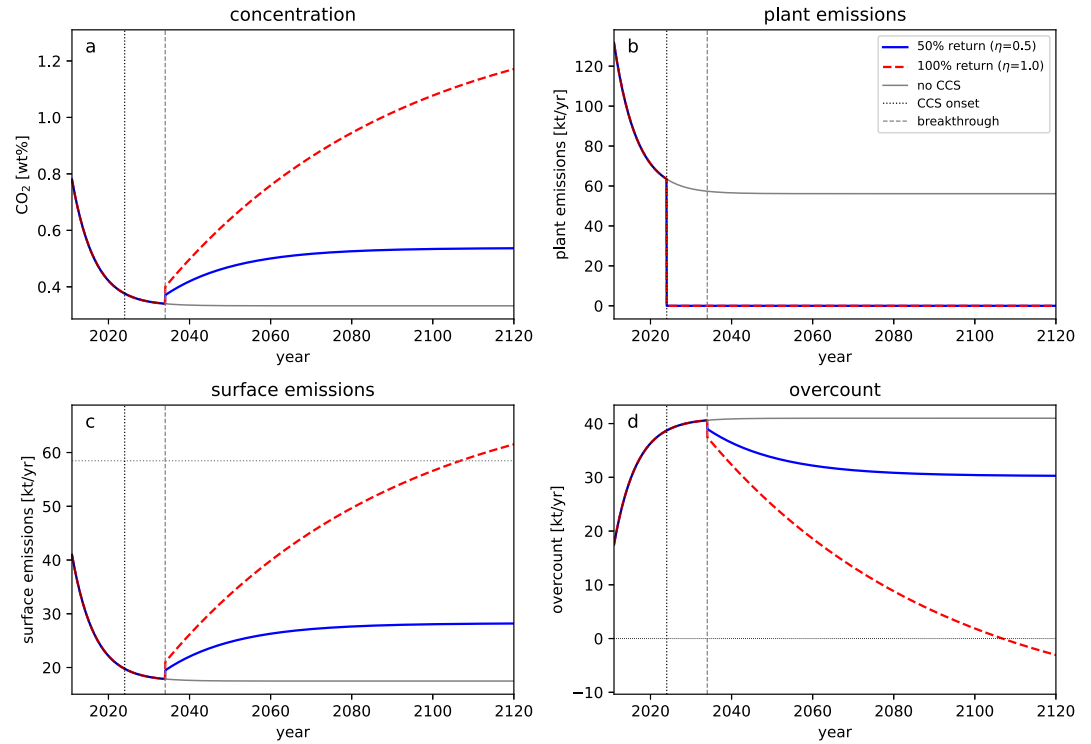


**Figure 10.** Effect of 100% CO<sub>2</sub> injection on the median calibrated Rotokawa model (non-reversal posterior subset), projected to 2150. CO<sub>2</sub> injection begins in 2024 with a 10-year breakthrough delay. Two return fractions are shown:  $\eta = 0.5$  (50% permanently sequestered, solid blue) and  $\eta = 1.0$  (full return, dashed red). The no-CO<sub>2</sub>-injection baseline is shown in gray. Vertical lines mark CO<sub>2</sub> injection onset (dotted) and breakthrough (dashed). (a) Reservoir CO<sub>2</sub> concentration, (b) plant emissions, (c) surface emissions, and (d) overcount, which becomes negative for the full-return scenario around 2107. The horizontal dotted line in (c) is the pre-development surface emission rate  $Q_{\text{surf},0}$ .

This scenario is well-described by the piecewise dominant-mode approximation to the DDE, given by Equation 49, modified for an initial condition that reflects an adjusted reservoir concentration at the time CO<sub>2</sub> capture begins,  $C(t_{\text{CO}_2})$ .

$$C(t) = \begin{cases} C_{\infty}^{(0)} + (C_0 - C_{\infty}^{(0)})e^{-\beta_0 t}, & t < t_{\text{CO}_2} + \tau, \\ C_{\infty}^{(\tau)} + \frac{C(t_{\text{CO}_2}) - \alpha/\lambda_1}{1 + \beta_{\tau}\tau e^{\lambda_1\tau}} e^{-\lambda_1(t-t_{\text{CO}_2})}, & t \gg t_{\text{CO}_2} + \tau. \end{cases} \quad (49)$$

Figure 10 summarizes hypothetical CO<sub>2</sub> injection scenarios using parameters of the median Rotokawa model (Section 3.3). CO<sub>2</sub> capture and reinjection begin in 2024 ( $t_{\text{CO}_2} = 13$  yr after the start of production). A  $\tau = 10$ -year breakthrough delay has been used for illustration, although in practice this should be estimated for a particular field on the basis of tracer testing or modeling (Muskat, 1938). Two return fractions are considered:  $\eta = 0.5$  (half of the CO<sub>2</sub> permanently sequestered) and  $\eta = 1.0$  (all CO<sub>2</sub> eventually returns).

In both scenarios, the onset of CO<sub>2</sub> injection causes plant emissions to drop immediately to zero. Reservoir CO<sub>2</sub> concentration continues to decline along the pre-capture trend (Figure 10a). After breakthrough in 2034, the returning CO<sub>2</sub> arrests the decline and concentrations begin to recover toward a new equilibrium that depends on  $\eta$ . For  $\eta = 0.5$ , the equilibrium concentration is lower than  $C_0$ , reflecting permanent removal of half the stored CO<sub>2</sub>. For  $\eta = 1.0$ , the equilibrium is higher, indicating that CO<sub>2</sub> is being concentrated in the reservoir.

These scenarios also illustrate how overcount can become negative over time (Figure 10d). Following the onset of CO<sub>2</sub> injection, the overcount declines rapidly from its pre-injection value. At this time, the plant owner is not

being charged for emissions through the plant and so it is not immediately obvious how they are “overpaying” on emissions. However, as the overcount takes changes in surface emissions into account, and these remain considerably suppressed below the pre-development level (Figure 10c), arguably the plant operator could receive a credit for causing fewer emissions to enter the atmosphere. Later though, for  $\eta = 1.0$ , the overcount declines due to concentrating  $\text{CO}_2$  in the reservoir that raises surface emissions, and eventually it switches sign to become negative. At this time, the surface emissions exceed the pre-development baseline,  $Q_{\text{surf},0}$ . However, the operator would pay nothing under a plant-metering rule that shows all their  $\text{CO}_2$  being injected back into the reservoir. This is not always the case: for  $\eta = 0.5$ , the permanent sequestration of half the stored  $\text{CO}_2$  keeps the equilibrium concentration lower and the overcount remains positive, stabilizing at approximately  $30 \text{ kt yr}^{-1}$ .

#### 4.4. Long-Term Storage of $\text{CO}_2$ in Geothermal Systems

Traditional carbon capture and storage (CCS) in subsurface reservoirs would typically treat the storage target as a boundable container, wherein  $\text{CO}_2$  is injected, the pore space filled, and it is intended that  $\text{CO}_2$  is retained in the volume indefinitely. In a convecting geothermal system subject to dissolved phase injection, the storage container is a flow-through system with ongoing natural  $\text{CO}_2$  fluxes (Equation 17), so the relevant storage concepts are fundamentally different. Three dissolved-phase measures and one mineral-phase measure are useful for thinking about geothermal carbon storage.

Potential dissolved storage is the mass of  $\text{CO}_2$  the reservoir could hold if all liquid were saturated at the current pressure:

$$M_{\text{pot}}(t) = M C_s(P(t)), \quad (50)$$

where  $C_s(P)$  is the pressure-dependent solubility (Equation 18). Because production reduces reservoir pressure and hence  $C_s(P)$ , potential storage itself declines over time. Furthermore, boiling reduces the amount of liquid mass,  $M$ , that can dissolve  $\text{CO}_2$ , also reducing potential storage. On the other hand, calibration of models for Ngā Tamariki and Rotokawa yields low end values of  $M$  that suggest only a subset of the reservoir is participating in  $\text{CO}_2$  exchange and that ways might be found to increase this, for instance, through additional drilling.

Actual dissolved storage is the  $\text{CO}_2$  mass presently dissolved in the reservoir fluid:

$$M_{\text{act}}(t) = M C(t). \quad (51)$$

This quantity cannot exceed  $M_{\text{pot}}$  in a single liquid-phase system, and the gap  $M_{\text{pot}} - M_{\text{act}}$  represents the unused dissolved-phase capacity. Furthermore,  $M_{\text{act}}$  can remain constant despite losses via surface or plant emissions, as long as these are balanced by upflow or reinjection returns.

Storage change quantifies the net gain or loss of dissolved  $\text{CO}_2$  relative to initial conditions. In the absence of boiling-induced mass loss, this is defined as:

$$\Delta M(t) = M(C(t) - C_0). \quad (52)$$

Storage change is negative for diluting fields and positive for concentrating fields.

*Mineralized storage* accumulates through water-rock reactions and is independent of the dissolved-phase measures:

$$M_r(t) = \int_0^t \kappa(C(t') - C_r) dt'. \quad (53)$$

This integral grows monotonically provided  $C > C_r$  and represents the only form of permanent storage in the model.

These storage quantities are illustrated in Figure 11 for three scenarios.

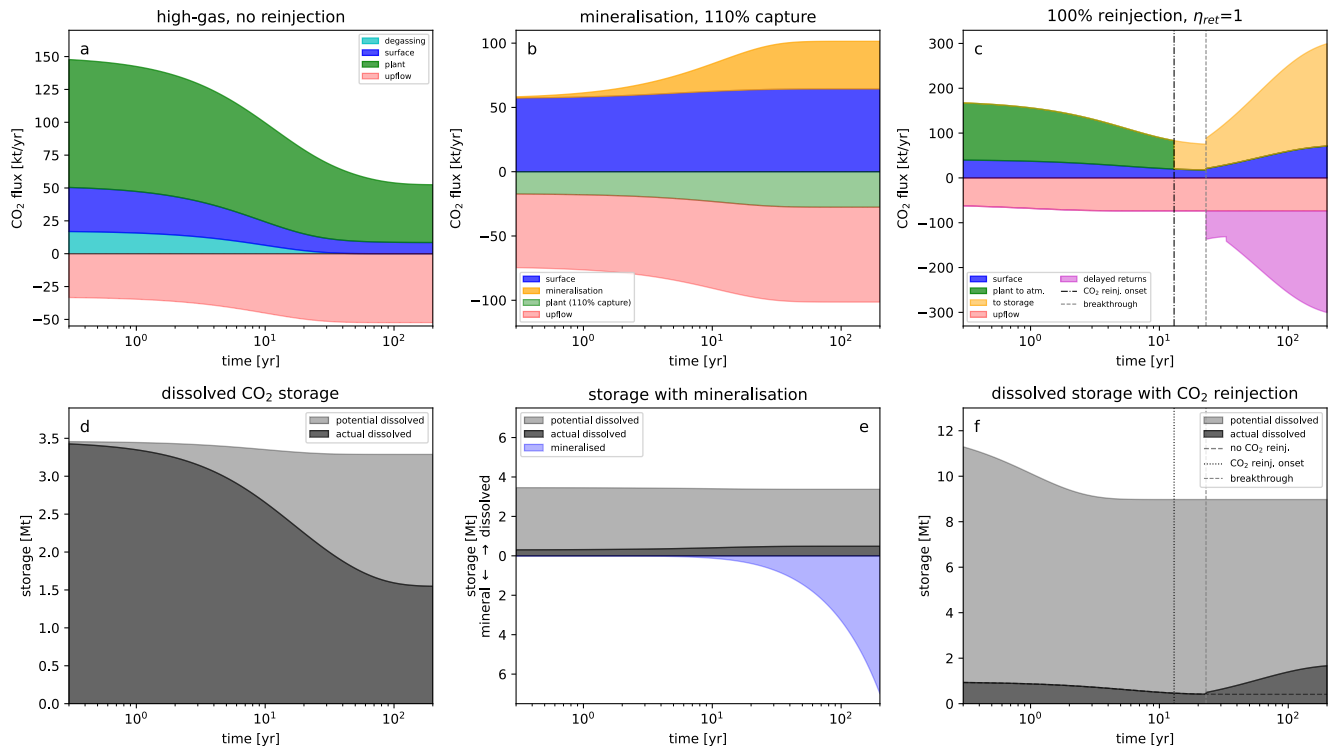


**Figure 11.** CO<sub>2</sub> fluxes (top) and storage (bottom) for three geothermal CO<sub>2</sub> scenarios. (a, d) A high-gas, solubility-constrained field with no reinjection. (b, e) A low-gas field with 110% CO<sub>2</sub> capture and mineralization ( $\kappa = M/5$  yr). (c, f) 100% CO<sub>2</sub> reinjection with a 10-year breakthrough delay before full return ( $\eta = 1$ ), using calibrated Rotokawa parameters.

#### 4.4.1. Scenario 1: High-Gas Production Without ReInjection

In a high-gas field without CO<sub>2</sub> reinjection (Figures 11a and 11d), production depletes the reservoir of CO<sub>2</sub> through a combination of degassing driven by pressure decline and direct plant emissions. Both actual and potential dissolved storage decline over time, with actual storage falling faster than the solubility limit. No CO<sub>2</sub> is stored permanently in this reservoir: instead, upflow CO<sub>2</sub> resides temporarily in the reservoir until it outflows or is extracted by wells. Actual storage reaches a new equilibrium value, about 50% of the pre-development amount, when the upflow, plant and surface fluxes balance each other at late time.

#### 4.4.2. Scenario 2: Mineralization With Negative Emissions

In a low-gas field where 110% of produced CO<sub>2</sub> is captured and reinjected ( $f_c = -0.1$ ), plus mineralization reactions are active (Figures 11b and 11e), the reservoir concentration rises above  $C_0$  because the extra CO<sub>2</sub> that is injected causes a concentrating trajectory. Actual dissolved storage increases correspondingly, although not by a large amount compared to the potential storage at saturation. Meanwhile, mineralization progressively converts dissolved CO<sub>2</sub> to a solid carbonate (Equation 53). The mineralization rate,  $\kappa(C - C_r)$ , starts near zero when  $C \approx C_r$  and accelerates as CO<sub>2</sub> accumulates, before reaching a steady rate once  $C$  approaches  $C_\infty$ . Thus, total mineral storage grows linearly at late time, exceeding 6 million tonnes after 200 years. If this mass of CO<sub>2</sub> was locked up as calcite, it would occupy about 4.1% of the pore volume initially filled by water. As mineralizing conditions are likely to be spatially variable with pH or cation availability, then this level precipitation could lead to local pore clogging issues if it concentrated along preferential flow pathways.

#### 4.4.3. Scenario 3: CO<sub>2</sub> Reinjection With Delayed Breakthrough

This scenario considers 100% of produced CO<sub>2</sub> is reinjected into the median calibrated Rotokawa reservoir starting 13 years after production begins (Figures 11c and 11f). A 10-year breakthrough delay separates injection from the return of stored CO<sub>2</sub> to the production zone, and all injected CO<sub>2</sub> eventually returns ( $\eta = 1$ ). Because the Rotokawa reservoir temperature (335°C) exceeds the range of validity of the linear solubility approximation

(Equation 18), potential storage is computed using the thermodynamic model of Mao et al. (2013). Plant emissions drop to zero at the onset of reinjection but surface emissions persist unchanged. After breakthrough, returning CO<sub>2</sub> arrests the decline in reservoir concentration, which then recovers toward a new, higher equilibrium (Section 4.3). Actual dissolved storage temporarily dips during the delay window when CO<sub>2</sub> is being extracted from the reservoir but returns have not yet arrived. After breakthrough, CO<sub>2</sub> concentration increases again.

#### 4.4.4. Calibrated Models

Model calibration at Rotokawa and Ngā Tamariki constrains values of  $M$ ,  $C_0$  and hence order of magnitude estimates of initial CO<sub>2</sub> dissolved in the participating reservoir. For Rotokawa, the posterior median is 0.97 MtCO<sub>2</sub> (90% credible interval: 0.67–1.28 MtCO<sub>2</sub>). At the same time, cumulative plant emissions charged under the ETS from 2011 to 2023 at Rotokawa total 1.1 Mt, similar to the dissolved storage. However, the reservoir is clearly not depleted of CO<sub>2</sub>, as attested by plant emissions of 60–70 kt yr<sup>−1</sup>. The discrepancy is explained by sustained replenishment of CO<sub>2</sub> by deep upflow and reduced surface emissions, although these effects are not recognized under the present emissions charging regime.

## 5. Conclusions

The increasing adoption of CO<sub>2</sub> capture and reinjection at geothermal power plants, and the associated greenhouse gas inventories and emissions penalties these attract, necessitates the development of physics-based accounting frameworks. This study has developed a lumped-parameter model for CO<sub>2</sub> fluxes and storage in geothermal reservoirs. The model tracks pressure evolution, dissolved CO<sub>2</sub> concentration, and the partitioning of emissions between the power plant and the Earth's surface. Closed-form exponential and related solutions are obtained to estimate net emissions contributions from reservoir degassing, CO<sub>2</sub> reinjection with delayed breakthrough, reversal of outflow, and mineralization reactions. Calibrated against emissions data from Rotokawa and Ngā Tamariki, the model forecasts how CO<sub>2</sub> concentrations evolve over decades of production and at what level emissions will eventually stabilize.

The primary conclusion of this study is that CO<sub>2</sub> storage in geothermal systems is fundamentally dissimilar to traditional CCS. First, some geothermal systems receive a continuous supply of CO<sub>2</sub> from depth that, while resident in the reservoir for a time, is eventually discharged into shallow aquifers or the surface. Accounting for the anthropogenic effect of CO<sub>2</sub> reinjection must include alteration of the natural throughput. For instance, production without reinjection suppresses surface emissions, so that CO<sub>2</sub> solely-metered through the plant may significantly overcount (and hence overcharge) the net emissions change. Equally, 100% reinjection of captured CO<sub>2</sub> does not eliminate the anthropogenic effect but rather reallocates it from a plant emission to a surface one. If this is not accounted for, operators may end up undercounting their true emissions.

Second, geothermal reservoirs are not generally bounded containers for the permanent storage of CO<sub>2</sub>, which is often an adequate concept for CCS in gas fields or saline aquifers. Naturally-fluxing CO<sub>2</sub> is only resident in the reservoir for a specified time ( $t_{\text{res}}$ ) and it follows that the same applies for reinjected CO<sub>2</sub>. Therefore, active reinjection is required to maintain elevated levels of CO<sub>2</sub> storage in a geothermal reservoir over the long-term. Designs to achieve such long-term storage will need to either exploit mineralization that is effective over timescales shorter than  $t_{\text{res}}$  or reinject at distance to ensure a delayed return ( $\tau$ ).

The implication is that emissions accounting based on plant metering can systematically overcount the anthropogenic effects of geothermal production and this unfairly penalizes an important source of low-carbon energy. Although these simplified lumped-parameter models can match and explain emissions trends and infer unobserved surface or unobservable baseline emissions, they are not sufficient on their own to support changes to regulation or field-specific corrections to emissions charges. Several advances are needed. First, detailed studies of individual fields should be undertaken, as the sign and magnitude of the overcount depend on reservoir size, recharge, CO<sub>2</sub> content, and reinjection strategy. Second, improved monitoring of surface CO<sub>2</sub> fluxes is important to provide direct observational constraints on the behaviors inferred here, including early-time degassing and the suppression or enhancement of natural emissions during production. Repeat soil flux surveys, such as those conducted by Bloomberg et al. (2014) and Yang et al. (2024), are one path forward, although continuous survey methods might also be adopted from terrestrial carbon cycle studies, such as eddy covariance towers. Third, more detailed numerical models of CO<sub>2</sub> transport for individual fields, building on the approaches of M. O'Sullivan et al. (2021) and J. O'Sullivan et al. (2025), are needed to resolve spatial heterogeneity, gas cap dynamics, and

near-surface transport processes that the lumped-parameter framework neglects. Together, these steps could provide regulators with the confidence to move toward an emissions accounting framework based on true anthropogenic impact rather than the plant-metering rules currently in use in New Zealand.

The framework developed here can be generalized beyond the two fields used to demonstrate it. Governing equations for pressure, dissolved CO<sub>2</sub> and the partitioning of emissions (Sections 2.2–2.4) make no assumptions unique to Rotokawa or Ngā Tamariki, and transfer to other producing systems primarily through recalibration. For new cases, the requirements are coincident production and emissions time series data to calibrate against, as well as constraints on the values of lumped parameters. Modifications to the equations may be warranted where the physics omitted from the model is thought to dominate, for example, thermal effects of CO<sub>2</sub> reinjection, or gas-cap and/or two-phase behavior. In practice, the model's value for policy is that it quantifies the overcounted (Equations 46 and 47) gap between plant-metered emissions and actual changes in a field's anthropogenic CO<sub>2</sub> throughput. Thus, a field-calibrated model is a useful tool for both operators and regulators to set a fair price geothermal CO<sub>2</sub> emissions.

## Appendix A: Thermodynamic Functions

This appendix presents approximate expressions for CO<sub>2</sub> solubility and its derivatives (Figure A1), derived from the thermodynamic model of Duan and Sun (2003). The underlying model is for CO<sub>2</sub> in pure water; the gas phase is treated as pure CO<sub>2</sub>, so the controlling pressure is the total reservoir pressure rather than a separately tracked CO<sub>2</sub> partial pressure, and salinity is not included. Mixture and partial-pressure effects from steam or other NCGs are therefore not represented.

Equation 18 expresses solubility as a linear function of pressure with a slope parameter whose temperature dependence is closely approximated by a quadratic expression

$$\left. \frac{dC_s}{dP} \right|_T = \sum_{i=0}^2 c_i T^i, \quad (\text{A1})$$

where  $c_i = [4.5848 \times 10^{-3}, -3.3141 \times 10^{-5}, 1.3104 \times 10^{-7}]$ .

For systems that are boiling, pressure and temperature follow the saturation curve. CO<sub>2</sub> solubility in the pressure range 5–15 MPa can be approximated by the following cubic expression accurate to 1.2%

$$C_s(P, T_{\text{sat}}(P)) = \sum_{i=0}^3 c_i P^i, \quad (\text{A2})$$

where  $c_i = [6.3416 \times 10^{-2}, -2.1793 \times 10^{-2}, 3.7815 \times 10^{-3}, -1.6108 \times 10^{-4}]$ . The expression is approximately linear in the pressure range 3–11 MPa with the following expression also accurate to 1.2%

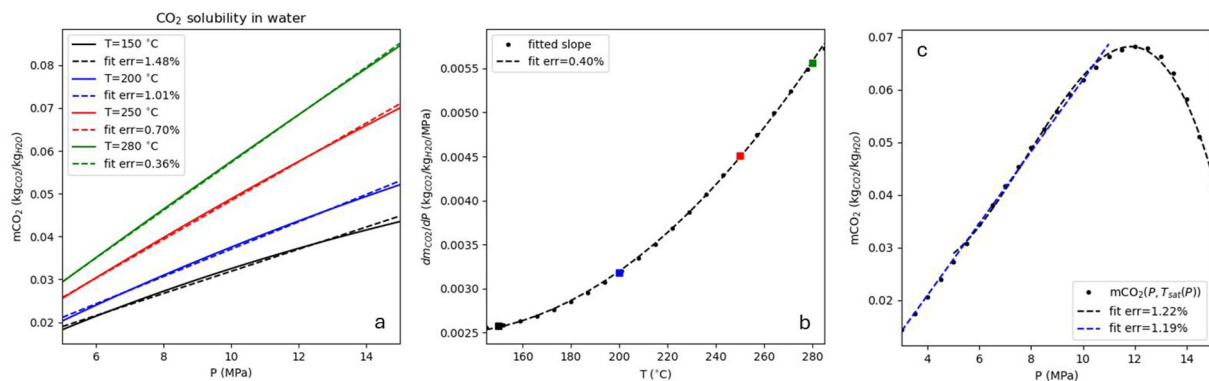


**Figure A1.** CO<sub>2</sub> solubility approximations derived from the thermodynamic model of Duan and Sun (2003). (a) Full solubility (solid curves) and its linear-in-pressure approximation (dashed, Equation 18) over 5–15 MPa for four isotherms; annotated percentages are the fit errors. (b) Linear slope parameter in (a) as a quadratic function of temperature. (c) Solubility along the boiling curve (solid points, full model) with a cubic fit (black dashed) and a linear fit (blue dashed) valid for 3–11 MPa.

$$C_s(P, T_{\text{sat}}(P)) = \sum_{i=0}^1 c_i P^i, \quad (\text{A3})$$

where  $c_i = [-6.3404 \times 10^{-3}, 6.8163 \times 10^{-3}]$ .

## Conflict of Interest

The author declares no conflicts of interest relevant to this study.

## Availability Statement

The lumped-parameter model, the Bayesian calibration routines, and the scripts that generate all figures in this study, together with the compiled plant-emissions time series used for calibration, are archived on Zenodo and openly available (Dempsey, 2026).

## Acknowledgments

I thank three anonymous reviewers and the Associate Editor for their careful assessment of this manuscript and comments that improved it. This work was supported by the New Zealand Government through the Ministry of Business, Innovation and Employment (MBIE), under contract UOC2456 for the Endeavour Research Programme “Derisking Carbon Dioxide Removal at Megatonne Scale in Aotearoa.” Open access publishing facilitated by University of Canterbury, as part of the Wiley - University of Canterbury agreement via the Council of Australasian University Librarians.

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