Modeling Lithium Brine Re-Injection for a DLE Brine Operation at the Salar de Atacama

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Hydrological issues associated with brine extraction to produce potash and lithium at the Salar de Atacama in Northern Chile are complex, but often over-simplified as "water unavailability". There are aspects to the situation that are logistical, political, economic, environmental, and commercial, but there is one central feature of the "drama in the Atacama" which is technical. That feature is the concern that brine extraction with evaporative processing that removes the water of the brine from the basin's aquifers could cause imbalances in the hydrology of the basin, impacting the stability of lower salt content lagoons at the periphery of the salar.[1, 2]

But if brine extraction operators in the Salar de Atacama could extract lithium from brine without evaporating most of the water, leaving potash in the brine, could the brine be re-injected back in the ground in a way that does not disrupt water tables? This could be enabled by a direct lithium extraction (DLE) technology solution. We have published multiple articles on this topic in the last year with differentiated perspectives focused on technical solutions to technical aspects of the lithium brine hydrology and extraction.[3, 4]

Zelandez has led a group of like-minded folks who share an interest in the technical aspects of the problem to understand how a DLE and brine re-injection strategy might work in the Salar de Atacama. This particular site for our studies was chosen because it is by far the most scrutinized lithium brine extraction site in the world, is the source of most lithium from brine, and as a result also has the most public hydrology data associated with it. That group includes:

Leonard Zourek, a Masters student at ETH Zurich in Switzerland. He wrote a chapter of his thesis on Salar de Atacama brine re-injection hydrology, building his own MODFLOW models using public data. The focus of his work was to understand if depletive brine extraction in the salar nucleus would eventually lead to brine levels dropping near sensitive lagoons.

Steve Shikaze and Steve Murray, expert hydrology modelers who build hydrology models for a living for lithium brine operations at Matrix Solutions. The focus of their work was to understand the dynamics of fresh & spent brine mixing after lithium was removed using a DLE technology and brine re-injected, and to see if that mixing might cause issues for a DLE operation.

With their permissions, we are publishing the products of their high-level models here for free and in full. Our intention for doing this is that the frameworks and ways of thinking demonstrated in these models may be helpful for developing preliminary understandings of what is possible for lithium brine development in South America and beyond. These studies should be considered preliminary and academic, but are also specific enough that they show where strings might be pulled to unravel more sophisticated insights via more detailed modeling.

There is nothing inherently "wrong" with evaporative brine processing as long as water availability for plants, animals, and humans is not impacted. However, there is significant interest in applying DLE to brine operations across the Lithium Triangle, and we hope that these models will provide helpful starting points for thinking about spent brine re-injection to either protect sensitive ecosystems, or at least prevent fresh and spent brine from mixing, as this could hurt project economics. We invite constructive feedback.

Acknowledgements

Thank you to Leonard Zourek of ETH Zurich, Steve Shikaze of Matrix Solutions, and Steve Murray of Matrix Solutions for their time and energy focused on understanding the solutions to these interesting and complex challenges. Thank you also to Zelandez team members Fernando Lourenco and Murray Brooker.

References

(1) Grant, 2020. Is Lithium Brine Water? URL.
(2) Grant, Hersh, *et al.*, 2020. "Is Lithium Brine Water?" – The Anti-Webinar. URL.
(3) Grant, Morgan, 2019. Re-Injection Enhanced Production for Direct Lithium Extraction (DLE) Projects. URL.
(4) Grant, Barros, 2020. Chile's Lithium Industry May Need a Tech Upgrade. URL.

Modelling Reinjection Of Spent Brine From Direct Lithium Extraction

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The work described in this document forms a part of my thesis to obtain the degree of MSc. Environmental Sciences from ETH Zurich, Switzerland.

Abstract

Current lithium (Li) production from salar brines relies on the evaporation of large volumes of water from brine, raising concerns about possible impacts on lagoon ecosystems in the mixing zone, at the edge of the salar nucleus. An application of Direct Lithium Extraction (DLE) to salar brines could reduce the need for evaporation, leaving large volumes of brin with less lithium in it. This study uses a constant-density MODFLOW model conceptually representing a part of the Salar de Atacama, Chile, to test whether spent DLE brine could be strategically reinjected into the upper halite aquifer to reduce the inflow of water from the mixing zone into the salar nucleus. It identifies that brine reinjection of up to around 12 L/s into a 500m-wide stretch could reduce inflow from the mixing zone and increase outflow to the salar nucleus. At higher rates, increased evaporation from the water table ("phreatic evaporation") makes brine reinjection less efficient. Furthermore, high reinjection rates can lead to flooding of the surface in the reinjection area, which can be mitigated by distributing the total reinjection flow among a higher number of wells. The most critical effect of high reinjection rates from a conservation perspective is that brine can flow into the mixing zone, threatening the water quality of its brackish water ecosystems. The vulnerability of the mixing zone is especially high in summer, when its water levels are lower, seasonally limiting safe reinjection rates. The design of a reinjection strategy will critically depend on the hydraulic conductivity of the brine-receiving layer. An accurate and high-resolution topographic survey of the model area is fundamental to correctly estimate evaporation from the water table. Reinjection will need to be accompanied by constant monitoring of water levels during operation to prevent brine flow into the mixing zone. Despite the limitations of this model (constant density, small model area, constant heads at the model boundaries, rough characterisation of hydraulic properties), its results are valuable for future work, as they point out important limitations and trends which spent DLE brine reinjection will face. In this sense, this study is meant as a starting point for modelling spent DLE brine reinjection which should be expanded and improved by future modelling work. Any reinjection project must avoid the inflow of brine into the mixing zone, as this would damage the very ecosystems DLE, in principle, allows to protect. When this is accounted for, this study finds that brine reinjection in the salar nucleus could mitigate potential impacts of depletive brine extraction and evaporation on the mixing zone ecosystems.

Contents

1 Introduction

Lithium extraction from salt lake (*salar* in Spanish) brines traditionally relies on an evaporative process to remove undesired salts and concentrate dissolved Li salts in the brine. Most of the water contained in brines is evaporated during this process. Direct Li extraction (DLE) describes a range of technologies which aim to selectively extract Li from salt lake or other brines without the need for prior evaporation. An application of DLE would drastically change the water balance of the Li extraction process, since it would strongly reduce the loss of water to evaporation. This scenario would generate high volumes of delithiated brine - a challenge from the perspective of disposal but also an opportunity to return water to the salar and mitigate the drawdown induced by pumping.

Given the hydrogeological functioning of many salares, it might also be an opportunity to mitigate potential impacts on important ecosystems at their margin. This is where low-salinity water, recharged at higher elevations, rises to the surface due to the density difference with the underlying brine of high salinity (see Fig. 1). The lagoons that are formed as a result of this flow behavior consist of brackish water and are important breeding grounds for many waterbirds, notably flamingos (Gajardo and Redón, 2019). As shown in Fig. 1, much water is evaporated in the mixing zone, but some flows into the salar nucleus. This flow could be further increased by brine extraction from the nucleus, which leads to a drawdown of the water table near the pumping location.

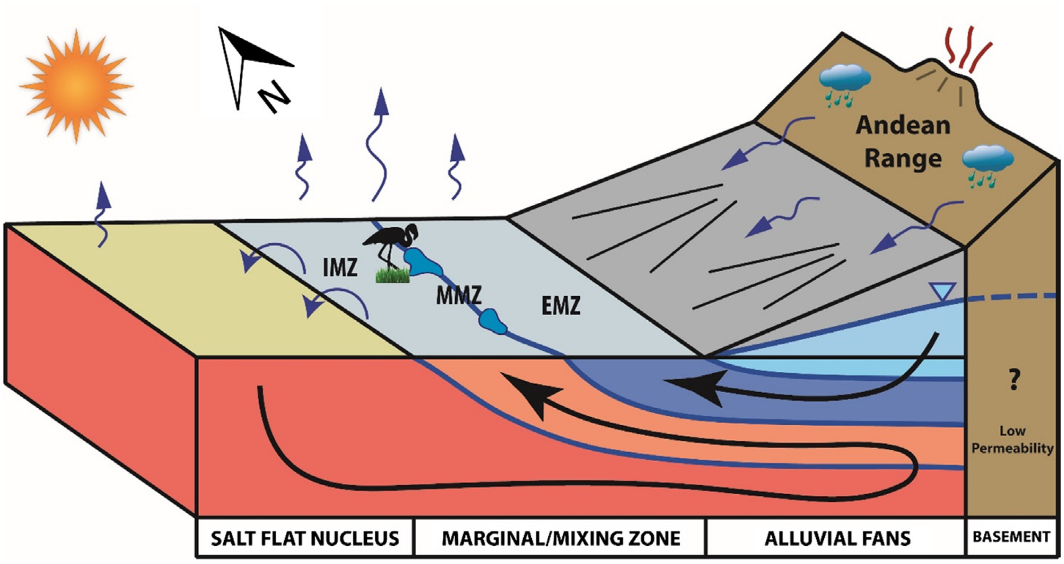


Figure 1: Schematic representation of freshwater (blue) overlying brine (red), separated by a "mixing zone" of intermediate salinity (orange). Figure from Marazuela et al. (2018)

Whether and at which time scale this drawdown propagates itself to the nucleus margin depends on the salar's characteristics and the applied pumping stress (J. Houston et al., 2011). Generally, however, it can be assumed that the removal of high volumes of brine from the nucleus aquifer is more likely to lead to such a drawdown than the removal of low volumes. Since DLE produces large volumes of spent brine, the net removal of brine from the salar could be lowered by reinjecting the brine. Furthermore, it could be strategically reinjected to the salar nucleus to reduce the inflow of water from the mixing zone. Conceptually this would involve reducing the hydraulic gradient near the nucleus margin by creating a groundwater mound through reinjection. This reinjected brine would then flow back into the salar nucleus instead of water from the mixing zone, shielding the mixing zone from the pumping-induced drawdown in the nucleus. However, if the groundwater mound is too high and the hydraulic gradient is reversed, reinjected brine could begin to flow off into the mixing zone, too, which would upset the water chemistry in its brackish water ecosystems. The creation of a groundwater mound could itself be a challenge, because it would have to exist against two resistances: evaporation rates rise when the water table gets closer to the surface and water flow away from the mound increases with the hydraulic gradient it creates.

This study aims to test the feasibility of the concept of strategically reinjecting DLE brine close to the nucleus margin using a constant-density numerical groundwater model of a part of the Salar de Atacama (SdA) in Northern Chile.

2 Methods

A MODFLOW-2005 model (Harbaugh, 2005; Harbaugh et al., 2017) was constructed using the ModelMuse graphical user interface (GUI) (Winston, 2019). The model is 500m wide, 5000m long and 100m deep. It is located in the south-western SdA and covers the transition from the nucleus into the internal mixing zone (Fig. 2). An overview of the model layers and boundary conditions (BCs) is shown in Fig. 3.

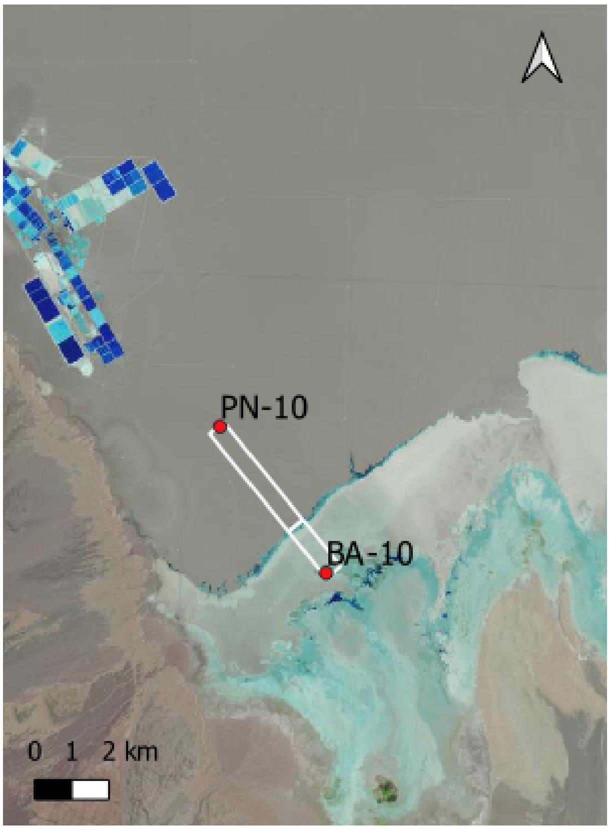


Figure 2: Locations of the model and of two observation wells. The white line crossing the model separates the nucleus (NW) and mixing zone (SE), which were modelled as subzones with different hydraulic conductivities. Satellite image from Amphos21 (2018).

2.1 Hydrostratigraphy and discretisation

The model surface elevation is set to 2300 masl, corresponding to the average elevation of the SdA nucleus. The hydrostratigraphic layers are similar to those defined by Marazuela et al. (2019a), i.e a 20m-thick upper halite, followed by a 30m-thick clay aquitard and a lower halite down to 100m below surface. The lower boundary of 100m below surface is a modelling choice and does not represent the contact with the bedrock. The uppermost 3m of the model are discretised into six 0.5m MODFLOW layers to accurately represent the effects of evaporation and reinjection. The remaining 17m of the upper halite, and the two lower layers are represented with one MODFLOW layer each, resulting in a nine-layer MODFLOW model. The upper halite layers are modelled as convertible layers, the lower two layers as confined layers. "Convertible" is the terminology used in MODFLOW's Layer-Property Flow package to represent unconfined layers. Cells in convertible layers are unconfined unless the head in the cell exceeds the cell top and they convert to confined cells.

Hydraulic conductivity is higher in the nucleus than in the mixing zone for the upper halite, and lower in the lower two layers (Fig. 3). These values correspond to the values Marazuela et al. (2019a) assigned to the relevant hydraulic conductivity zones (KA12b and KA9) in their regional flow model of the SdA. Vertical hydraulic conductivity (K_z) was defined as $0.1K_x$.

The model grid cell size for all well scenarios is 20m x 20m. To adequately represent reinjection using a 2m-wide trench, models of trench reinjection use a grid resolution of 2m x 20m.

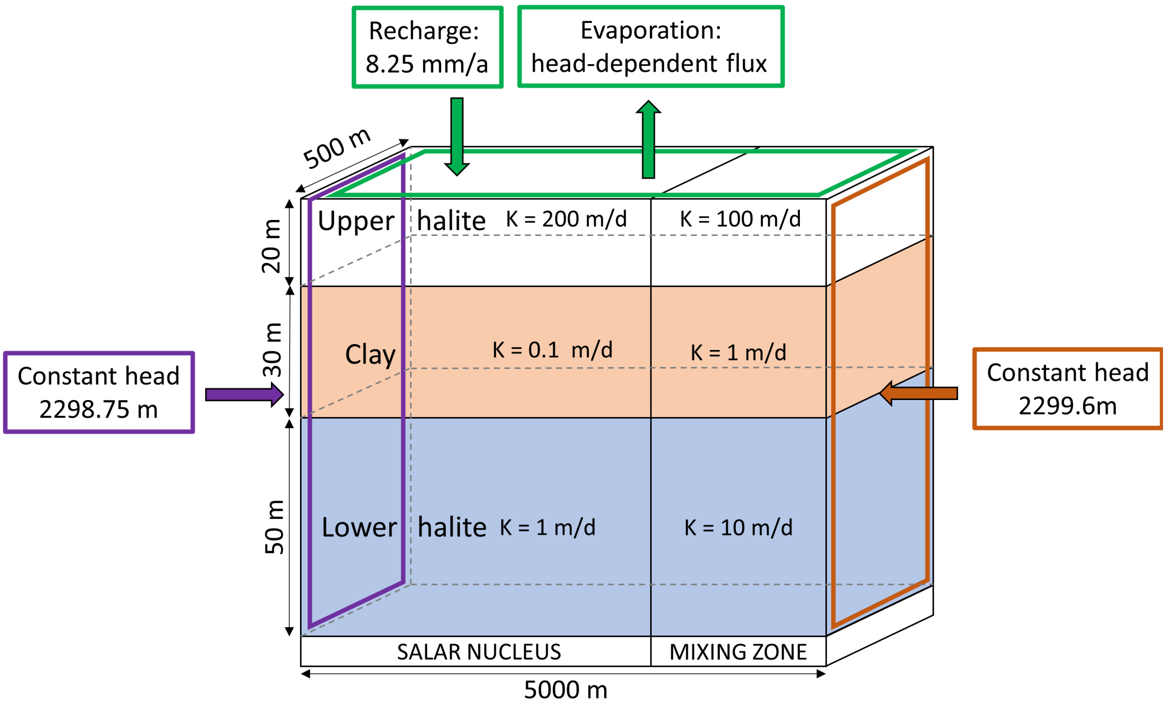


Figure 3: Schematic of the numerical model with dimensions, layers, hydraulic conductivities and BCs.

2.2 Boundary conditions (BCs)

The model bottom and the long sides are no-flow boundaries.

A constant-head BC is imposed at all active cells at the nucleus and mixing zone ends of the model with the time-variant specified-head (CHD) MODFLOW package. The prescribed head of 2298.75 masl at the nucleus end is taken from the phreatic surface contour map from Boutt et al. (2016) (a detail of which can be found in Fig. 6). The head of 2299.6 masl at the mixing zone end is the mean value of hydraulic head observations in piezometer BA-10 (Albemarle Ltda. (2020), Fig. 16).

Recharge from precipitation onto the model surface is represented by a constant recharge rate of 8.125 mm/a using the MODFLOW Recharge (RCH) package. This corresponds to a precipitation of 12.5 mm/a multiplied with an infiltration coefficient of 0.65, a mean value for the two recharge zones A13-e and A10-2 from Marazuela et al. (2019a).

Evaporation is modelled as a head-dependent flux using the MODFLOW Evapotranspiration Segments (ETS) Package. The flux is calculated from the distance of the water table to a specified surface (here: the model top) and ranges from the potential evaporation rate (E_0) at or above this surface to zero at a specified extinction depth. The user specifies a number of points which define linear segments of the evaporation-depth relation. In this model, a five-segment linearisation of the curve established for the SdA nucleus by Grilli and Vidal (1986) is used (Fig. 4). The two other evaporation curves shown are tested in the sensitivity analysis (Section 3.3).

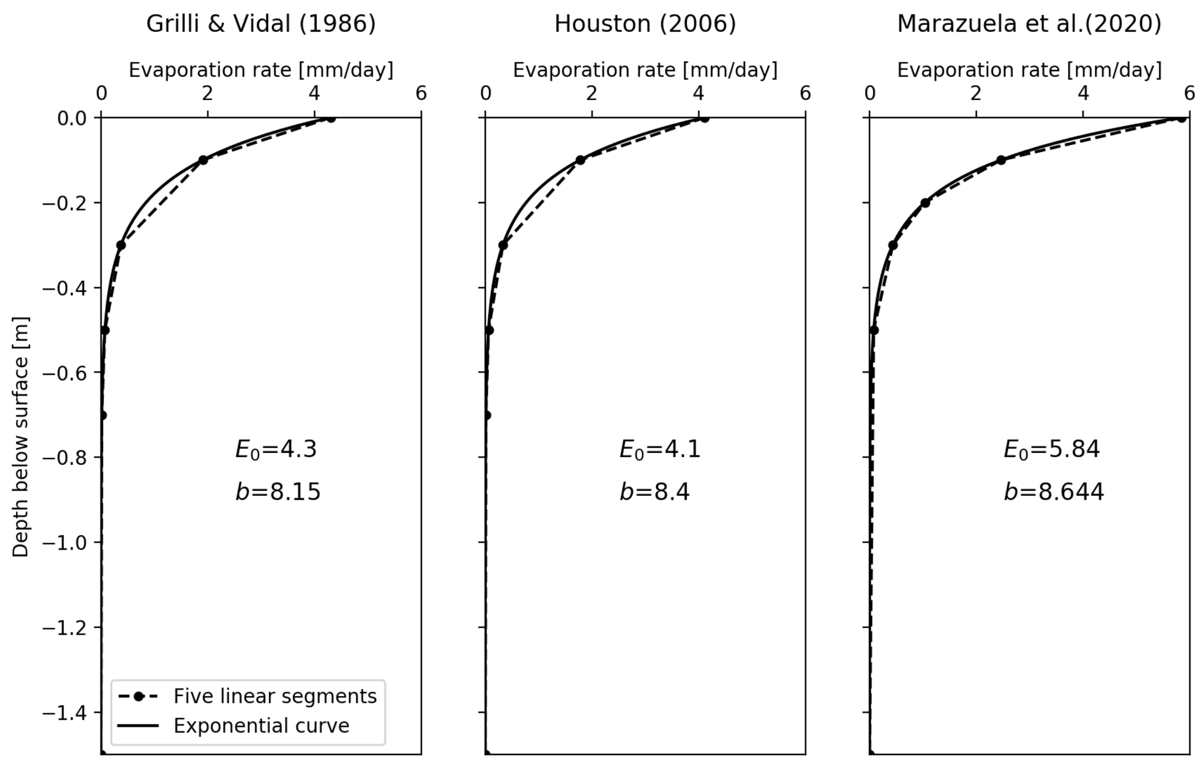


Figure 4: Exponential and linearly approximated relationships between water table depth below surface and evaporation rate. Fitting parameters for the exponential curves are printed.

The mathematical expression for the relationship between phreatic evaporation and depth of the water table below surface is:

$$E = E_0 * e^{(-b*z)}$$

where E_0 is the potential evaporation rate [mm/d], b is a fitting parameter and z is the (positive) depth of the water table below surface [m] (Marazuela et al., 2020).

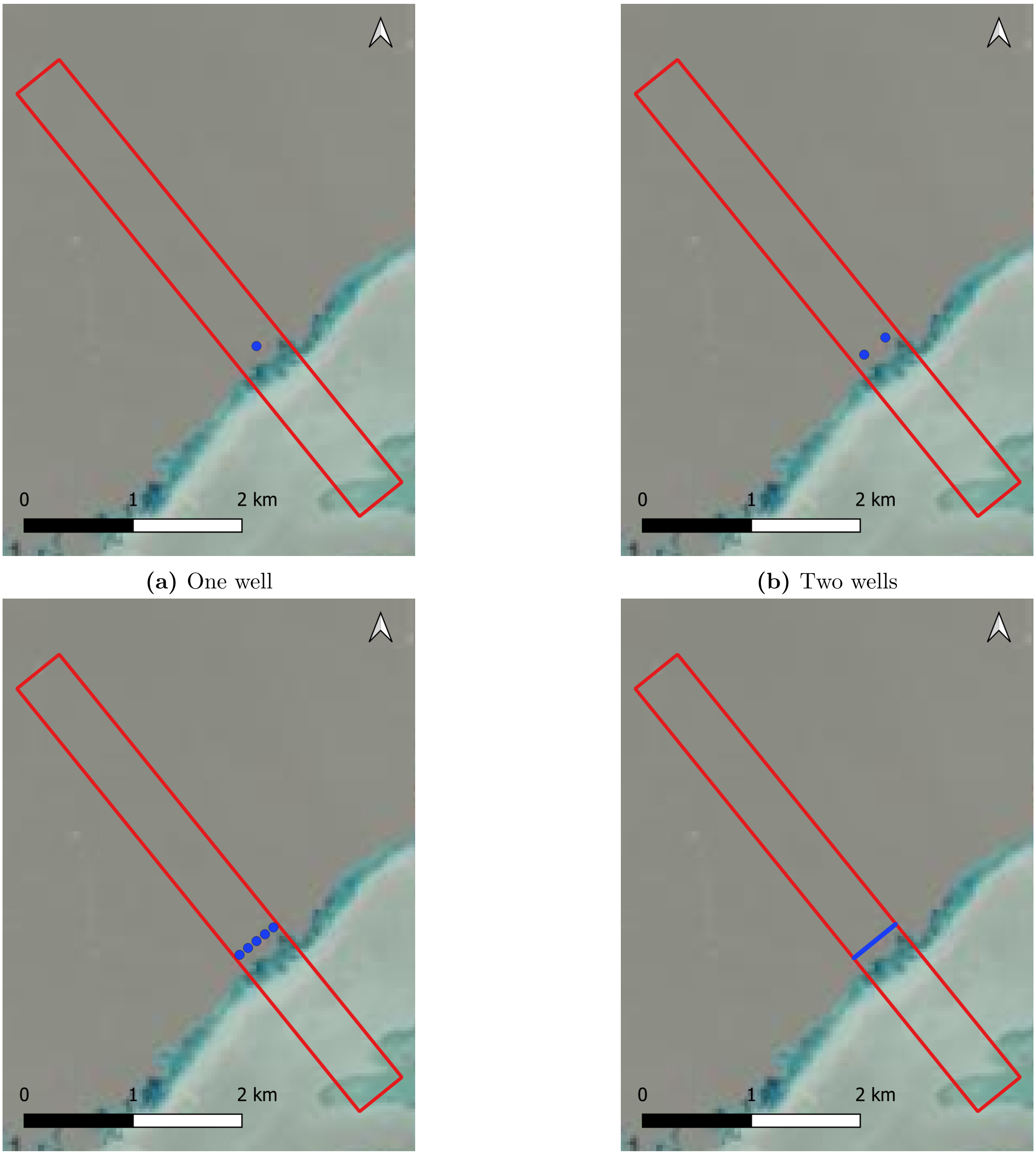
The Grilli and Houston equations are given in the respective articles (Grilli and Vidal, 1986; John Houston, 2006), Marazuela's equation was inferred from the description and lysimeter data provided in the supporting information to Marazuela et al. (2020). Extinction depth for all linearised curves is set to 1.5m below surface. Below this depth, evaporation drops to 0 mm/d.

Reinjection is modelled close to the salar nucleus margin, 200m inward from the visible boundary between nucleus and mixing zone. Three reinjection scenarios consist of reinjecting spent brine into the upper halite via one, two or five wells, a fourth scenario models reinjection via a 2m wide trench spanning the whole model width (Fig. 5).

Wells are modelled to inject water into the upper halite with the MODFLOW Well (WEL) package. Well screens conceptually range from 1m below surface to 11m below surface. Since the upper halite is discretised into seven MODFLOW layers, each reinjection well injects into five MODFLOW layers: the four 0.5m layers from 1-3m below surface and the 17m-thick layer starting at 3m below surface and going down to the top of the clay aquitard (20 m below surface). The upper two MODFLOW layers from 0-1 m below surface are modelled to receive no reinjection. The pumping rate applied to each layer is proportional to the layer's relative contribution to the screened length (conceptually 10m). Therefore, 80% of the reinjection flux is assigned to the lower layer (8m of screen), and 5% to each of the upper layers (0.5m of screen). However, since the lower layer is only represented by one MODFLOW layer, the reinjection flow is not actually vertically concentrated in the upper 8m of the model cell. Instead, the cell as a whole receives the inflow of 80% of the total reinjection rate and the hydraulic head responds uniformly inside the cell. This is why the well is only "conceptually" 10m long - MODFLOW treats the well reinjection as if it went from 1m below surface down to 20m below surface.

Reinjection via a trench does not have this vertical component. It is modelled as a 2m x 500m area receiving a homogeneous recharge into the uppermost active cell using the MODFLOW recharge (RCH) package.

The reinjection scenarios are modelled using a series of steady-state simulations. A first simulation with a reinjection rate of 0 L/s allows to establish the situation without reinjection ("base case"). It is followed by 25 steady-state simulations in which the total reinjection rate is increased up to 25 L/s in increments of 1 L/s.



(a) One well

(b) Two wells

(c) Five wells

(d) Trench (exaggerated line thickness)

Figure 5: The four reinjection scenarios simulated in this study. Satellite image from Amphos21 (2018).

2.3 Initial conditions

All model cells are assigned an initial head of 2299 masl, a value between the two heads at the constant-head BCs.

2.4 Solver

The finite difference equations are solved with the geometric multigrid (GMG) solver using the default settings (RCLOSE=1E-5, IITER=100, HCLOSE=1E-5, MXITER=100, ISM=0), resulting in mass balance discrepancies well below 1% for all simulations.

2.5 Postprocessing

To analyse flows at the mixing zone constant-head boundary, the software *Zonebudget* (Harbaugh, 1990) was used to compute local water budgets from MODFLOW model output files. Results were analysed and plotted with the Python package *floPy 3.3.0* (Bakker et al., 2016, 2018) in Python 3.7.6 as well as with ModelMuse 4.2 (Winston, 2019).

3 Results

3.1 Situation without reinjection

In the situation without reinjection, the flow pattern produced by this model is as expected from the constant head boundary conditions: water flows from the mixing zone boundary into the salar nucleus (Fig. 6). Agreeing with observations from Boutt et al. (2016), the hydraulic gradient is steeper in the mixing zone and flattens in the nucleus because of the higher hydraulic conductivity of the upper halite in the nucleus compared to the mixing zone.

The water balance of the model is dominated by the inputs and outputs at the constant-head boundaries (Table 1). Recharge from precipitation is a minor input to the water balance although studies by Boutt et al. (2016) and others have noted that short, significant precipitation events on the nucleus can cause rapid changes in the water level of several tens of cm. Evaporation is low because the water table is deeper than 0.5m below surface in most parts of the model, a depth at which evaporation is already strongly reduced (Fig. 4).

Table 1: Water balance of the modelled strip (500m x 5000m x 100m) in the scenario without reinjection (the "base case").

Input	**Flow [L/s]**	**Output**	**Flow [L/s]**
Mixing zone const. head	3.45	Nucleus const. head	3.34
Recharge from precipitation	0.64	Evaporation	0.75

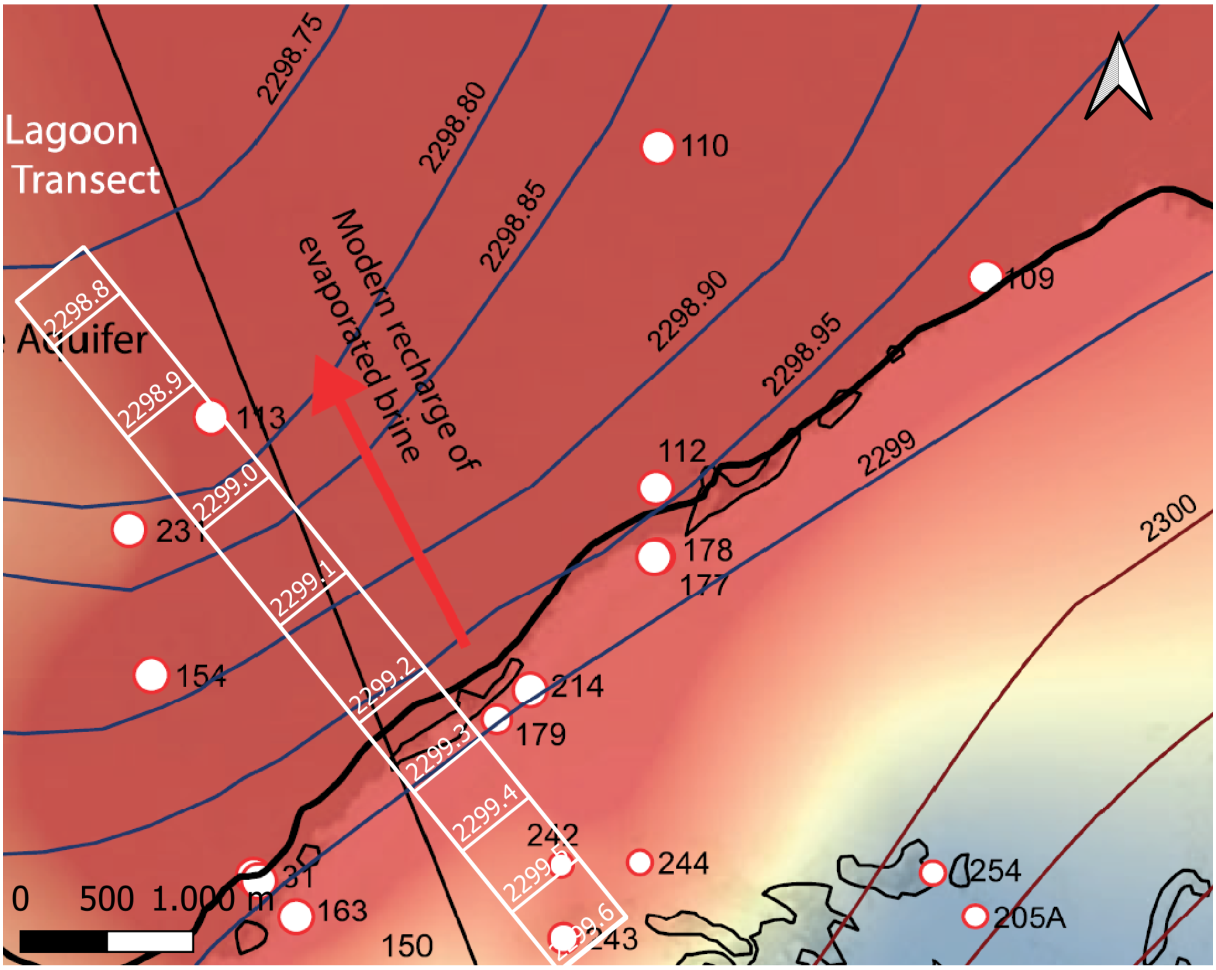


Figure 6: white lines: water table elevation contours [masl] from a steady-state simulation of of the situation without reinjection. Background image: water table elevations contours observed by Boutt et al., 2016 for January 2014, detail of Fig. 11 from that article.

3.2 Reinjection scenarios

3.2.1 Effects on the water table

The water table resulting from reinjecting 5, 10, 15, 20 and 25 L/s in the different scenarios is shown in Figure 7. The distribution of reinjection influences the water table close to the reinjection location, but the scenarios become undistinguishable a few hundred meters away from reinjection.

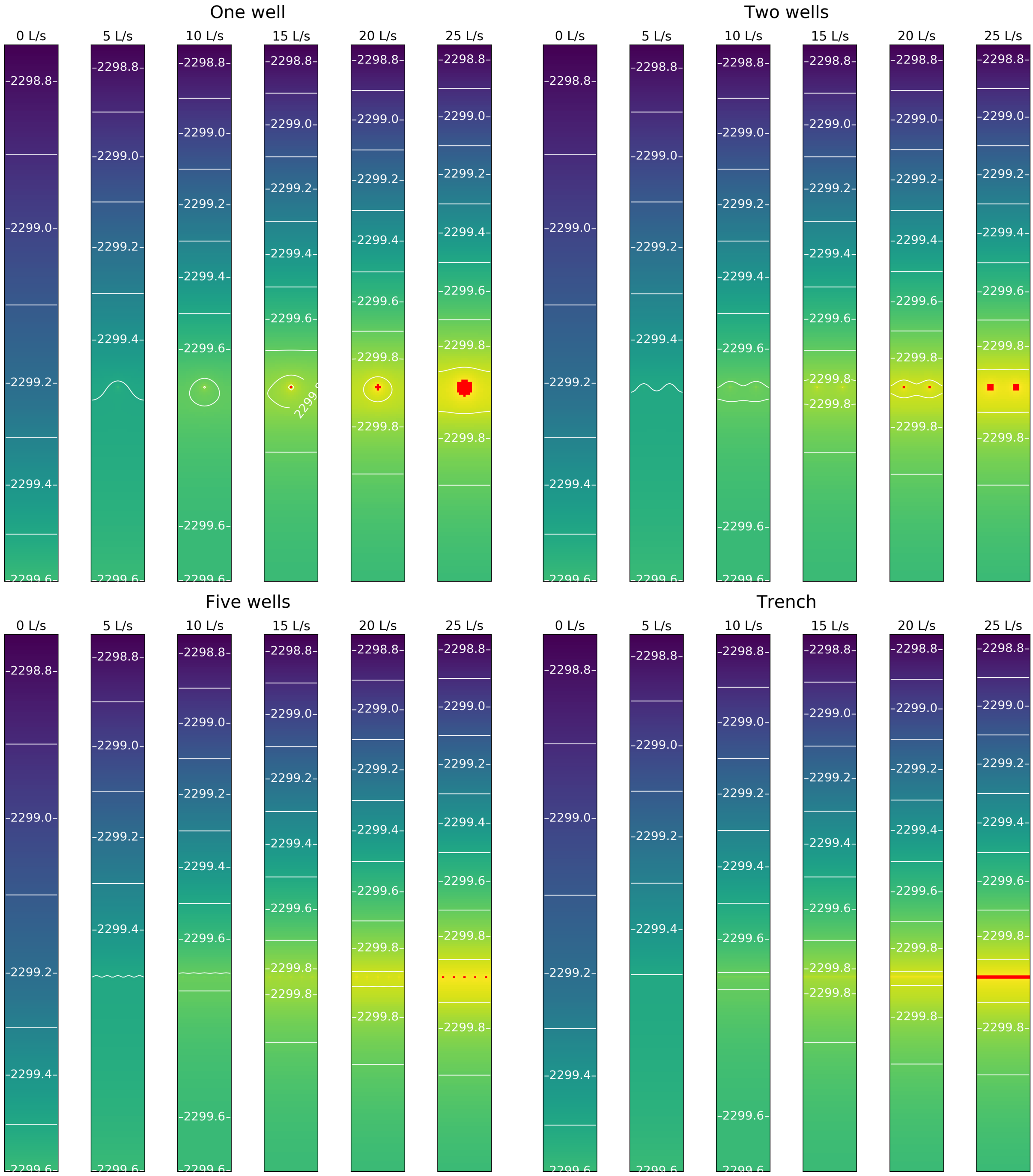


Figure 7: Plan view of the modelled strip with water tables resulting from steady state simulations of different reinjection rates for the four reinjection scenarios. Flooded cells (water table above model top) are masked in red.

In all scenarios, reinjection raises the water table, eventually leading to a reversal of the flow pattern. The reinjection location replaces the mixing zone boundary as the region with the maximum head. This means the flow is no longer unidirectional towards the nucleus, but bidirectional, towards the nucleus *and* the mixing zone. Depending on the volumes of reinjected brine involved, this could potentially affect the water chemistry of the mixing zone and thereby threaten the ecosystems it harbors.

All scenarios exhibit flooding beyond a certain reinjection rate, i.e. the water table elevation exceeds the model surface, indicating the limit of the aquifer's capacity to absorb high rates of localised reinjection. Flooding can be mitigated by using multiple wells or a trench: flooding first occurs at 15, 20 and 24 L/s for one, two and five wells, respectively. The trench spreads reinjection over a larger surface and floods at 21 L/s - later than one or two wells but earlier than five wells. This is because the trench only recharges *onto* the aquifer and does not reinject into depth.

Fig. 8 illustrates both effects using a cross-section through the model. Without reinjection, the hydraulic gradient points towards the nucleus end, and is steeper in the mixing zone than in the nucleus (due to the lower K in the mixing zone). Reinjection raises the water table. At 10 L/s, the head in the cell receiving the reinjection flow has exceeded the head at the mixing zone boundary, reversing the flow direction. At 15 L/s, the surface begins to flood.

Another observation can be made from Fig. 8 is that the marginal change in water table elevation tends to decrease. In other words, the difference in hydraulic head produced by reinjecting 5 instead of 0 L/s is higher than the difference between 10 and 15 L/s. This has two reasons: firstly, evaporation consumes more brine the closer the water table comes to the surface. Secondly, a higher groundwater mound leads to a higher hydraulic gradient, and thus more brine flowing off - including into the mixing zone, when the local minimum in head between reinjection and mixing zone end disappears. This behaviour points towards a loss of efficiency of reinjection and the risk of brine flow to the mixing zone at high reinjection rates.

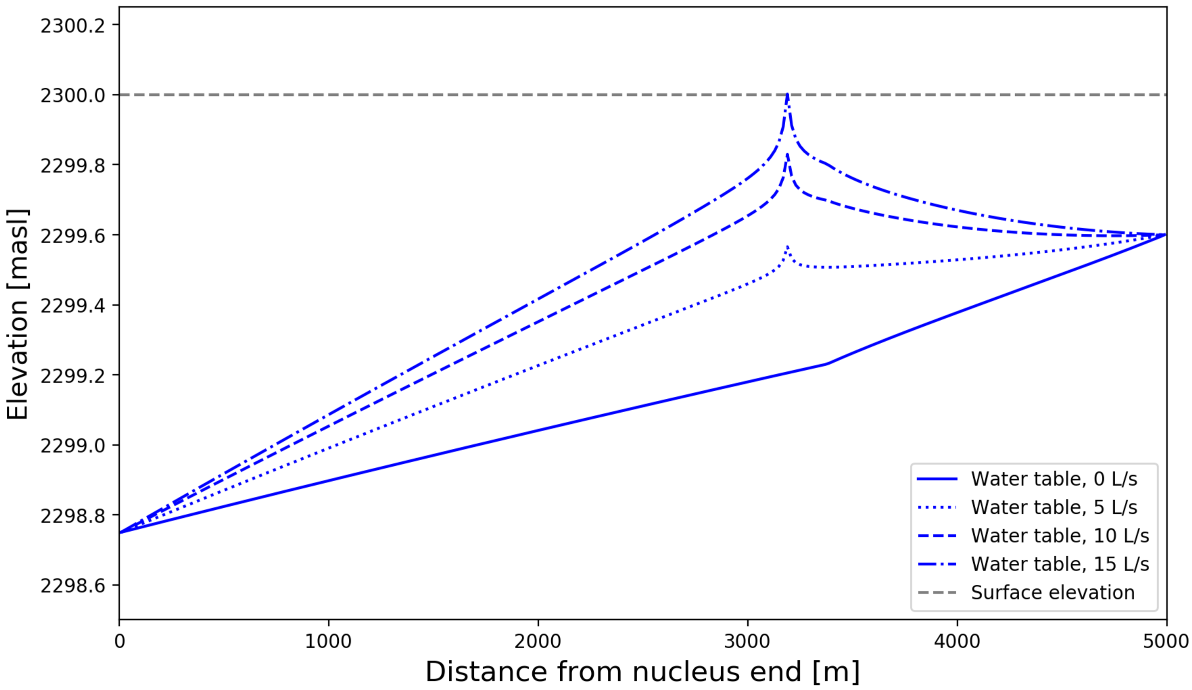


Figure 8: Cross-section of the water table elevation for different reinjection rates using one well. The cross-section contains the well cells and thus shows the local maximum effect of reinjection, which decreases towards the model boundaries.

3.2.2 Effects on the water balance

The rise in water table elevation also affects the water balance. Reinjected brine has three possible fates in this model: it can evaporate, flow into the nucleus or, at higher rates, flow into the mixing zone. The first sink for reinjected brine, evaporation, increases in response to reduced distance of the water table to the model surface (Fig. 9). The second sink for reinjected brine, outflow at the nucleus constant-head boundary, also increases due to the increased hydraulic gradient towards the nucleus end. As a response to the alteration of the hydraulic gradient by reinjection, the inflow from the mixing zone is reduced and can even go negative (outflow from the model to the mixing zone).

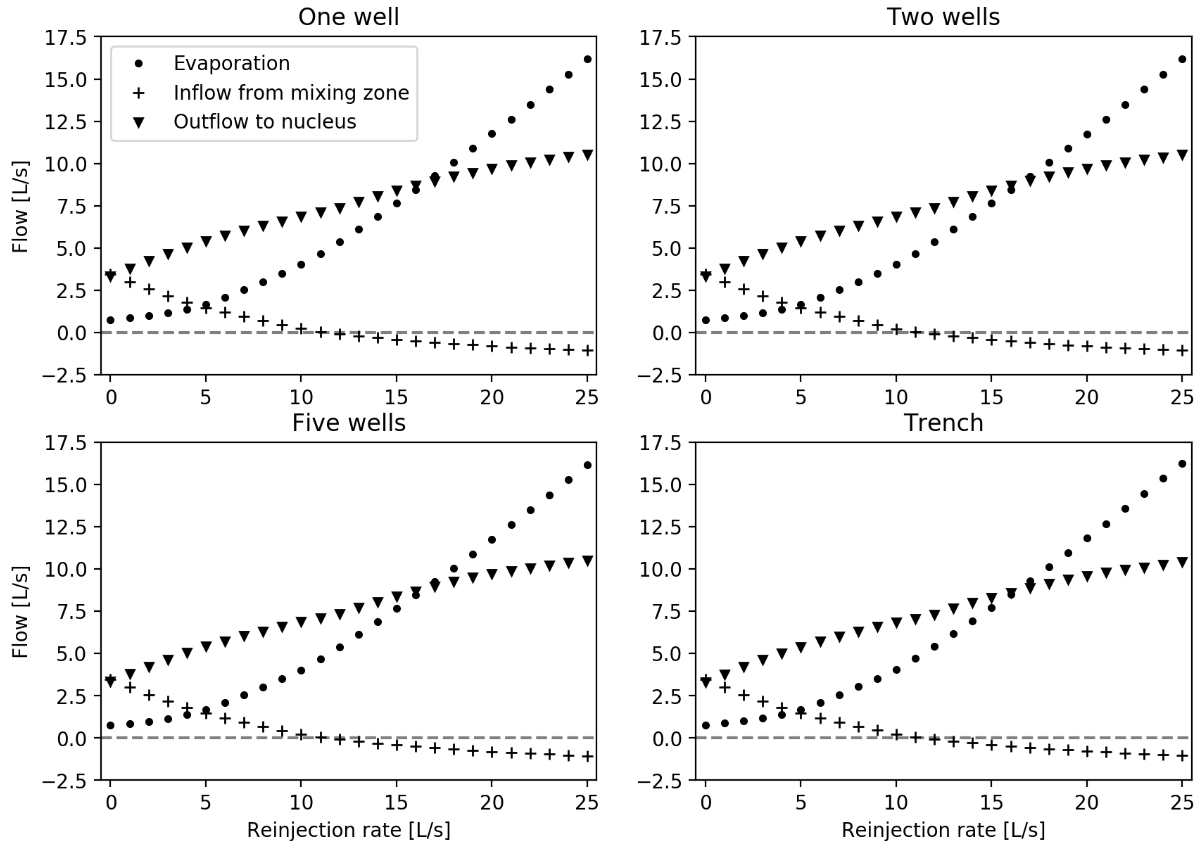


Figure 9: Evaporation output and flow through the nucleus and mixing-zone constant-head boundary vs. reinjection rate. Positive values designate inflow through the mixing zone constant-head boundary, and outflows at the nucleus constant-head boundary and by evaporation.

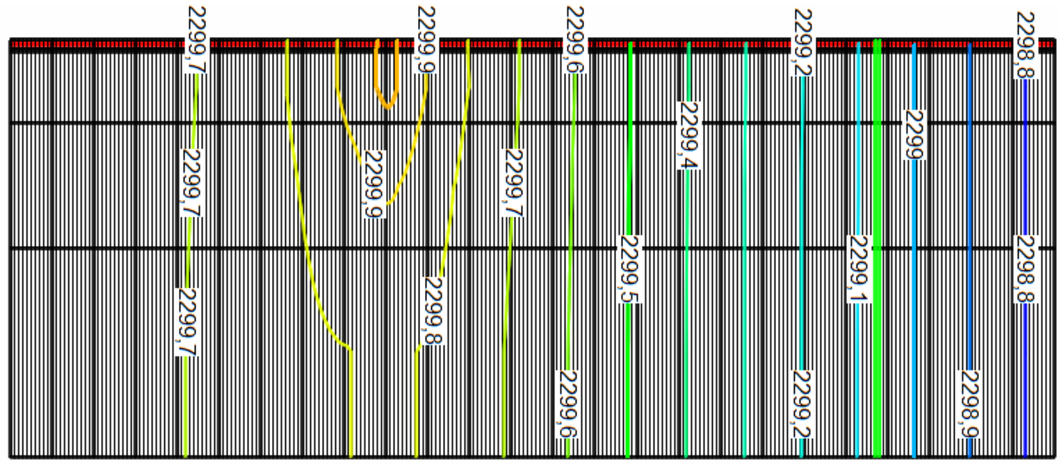
Two phases can be recognised: in an initial phase, up to a rate of 12 L/s, most reinjected brine flows out at the nucleus end, and practically stops inflow at the mixing zone end. Evaporation increases little. Beyond 12 L/s, evaporation consumes most additional brine due to the increasing proximity of the water table to the surface (or even flooding). Furthermore, the mixing zone boundary becomes a sink of brine, which is to be avoided.

Interestingly, the distribution of reinjection (single or multiple wells, trench) does not appreciably affect the model's water balance. This can be explained by the very local differences the distribution has on the water table (Fig. 7), which in turn is a result of the model's narrowness (500m) and the constant values of head imposed at the nucleus and mixing zone boundaries.

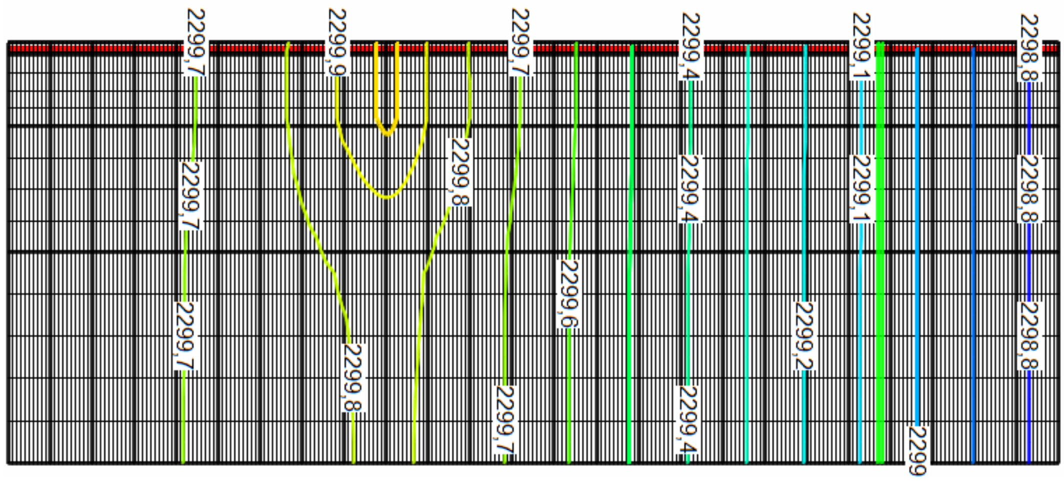
These local differences in water table are too small to influence evaporation, which is aggregated over the whole model surface.

3.2.3 Vertical effects of reinjection

The model results suggest reinjection affects hydraulic heads and thus flow in all model layers, i.e. the pressure increase reinjection into the upper halite creates there can be perceived in the clay and lower halite (Fig. 10a). This was also true for a model with higher vertical discretisation of all layers (19 instead of 9 MODFLOW layers), run for testing purposes (Fig. 10b). In a transient model with constant boundary conditions run over 100 years with a time step of 10 days this steady state would be reached within a year. This indicates that head and flow in the lower aquifers could be affected on time scales relevant for a DLE project.



(a) Using the model's vertical discretisation into 9 MODFLOW layers.



(b) Using a refined vertical discretisation into 19 MODFLOW layers.

Figure 10: Cross-sections of hydraulic head contours [masl] for reinjection of 25 L/s using one well. The mixing zone is at the right, nucleus at the left end. The bold black horizontal lines represent the boundaries between upper halite, clay and lower halite. Thin black horizontal lines represent the MODFLOW layers.

However, the flow through the lower layers is relatively low due to the lower hydraulic conductivities of the lower layers relative to the upper halite (Fig. 11).

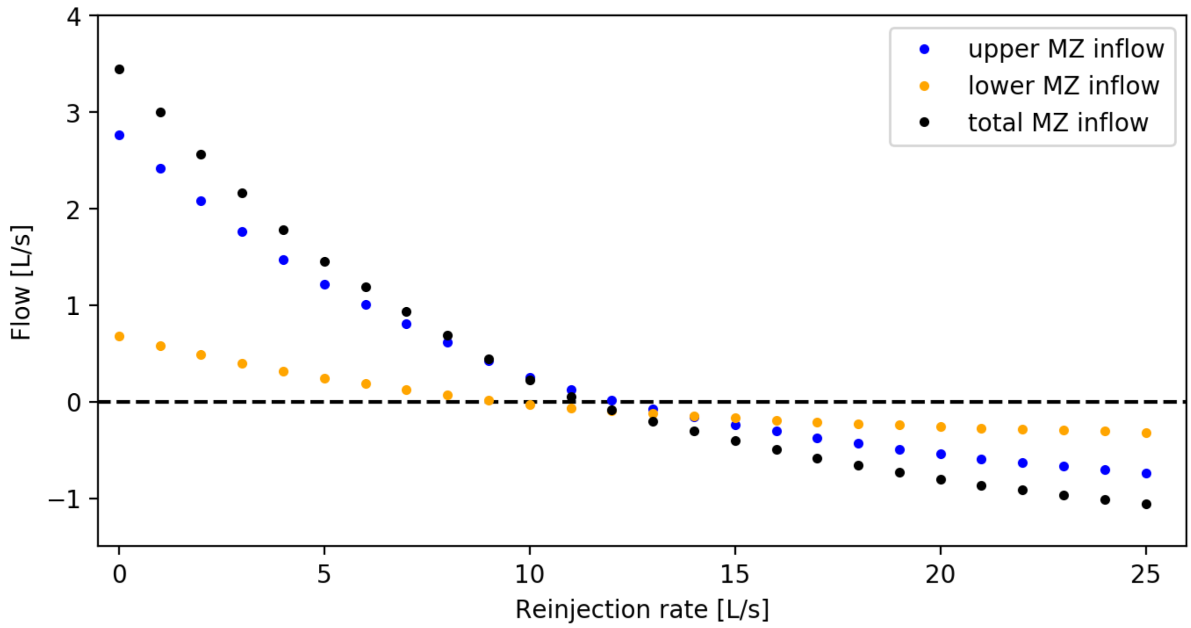


Figure 11: Inflow at the mixing zone constant-head BC for the upper halite and the lower layers (clay and lower halite) and the total inflow. Data from one well, reinjection scenarios are barely distinguishable.

3.3 Sensitivity analysis

3.3.1 Model topography

It is difficult to accurately characterise the topography of the small model area involved in this study, given that most publicly available digital elevation models (DEM) usually have coarse resolutions (e.g. 30 m) and exhibit considerable noise. Therefore, this study used a simplified, flat model topography of 2300 masl. This is quite consistent with ground elevation at observation wells within the model domain (BA-10, BA-11 and PN-16B in the mixing zone; PN-10 in the nucleus), reported by Albemarle Ltda. (2020).

The flat topography was constrasted with the topography IDAEA-CSIC (2017) used in their regional flow model of the SdA (and M.A. Marazuela's articles about the SdA; Marazuela et al. (2018, 2019a,b, 2020)). The original FEFLOW model was obtained as part of an annex to Amphos21 (2018) under the Chilean Law on Transparency. The elevation of all nodes of the model surface layer were extracted, and the model surface elevation was interpolated between these elevation points using the built-in *Triangle Interpolation* algorithm in ModelMuse (USGS, 2020)).

The two topographies agree in the nucleus, where both use an elevation of 2300 masl. However, they differ in the mixing zone, where SQM's topography, used by Marazuela and coauthors, rises up to 2305.3 masl (Fig. 12). Given the strong reduction of phreatic evaporation within the first 50 cm below surface, a higher surface elevation "shields" the water table, strongly reducing evaporation. Topography is therefore a key variable of model development due to its control on evaporation.

This can be observed in Fig. 13, where in the base case Marazuela's topography leads to a lower evaporation outflow compared to the flat topography. Since the reduced evaporation removes less water, the mixing zone constant-head BC can accommodate the steady-state flow through the model while providing less water, resulting in a lower mixing zone inflow with Marazuela's topography than with a flat topography. The higher surface elevation not only affects the base case, but also shields reinjected brine from evaporation, making reinjection more efficient in changing the water table. These factors explain why only 7 L/s are necessary to stop inflow from the mixing zone compared to 12 L/s for a flat topography.

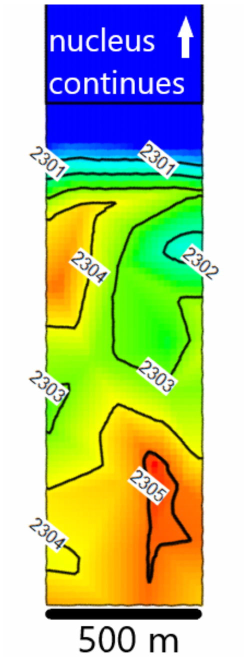


Figure 12: Surface elevation contours [masl] in the mixing zone of the reproduced topography by IDAEA-CSIC (2017). The nucleus continues at 2300 masl.

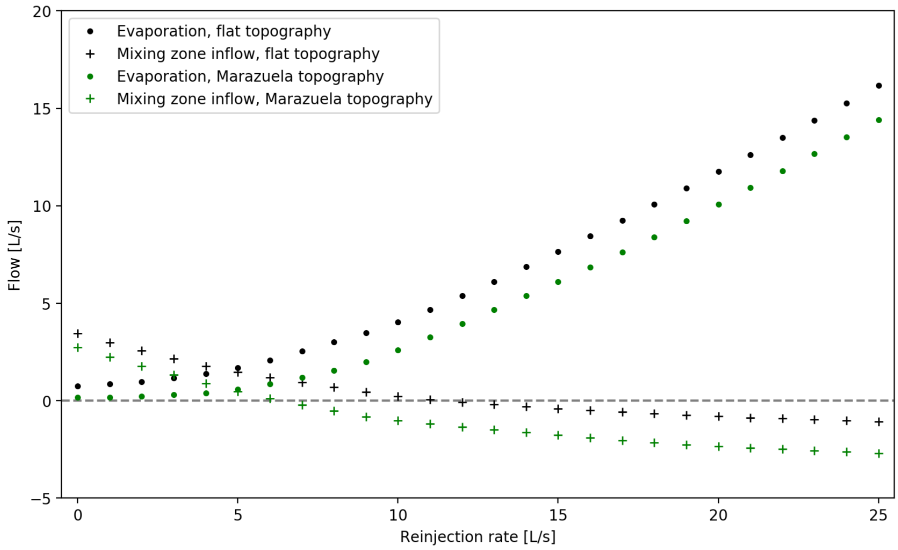


Figure 13: Evaporation and mixing zone input vs reinjection rate for the topographies. Results are shown for one well, the different well and trench scenarios are indistinguishable.

3.3.2 Hydraulic conductivity of the upper halite

The hydraulic conductivity (K) determines how much water flows through the model under a given hydraulic gradient. It also determines how well reinjected water flows away from the reinjection location. Therefore a lower K has a double effect: it leads to a lower water balance in the situation without reinjection and to a faster increase in evaporation upon reinjection, because locally the water table rises more for a given reinjection rate. Both effects can be appreciated in Fig. 14.

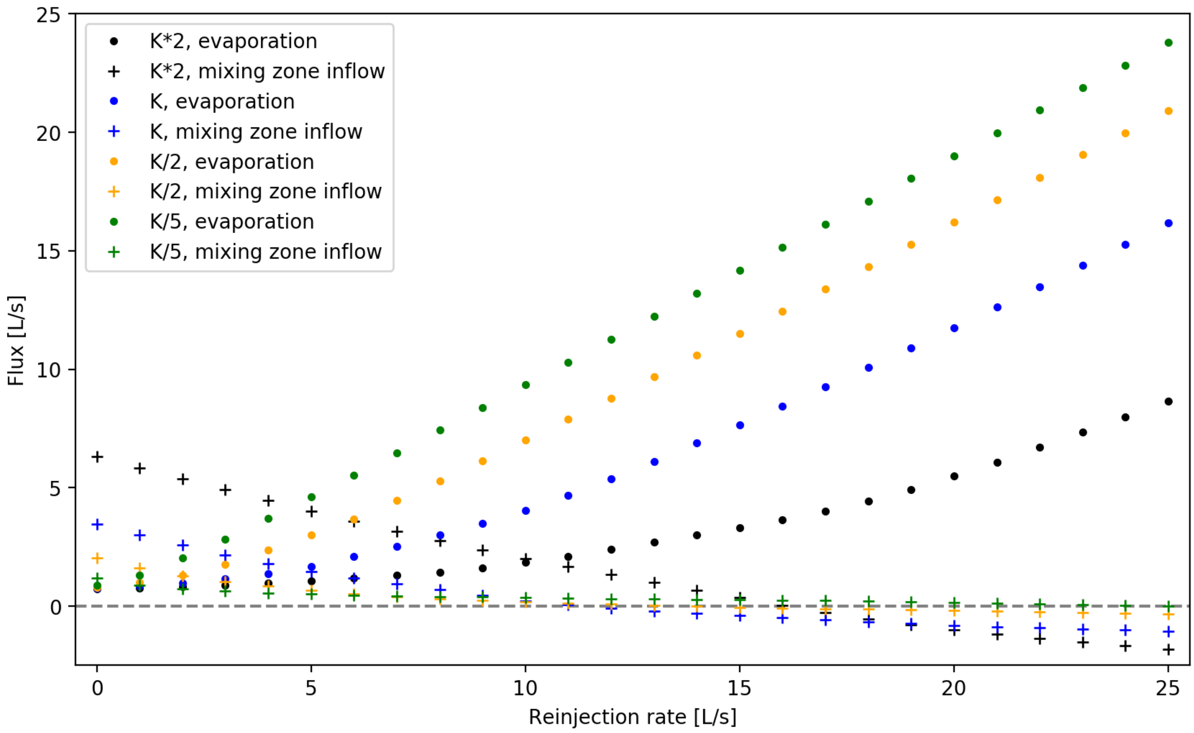


Figure 14: Evaporation and mixing zone input vs reinjection rate for 200, 50 and 20% hydraulic conductivity in the upper halite. Results are shown for one well, the different well and trench scenarios are indistinguishable.

Over time, reinjection would likely lead to a decreasing K near the reinjection location, due to salt precipitation as a result of evaporation. Depending on its magnitude, such a reduction of K can have a strong impact on the fate of reinjected brine: for a hydraulic conductivity of only 20% of the original value, most reinjected brine would evaporate because the aquifer can't absorb it fast enough, leaving almost no brine to be returned to the nucleus.

3.3.3 Evaporation function

Different authors have established relationships between water table depth and phreatic evaporation for the nucleus of the SdA. Usually, these curves are based on measurements of potential evaporation from evaporation pans and of phreatic evaporation from lysimeters. To capture this variability, two more curves were modelled in addition to the nucleus curve from Grilli and Vidal (1986):

- the curve for SdA nucleus brine evaporation from John Houston (2006)
- the fit for the SdA nucleus described in Marazuela et al. (2020)

As shown in Fig. 4, these curves have different potential evaporation rates, but largely agree in their extinction depth: at 0.6 m from the surface, evaporation is already below 1% of potential evaporation.

The formulation of the depth-evaporation relationship only moderately affects the results. Differences follow the different potential evaporation rates: Houston's curve leads to a lower evaporation than Grilli's curve, Marazuela's curve to higher evaporation. Interestingly, all curves agree that the threshold beyond which brine flows into the mixing zone is between 10 and 13 L/s.

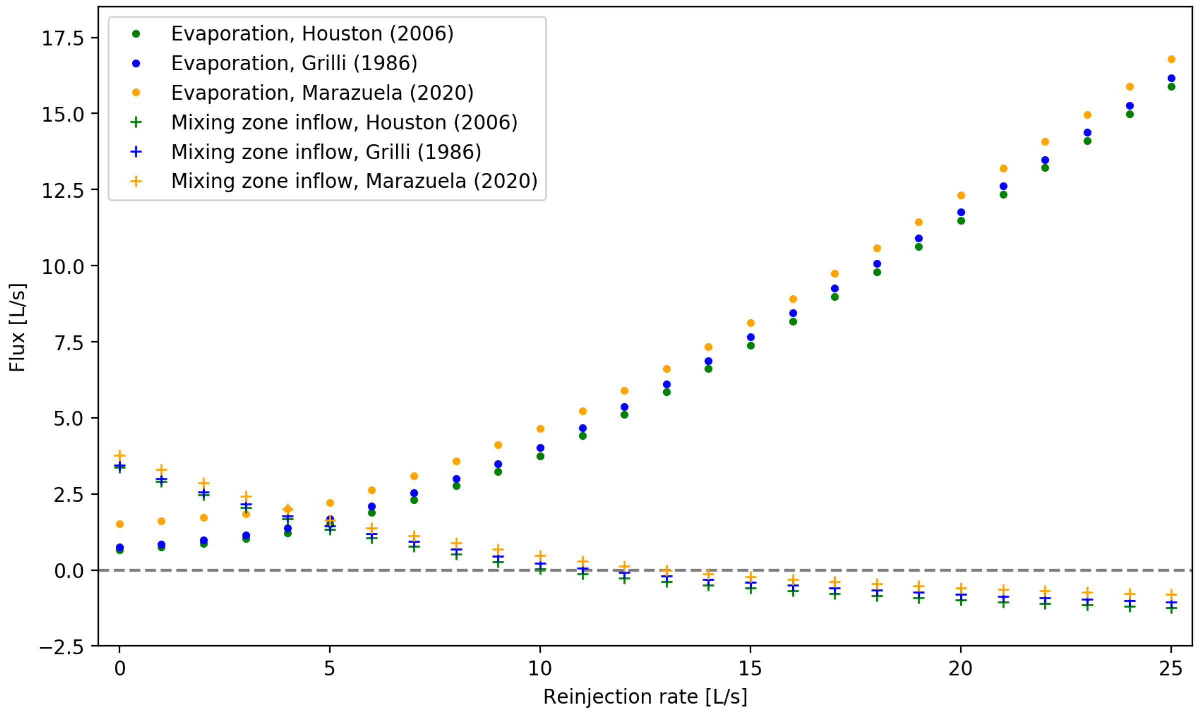


Figure 15: Evaporation and mixing zone inflow vs. reinjection rates for the three tested evaporation curves. Results are shown for one well, the different well and trench scenarios are indistinguishable.

3.3.4 Seasonal dynamics

A look at the historic records from well BA-10 (Fig. 16) reveals that high heads occur mostly during winter, when the evaporation rate is at its lowest. Conversely, in summer the head in the mixing zone is typically lowest and evaporation rates are high. These two trends have contrary effects, because a lower head in the mixing zone leads to a lower water table and thus a reduction of evaporation.

To represent typical summer and winter conditions, I modelled these two trends together. The maximum and minimum evaporation rates are set to 6.07 mm/d and 2.77 mm/d, according to the monthly fractions of annual pan evaporation of 11.6 % (January) and 5.3 % (July). These are average values from nine stations located in the Atacama desert above 1000 masl reported by John Houston (2006). The winter and summer mixing zone heads are 2299.4 m and 2299.8 m, roughly corresponding to the upper and lower ends of observed heads. While seasonal changes in potential evaporation rate are on the order of 50%, the strong reduction of evaporation within the first 50cm means that actual evaporation can vary by much more than 50% in response to a change in head of 20cm (Fig. 4).

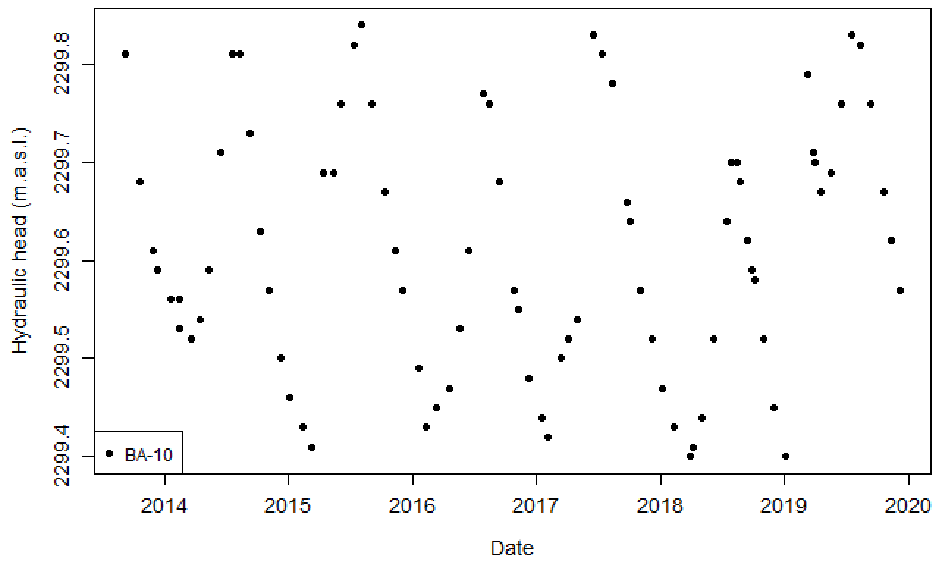


Figure 16: Historical observations of hydraulic head from shallow piezometer BA-10, close to the mixing zone end of the model, from Albemarle Ltda. (2020).

This is reflected in the outcome of the seasonal modelling: despite the lower evaporation rate in winter, total evaporation is higher in winter than in summer (Fig. 17). This is because the higher head at the mixing zone boundary brings the water table closer to the surface. As a consequence of the higher hydraulic gradient and evaporation, the inflow from the mixing zone is higher in winter than in summer. This means that in summer, a relatively small reinjection of 5 L/s would stop inflow from the mixing zone, with higher rates causing brine flow into the mixing zone. In winter, reinjection rates are not limited by this concern because the higher mixing zone head compared with the high evaporation close to the surface make the mixing zone less vulnerable to brine inflow.

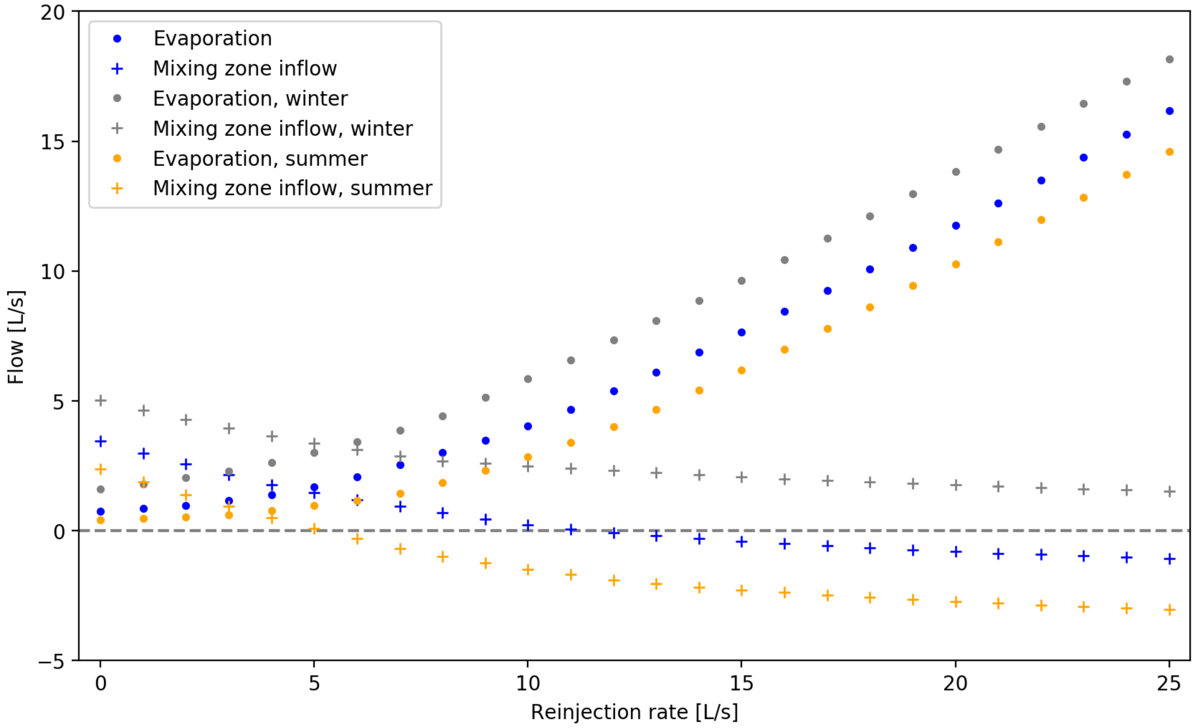


Figure 17: Evaporation and mixing zone inflow for typical situations in winter and summer compared to the mean situation. Results are shown for one well, the different well and trench scenarios are indistinguishable.

It is interesting to revisit the effect of topography in the context of seasonality 18. As previously discussed, the higher topography used by Marazuela shields brine from evaporation. This dampens seasonal differences: since brine in the mixing zone is mostly below extinction depth, it will only weakly be affected by variations in potential evaporation or water table rise than if it were within few decimeters from the surface. However, the difference in hydraulic head between winter and summer still affects the magnitude of inflow from the mixing zone and its vulnerability to brine inflow. Therefore, even under Marazuela's topography, the threshold reinjection rate producing inflow into the mixing zone drops from 9 L/s in winter to 4 L/s in summer.

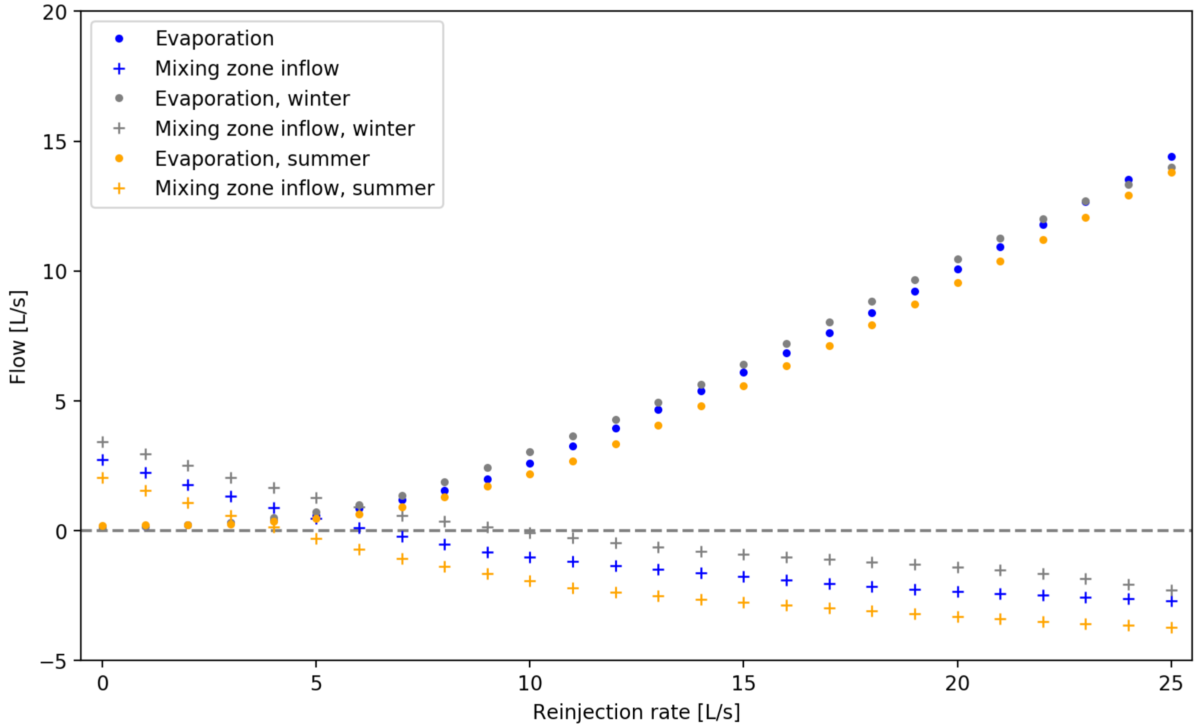


Figure 18: Evaporation and mixing zone inflow for typical situations in winter and summer **using Marazuela's topography**. Results are shown for one well, the different well and trench scenarios are indistinguishable.

3.3.5 Constant head at the nucleus boundary

Head records from well PN-10, located near the nucleus end of the model show that the head there does not follow a seasonal pattern. Instead, it has a general tendency to fall, which is interrupted by individual rainfall events, leading to recharge and sudden increases in head of up to 70cm (Fig. 19). The constant head imposed at the nucleus end of this model (2298.75 m) agrees with the piezometric surface from Boutt et al. (2016), shown in Fig. 6, but clearly corresponds to the higher end of the historic range of heads.

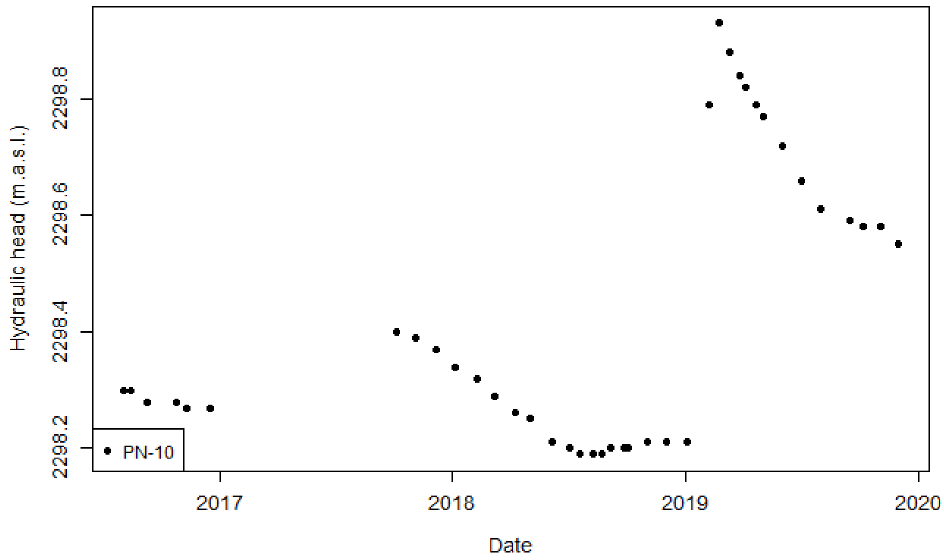


Figure 19: Historical observations of hydraulic head from well PN-10, close to the nucleus end of the model, from Albemarle Ltda. (2020).

Using a lower head at the nucleus end (2298.25 m), the flow through the model is higher as a result of the higher hydraulic gradient (Fig. 20). This higher flow has to be sourced from the mixing zone, since the only other source of water - recharge from precipitation - is kept constant in the model. Furthermore, evaporation is strongly reduced as a consequence of the lower water table elevation. The lower water table means more brine can be reinjected before brine starts flowing into the mixing zone (14 L/s compared to 11 L/s). This indicates that the risk of brine flow into the mixing zone can be mitigated by reinjecting in a region with stronger hydraulic gradient in the direction of the nucleus.

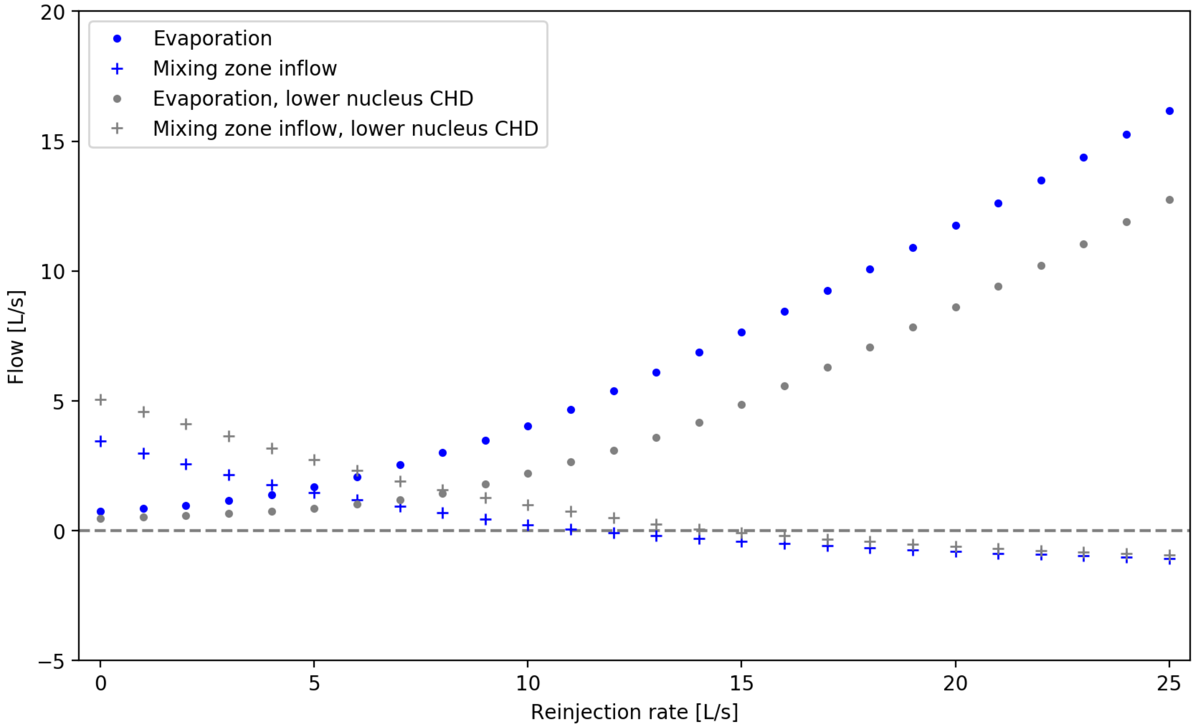


Figure 20: Evaporation and mixing zone inflow vs. reinjection rate for the default model and a lower head at the nucleus end. Results are shown for one well, the different well and trench scenarios are indistinguishable.

3.3.6 Grid cell size

The grid cell size is varied to test whether the model is able to reproduce the results independently of the grid cell size. This parameter is presented as a model quality parameter and has no direct physical implications for reinjection.

Fig. 21 shows that the effect of grid cell size choice on the model results is negligible compared to the effect of other model parameters. Here, quadratic cells with a side length of 10m and 50m are constrasted with the 20m used in this study. For the trench, the 2m x 20m cells are compared to 2m x 50m and 2m x 100m cells.

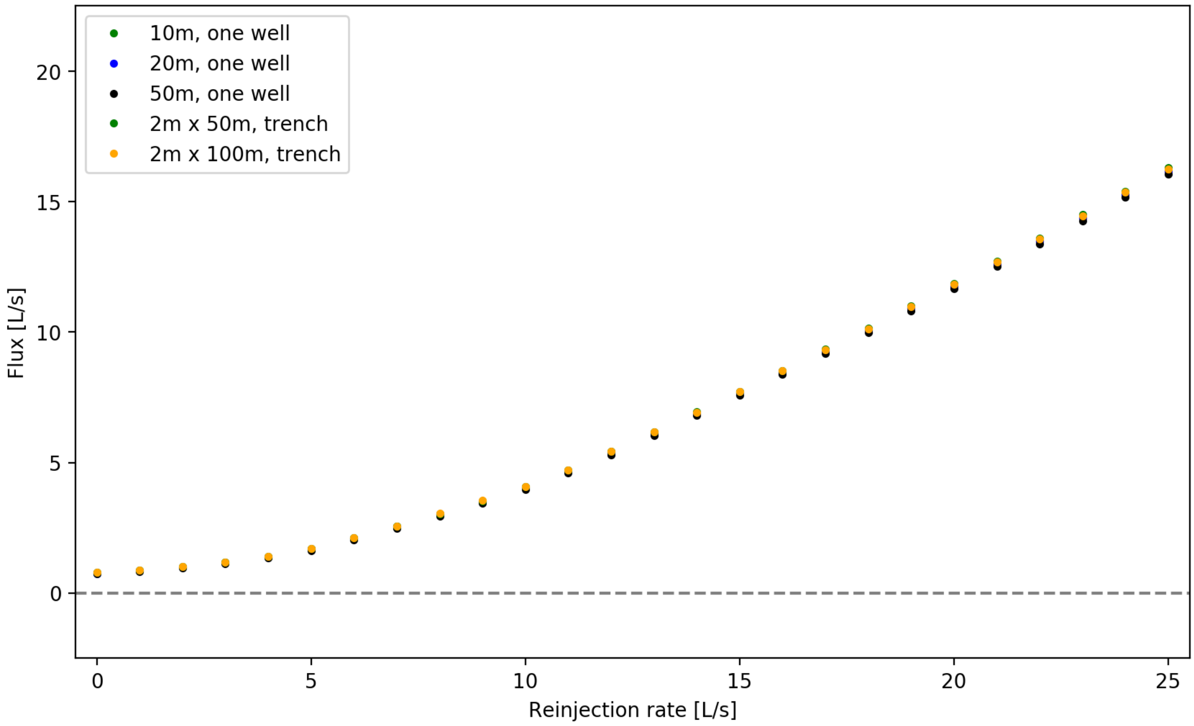


Figure 21: Evaporation for different grid cell sizes. Results are shown for one well.

4 Discussion

Model limitations The model makes some important assumptions, which are simplifications of an actual salar, in order to gain general insights into the effects of brine reinjection. This model is not intended to be used for any permitting or monitoring at the SdA. Most importantly, it is a constant density model which does not explicitly model the effect of the brine-freshwater interface. This interface marks the transition from brine to brackish and fresh water, which have different densities. The density difference forces less dense fresh and brackish water in the mixing zone to rise when it comes into contact with the brine body, forming lagoons and zones with shallow groundwater where evaporation is high. Thus, the variable-density effect reduces the flow from the mixing zone into the salar because instead of simply flowing into the salar, water in effect rises and evaporates. The lack of representation of this variable density effect means that the model overestimates the flow from the mixing zone into the nucleus. This high flow has to leave the model somewhere, and since evaporation is controlled (and limited) by the water table elevation, most water leaves the model at the nucleus boundary. A variable-density model would likely produce less inflow at the mixing zone end, because the denser brine body "blocks" its flow into the nucleus, making evaporation the main water sink of the model. This would agree better with the prevailing conceptual understanding of flow in salar systems, where density contrasts play a decisive role in forcing freshwater to discharge and evaporate (Marazuela et al., 2019a; Munk et al., 2020). The higher density of brine could also be important for its mixing behaviour with brackish mixing zone waters if brine flow to the mixing zone were to happen. The effect of variable fluid density on flow could be addressed by using a variable-density model code like SEAWAT (Langevin et al., 2008).

Another limitation of the model is that the hydraulic heads imposed at the model boundaries are not allowed to change in response to reinjection. In reality, the head at the location of the model boundary would of course respond to an influence of reinjection. However, in this study, the purpose of the constant head BCs is to produce and monitor flow across the boundaries and especially to identify the threshold reinjection rate causing brine flow into the mixing zone. So, while in a natural system the boundary would respond to reinjection by a change in head, the change in flow at the boundary, which this model monitors, is still indicative of the effect reinjection has at that location.

Finally, the small width of the model (500m) is not sufficient to fully model the effect of reinjection in this dimension, which is indicated by the hydraulic head contours reaching the long model boundaries in Fig. 7. This explains why the differences between the distributions of reinjection are quite small. A wider model would allow these differences to fully unfold and be assessed.

Despite these simplifications, the trends and limitations acting on reinjection of spent DLE brine this model helps identify are valuable information for a potential implementation of DLE with spent brine reinjection. Any DLE project would require a more detailed site-specific characterisation of the hydrogeology as well as extra model features, like variable-density flow and a larger model domain. This model is a first attempt at modelling reinjection, and should be modified and expanded by future modelling work. Despite its simplifications, it allows to identify key constraints for reinjection of spent DLE brine which should be addressed by future work and taken into account during the operation of DLE brine reinjection to avoid negative impacts on the ecosystems in the mixing zones of salares.

Response of lower layers The response of the lower layers to reinjection in this model is not very well constrained. The assumption of a uniform constant head throughout the whole profile at the nucleus and mixing zone boundaries is a simplification made in the absence of head observations from the lower layers. In reality, heads and flow patterns in the lower layers can be expected to differ from the upper halite, not least due to the presence of fluids of different densities. The response of lower layers to reinjection should therefore be understood as a mere indication that lower layers could be affected by reinjection, but not as an accurate description of *how* they would be affected.

Topography Topography controls phreatic evaporation. If the terrain rises in the mixing zone, the flat topography of this model overestimates evaporation. Indeed, Marazuela's (higher) topography shields brine from evaporation in the mixing zone, leading to brine flow into the mixing zone at lower reinjection rates (Section 3.3.1). This limits the rates at which DLE could operate. Given the criticality of evaporation for a reinjection model, any further modelling effort should be based on high-resolution and high-accuracy digital elevation models of the region of interest.

Hydraulic conductivity Hydraulic conductivity has a strong effect on the feasibility of reinjection (Fig. 14). There are two sources of uncertainty regarding K: quantifying it accurately based on hydraulic tests and quantifying its reduction over time by reinjection-induced salt precipitation. If one or both of these reasons led to the real hydraulic conductivity being only 20% of the original K value, this would essentially render reinjection into the upper halite impossible because reinjected brine would not be removed fast enough. Possible solutions to this problem could be the usage of well screens starting further down from the surface, the reinjection into a region with a higher hydraulic gradient (i.e. closer to the location of brine extraction) or reinjection into lower, confined layers. An assessment of the latter option would however require a dedicated modelling effort based on a more detailed characterisation of these layers.

Evaporation function The uncertainty stemming from the depth-dependence of evaporation is small compared to other model parameters. The differences in potential evaporation between the curves are dampened by the sufficiently large distance of the water table to the surface. The present model assigned one evaporation curve to the whole model surface, despite the curve having been established by the authors for the SdA nucleus. This approach was chosen since most of the model domain covers the nucleus. For a more accurate model, field measurements of phreatic evaporation in both the nucleus and mixing zone could be used to define two evaporation curves for the respective model zones. Given the marked reduction of evaporation rates with fluid density (John Houston, 2006), it would be interesting to explicitly include this relationship in a variable-density model.

Seasonal dynamics The vulnerability of the mixing zone to brine inflow varies seasonally and is highest in summer, when its water levels are lowest. Any reinjection would therefore need to be accompanied by a constant monitoring of water levels in the mixing zone and constantly adjust rates and locations of reinjection to prevent brine inflow into the mixing zone. The seasonal variation in reinjection capacity might mean DLE would need to operate in a seasonal manner even though its process, unlike the evaporative one, does not inherently depend on evaporation rates and temperatures. A possible strategy to reinject at high rates without risking brine inflow into the mixing zone in summer would be to move the reinjection infrastructure further into the nucleus permanently or seasonally.

Constant head at the nucleus end The hydraulic head at the nucleus end in reality can be expected to vary in response to precipitation events and pumping stresses from the brine production areas, but generally has a decreasing trend according to its historical head records (Fig. 19). A decrease in nucleus head allows for higher rates of reinjection without inflow to the mixing zone, since reinjected brine is "pulled" into the nucleus. However, it also leads to a higher base case inflow from the mixing zone in response to the higher hydraulic gradient. As long as this increased inflow is mitigated by brine reinjection, there should be no negative impact on the mixing zone ecosystems, and a local drawdown in the nucleus could help prevent high reinjection rates affecting the mixing zone. In other words, if more brine needs to be reinjected than is possible while avoiding mixing zone inflow, reinjection can be increased by moving it closer to the drawdown induced by brine reduction. Conversely, reinjection might be limited for some months following an event of recharge by rainfall due to the increase in head in the nucleus.

Scaling up reinjection The volumes of brine being pumped out of the SdA are much higher than the reinjection rates modelled in this study (0-25 L/s): SQM and Albemarle plan to reach maximum brine extraction rates of 1700 L/s and 442 L/s in the coming years (IDAEA-CSIC, 2017). Under the modelled conditions, a stretch of 500m width permits reinjection on the range of 10 L/s. Naively scaling this result up indicates that reinjection of 1000 L/s of brine would require wells or a trench to be installed along 50 km of the nucleus margin. Of course, an assessment of reinjection along longer stretches of the SdA nucleus margin would require a more complex model, considering local variations of topography, hydraulic properties and hydraulic gradients. However, this simple calculation shows that reinjection with the tested well and trench scenarios would require a considerable effort in terms of building reinjection infrastructure (wells or trenches). This makes it likely that DLE projects will look at the possibility to move reinjection further into the salar and/or into lower layers, which could reduce the risk of brine flow into the mixing zone and in the case of lower layers, the brine loss to evaporation.

The location of reinjection in this model (200m inward from the nucleus edge) was chosen because it is far away from the brine extraction zones, maximally delaying a potential dilution of lithium-rich by lithium-poor brine, and close to the mixing zone ecosystems, so that a groundwater mound would be a close to the object of interest. The location of reinjection was not varied in this study, but is of course a variable in the design of a reinjection concept. Moving the reinjection site further inward to the salar nucleus, and closer to the production areas would likely allow for higher rates of brine reinjection without provoking brine inflow into the mixing zone, as the hydraulic gradient towards the nucleus would be steeper. Higher reinjection rates would allow the reinjection of a certain volume with less reinjection infrastructure (wells or trenches). On the other hand, a reduced distance between brine production and brine reinjection areas can be expected to reduce the time it takes lithium-poor brine to reach extraction wells. However, this topic was not modelled in the present study and will need to be addressed by future work.

Other concerns with reinjection of spent DLE brine This study is purely focusing on understanding *flow*, and did not consider *transport* or *reaction.* Phenomena like the mixing of Li-depleted with Li-rich brine causing brine dilution or the introduction of trace contamination from e.g. organic solvents used in some DLE techniques lie beyond its scope. Furthermore, it did not consider the effect of salt precipitation on hydraulic conductivity, geochemical interactions between spent DLE brine and the aquifer matrix or mechanical alterations of the aquifer by reinjection, especially when using pressurised wells (the last two concerns were raised by Flexer et al. (2018)). These concerns will need to be addressed by future work using site-specific information.

5 Conclusion

Results from this model suggest that reinjection of spent DLE brine is feasible under the modelled conditions. Most importantly,

- a groundwater mound can be maintained against evaporation
- inflow from the mixing zone can be reduced
- some spent brine flows back into the nucleus, partly balancing the effect of brine extraction on the nucleus' water balance.

The distribution of reinjection affects at which rates and where flooding occurs. However, due to the characteristics of the present model it has almost no effect on the water balance because it leads to very localised differences in water table, which are negligible when taking into account the entire model area.

Reinjection is efficient in reducing the inflow from the mixing zone at rates below a threshold. At higher rates, additional reinjected brine mostly evaporates and/or flows into the mixing zone, which has to be prevented to avoid perturbations of the water chemistry of the mixing zone's brackish water ecosystems.

If hydraulic conductivity is much lower than expected or is reduced strongly by salt precipitation, reinjection into the upper halite becomes difficult, since the aquifer can't absorb the flow quickly enough. The surface would flood and reinjected brine almost totally evaporate, reducing the water balance advantage DLE has over evaporative Li extraction.

Seasonal conditions, notably the hydraulic head in the mixing zone, control the mixing zone's vulnerability to brine inflow and limit the rates that can be reinjected. An implementation of DLE would have to carefully monitor these heads and adapt the reinjection rates and locations according to them.

A high-resolution, high-accuracy DEM of the area of interest would reduce uncertainties in modelling evaporation, which is strongly influenced by the topography.

The lower layers might be affected by reinjection into the upper halite on time scales relevant to a DLE project. They need to be characterised and modelled in more detail than was done in this study.

This study has some important limitations, which limit its applicability to actual salar systems. Most notably, it does not include the effect of variable density on flow, models a small area in which pumping stresses can affect the model boundaries and the effects of different reinjection scenarios cannot fully unfold, and simplifies the complex hydrogeology, especially of the mixing zone, into six zones of uniform hydraulic conductivity. Future modelling of spent DLE brine reinjection should address these simplifications. This work is intended as a first step towards modelling spent DLE brine reinjection and aims to highlight important factors and limitations that need to be taken into account by future reinjection approaches.

DLE offers the potential to mitigate negative effects of brine extraction on salars' water balance and mixing zone ecosystems, but could also damage these ecosystems by brine inflow. The key trends identified in this work together with the proposed model improvements will help to make sure this potential is fulfilled while conserving the mixing zone ecosystems.

References

Albemarle Ltda. (2020). *Informe Anual N°4 - Plan de Seguimiento Ambiental Hídrico.*

Amphos21 (2018). *Estudio de Modelos Hidrogeológicos Conceptuales Integrados Para Los Salares de Atacama, Maricunga y Pedernales.* Tech. rep.

Bakker, Mark et al. (2016). "Scripting MODFLOW Model Development Using Python and FloPy". In: *Groundwater* 54.5, pp. 733–739. DOI: 10.1111/gwat.12413.

Bakker, Mark et al. (2018). *FloPy v3.2.9: US Geological Survey Software Release.* U.S. Geological Survey. DOI: 10.5066/F7BK19FH.

Boutt, David F. et al. (2016). "Rapid Recharge of Fresh Water to the Halite-Hosted Brine Aquifer of Salar de Atacama, Chile: Rapid Recharge of Fresh Water to the Salar de Atacama, Chile". In: *Hydrological Processes* 30.25, pp. 4720–4740. DOI: 10.1002/hyp.10994.

Flexer, Victoria et al. (2018). "Lithium Recovery from Brines: A Vital Raw Material for Green Energies with a Potential Environmental Impact in Its Mining and Processing". In: *Science of The Total Environment* 639, pp. 1188–1204. DOI: 10.1016/j.scitotenv.2018.05.223.

Gajardo, Gonzalo and Stella Redón (2019). "Andean Hypersaline Lakes in the Atacama Desert, Northern Chile: Between Lithium Exploitation and Unique Biodiversity Conservation". In: *Conservation Science and Practice* 1.9. DOI: 10.1111/csp2.94.

Grilli, A. and F. Vidal (1986). "Evaporación Desde Salares: Metodología Para Evaluar Los Recursos Hidricos Renovables. Aplicación En Las Regiones I y II." In: *Revista de la Sociedad Chilena de Ingenería Hidráulica* 1.2.

Harbaugh, Arlen W. (1990). *A Computer Program for Calculating Subregional Water Budgets Using Results from the U.S. Geological Survey Modular Three-Dimensional Finite-Difference Ground-Water Flow Model.* Tech. rep. 90-392.

Harbaugh, Arlen W. (2005). "MODFLOW-2005, the U.S. Geological Survey Modular Groundwater Model - the Groundwater Flow Process". In: *U.S. Geological Survey Techniques and Methods 6-A16.* URL: https://pubs.er.usgs.gov/publication/tm6A16 (visited on 07/13/2020).

Harbaugh, Arlen W. et al. (2017). *MODFLOW-2005 Version 1.12.00, the U.S. Geological Survey Modular Groundwater Model.* U.S. Geological Survey. DOI: 10.5066/F7RF5S7G.

Houston, J. et al. (2011). "The Evaluation of Brine Prospects and the Requirement for Modifications to Filing Standards". In: *Economic Geology* 106.7, pp. 1225–1239. DOI: 10.2113/econgeo.106.7.1225.

Houston, John (2006). "Evaporation in the Atacama Desert: An Empirical Study of Spatio-Temporal Variations and Their Causes". In: *Journal of Hydrology* 330.3-4, pp. 402–412. DOI: 10.1016/j.jhydrol.2006.03.036.

IDAEA-CSIC (2017). *Informe: Cuarta Actualización Del Modelo Regional de Flujo Del Salar de Atacama.*

Langevin, C. D. et al. (2008). *SEAWAT Version 4: A Computer Program for Simulationof Multi-Species Solute and Heat Transport.* Tech. rep.

Marazuela, M.A. et al. (2018). "3D Mapping, Hydrodynamics and Modelling of the Freshwater-Brine Mixing Zone in Salt Flats Similar to the Salar de Atacama (Chile)". In: *Journal of Hydrology* 561, pp. 223–235. DOI: 10.1016/j.jhydrol.2018.04.010.

Marazuela, M.A. et al. (2019a). "Hydrodynamics of Salt Flat Basins: The Salar de Atacama Example". In: *Science of The Total Environment* 651, pp. 668–683. DOI: 10.1016/j.scitotenv.2018.09.190.

Marazuela, M.A. et al. (2019b). "The Effect of Brine Pumping on the Natural Hydrodynamics of the Salar de Atacama: The Damping Capacity of Salt Flats". In: *Science of The Total Environment* 654, pp. 1118–1131. DOI: 10.1016/j.scitotenv.2018.11.196.

Marazuela, M.A. et al. (2020). "Towards More Sustainable Brine Extraction in Salt Flats: Learning from the Salar de Atacama". In: *Science of The Total Environment* 703, p. 135605. DOI: 10.1016/j.scitotenv.2019.135605.

Munk, Lee Ann et al. (2020). *Hydrogeologic and Geochemical Distinctions in Salar Freshwater Brine Systems*. Preprint. EarthArXiv. DOI: 10.31223/osf.io/j3pu6.

USGS (2020). *ModelMuse Help - Interpolation Methods*. URL: https://water.usgs.gov/nrp/gwsoftware/ModelMuse/Help/index.html?interpolation_methods.htm (visited on 07/17/2020).

Winston, Richard B. (2019). *ModelMuse Version 4: A Graphical User Interface for MODFLOW 6*. Tech. rep. USGS.

Preliminary Brine Re-Injection Scenario Modeling in a DLE Implementation Context

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December 2020

1 METHODS

Matrix Solutions Inc. (Matrix) has partnered with Jade Cove and Zelandez to evaluate the effects of re-injection of lithium brine solution leftover from direct lithium extraction (DLE) processes from groundwater deposits found in salt lake (salar) basins. A numerical groundwater flow and brine transport model has been developed to examine the effect of brine re-injection into the subsurface of the salar or adjacent brine-freshwater interface area. The model can be used to evaluate how the re-injection of spent brine (i.e. brine with lithium removed by DLE) might affect the extraction of lithium in the salar nucleus. This preliminary evaluation is provided here using a numerical model of a salar system and is based on previously published investigations of salar systems. Nothing in this document should be construed as a recommendation or as pertaining to a specific jurisdiction, project, operation, or technology company. The model is focused on DLE and brine re-injection on the Salar de Atacama because there is more public data on this hydrological system in the context of lithium brine than any other system.

1.1 Conceptual Model

This conceptual model for this evaluation is based on the groundwater flow system formed between a salar and adjacent upland area. A mixing zone exists where freshwater from upland areas and brine from the nucleus interact. This model is based on the conceptual and numerical models developed and applied by Zourek (2020) and informed by the research of Marazuela (2018, 2019). A diagram of the conceptual flow system for this study is presented in Figure 1.

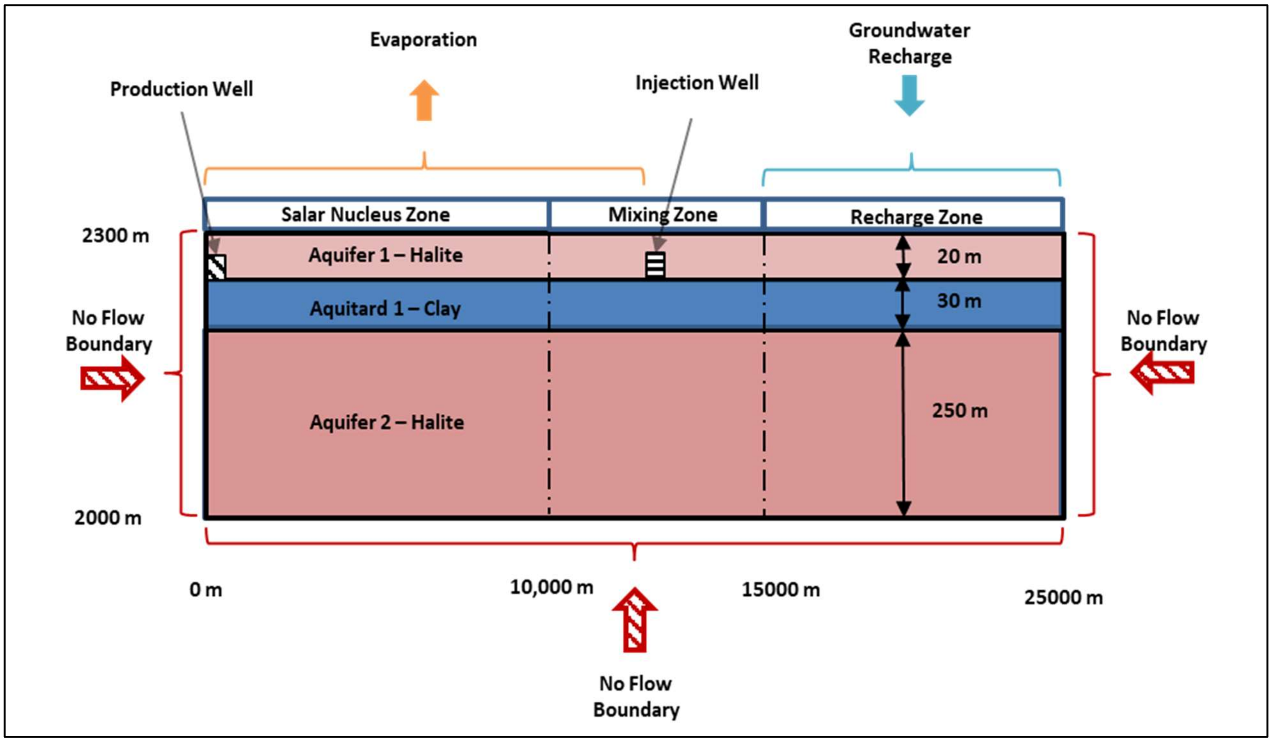

Figure 1 – Salar Basin Cross Section Conceptual Model

A production well extracting lithium rich brine is conceptualized at the start of the conceptual cross section and an injection well re-injecting lithium-poor brine is conceptualized within the mixing zone extent of the section in either the first or second halite layer.

1.1.1 Geologic structure and properties

The geologic structure of this salar basin is a simplified three-layer system based on the research of Zourek (2020). The physical properties of this system, including hydraulic conductivity and storage, are based on Zourek (2020) and Marazuela (2018 2019).

Table 1 Geologic Properties

			Hydraulic Conductivity (m/d)		Storage	
Layer Number	Layer Type	Thickness (m)	Horizontal (K_{xy})	Vertical (K_z)	Specific Yield () and Effective Porosity	Specific Storage (m^{-1})
Layer 1	Halite (Aquifer)	20	200	20	0.05	5.00E-03
Layer 2	Clay (Aquitard)	30	0.1	0.01	0.015	1.00E-05
Layer 3	Halite (Aquifer)	250	1	0.1	0.015	1.00E-05

1.2 Numerical Model

The numerical model constructed and evaluated was implemented using the United States Geologic Survey (USGS) SEAWAT program for variable density groundwater flow and solute (brine) transport.

1.2.1 Model Dimensions and Resolution

A two-dimensional (cross section) numerical model has been developed for this evaluation. The lateral and vertical extents of the model (25 km and 300 m, respectively) were selected to evaluate the effects of brine pumping and re-injection in a typical salar system. These model dimensions were chosen to ensure that the locations of re-injection evaluated within the mixing zone are sufficiently far away from the boundaries of the model that the boundaries do not affect the predictions of the model in these locations.

The salar basin cross section was represented in the numerical model (SEAWAT) with a fixed cell size in the x, y extent and a variable cell thickness in the vertical (z) dimension. Cell thicknesses range from 2 m in the upper aquifer to 10 m in the lower aquifer. These values were selected to provide appropriate grid resolution to represent the physical processes governing the variable density groundwater flow system.

1.2.2 Initial conditions

An initial groundwater level of 2,300 m (water level at ground surface) is assigned in the model. For brine transport, the background concentrations of the brine constituents are represented by total dissolved solids (TDS) and assigned 330,000 mg/L. At lateral distances between 12,500 to 25,000 m, this initial TDS value is reduced to 6,500 mg/L within the first halite layer and clay layer to represent lower brine concentrations due to mixing of the nucleus brine with freshwater recharge from outside the salar. The background concentrations of lithium is set to 2,000 mg/L in all areas except in the first halite layer and clay layer from 12,500m to 25,000 m where it is set to 5 mg/l represent lithium concentrations in the mountain regions receiving freshwater recharge.

From these initial conditions the model was run for a period of 220 years to provide the model time to equilibrate from these initial conditions to a long-term average condition. This long-term average condition represents the starting point for model simulations to evaluate the effects of brine re-injection.

1.2.3 Boundary Conditions

No flow boundary conditions are assigned along the sides and bottom of the modelled cross section. These conditions mean that no groundwater may flow in or out of the model along these sides of the model. Along the top of the model a depth dependent evaporation boundary condition was applied from 0- 12,500 m along the cross section. From 15,000 to 25,000 m along the section a recharge boundary condition is applied. Within the 12,500 to 1500 m along the section no evaporative or recharge function boundary condition is applied consistent with the approach used in the Marazuela 2018 salar cross section model. Groundwater recharge rates are similar to those implemented Marazuela (2019). Evaporation rates are similar to those implemented by Grilli (1986) and Houston (2006) and are representative for the environment based on available literature, see Table 2 Boundary Condition Values. Model boundary conditions are shown in Figure 1.

Table 2 Boundary Condition Values

Boundary Condition	Rate (mm/year)
Groundwater Recharge	15
Evaporation	1,500

2 MODEL APPLICATION

2.1 Validation

The water balance of the model was evaluated to ensure that the balance of inflows and outflows to the system was consistent with the conceptual model and rates of recharge and evaporation reported. The water balance of the model used to generate the initial conditions of the scenario models is presented in Table 3.

Table 3 - Long Term Water Balance (220 Years)

Water Balance Component	Inflows (kg/year)	Outflows (kg/year)
Storage	1.15E+07	6.77E+06
Recharge	7.64E+07	0.00E+00
Evapotranspiration	0.00E+00	7.95E+07
Change in Fluid Mass as a Result of Concentration Change (DCDT)	4.39E+06	5.73E+06
Total of Components	9.23E+07	9.20E+07
Error (%)	0.0%	

The long-term water balance illustrates that recharge and evapotranspiration are approximately in balance with one another, as expected over the long term run because no other sources of water flow in or out of the model are present.

Further model scenarios were evaluated in terms of the flow and brine balance to ensure a numerically sound solution was achieved by the model. In the case of flow and brine transport the error of the model was less than 1% and is not considered significant.

2.2 Re-injection Scenarios

A series of five different lithium brine production and re-injection scenarios were simulated to evaluate the effect that brine re-injection has on lithium production over a 30-year period. These scenarios all used a fixed brine extraction rate of 15 L/s and a re-injection rate that varied from 0-15 L/s. An additional scenario which evaluated re-injection within the deeper second aquifer was also evaluated. The scenarios considered are summarised in Table 4. The production and re-injection locations are illustrated on Figure 1 .

Table 4 Model Scenarios

<table>
<tr><th>Scenario Number</th><th>Scenario Description</th><th>Pumping Rate (L/s)</th><th>Injection Rate (L/s)</th><th>Production Location</th><th>Injection Location</th></tr>
<tr><td>1</td><td rowspan="3">Production with re-injection in upper halite unite (layer 1)</td><td>15</td><td>15</td><td rowspan="5">At 83 m along the cross section, from 10-20 m bgs within upper halite unit (layer 1)</td><td rowspan="3">12,500 m along cross section from 10-20 m bgs within the upper halite unit (layer 1)</td></tr>
<tr><td>2</td><td>15</td><td>10</td></tr>
<tr><td>3</td><td>15</td><td>5</td></tr>
<tr><td>4</td><td>Production with no re-injection</td><td>15</td><td>0</td><td>N/A</td></tr>
<tr><td>5</td><td>Production with re-injection at depth in lower halite unit (layer 3)</td><td>15</td><td>5</td><td>12,500 m along section (middle of mixing zone), from 55-65 m bgs within the lower halite unit (layer 3)</td></tr>
</table>

2.3 Scenario Results

The following sections summarize the results of the scenarios, which are compared based on lithium concentrations at the extraction well, lithium mass recovery, and distribution of lithium mass within the salar system.

2.3.1 Production Well Pumping Rates

For all model scenarios the constant pumping rate of 15 L/s at the production well results in drawdown of groundwater levels in the surrounding area of the cross section. A maximum drawdown of approximately 6.7 and 10.7 meters is predicted for scenario 1 and 4 respectively through the 30-year simulation period. In scenarios with re-injection rates of 0 to 5 L/s, the groundwater levels in the vicinity of the production well eventually drop below the well screen forcing lower pumping rates to be achieved. In those scenarios with 10 to 15 L/s re-injection the groundwater levels around the production well are maintained above the well screen and pumping rates are maintained at the prescribed 15 L/s through the 30-year period. The pumping rates achieved in all scenarios are presented in Figure 2.

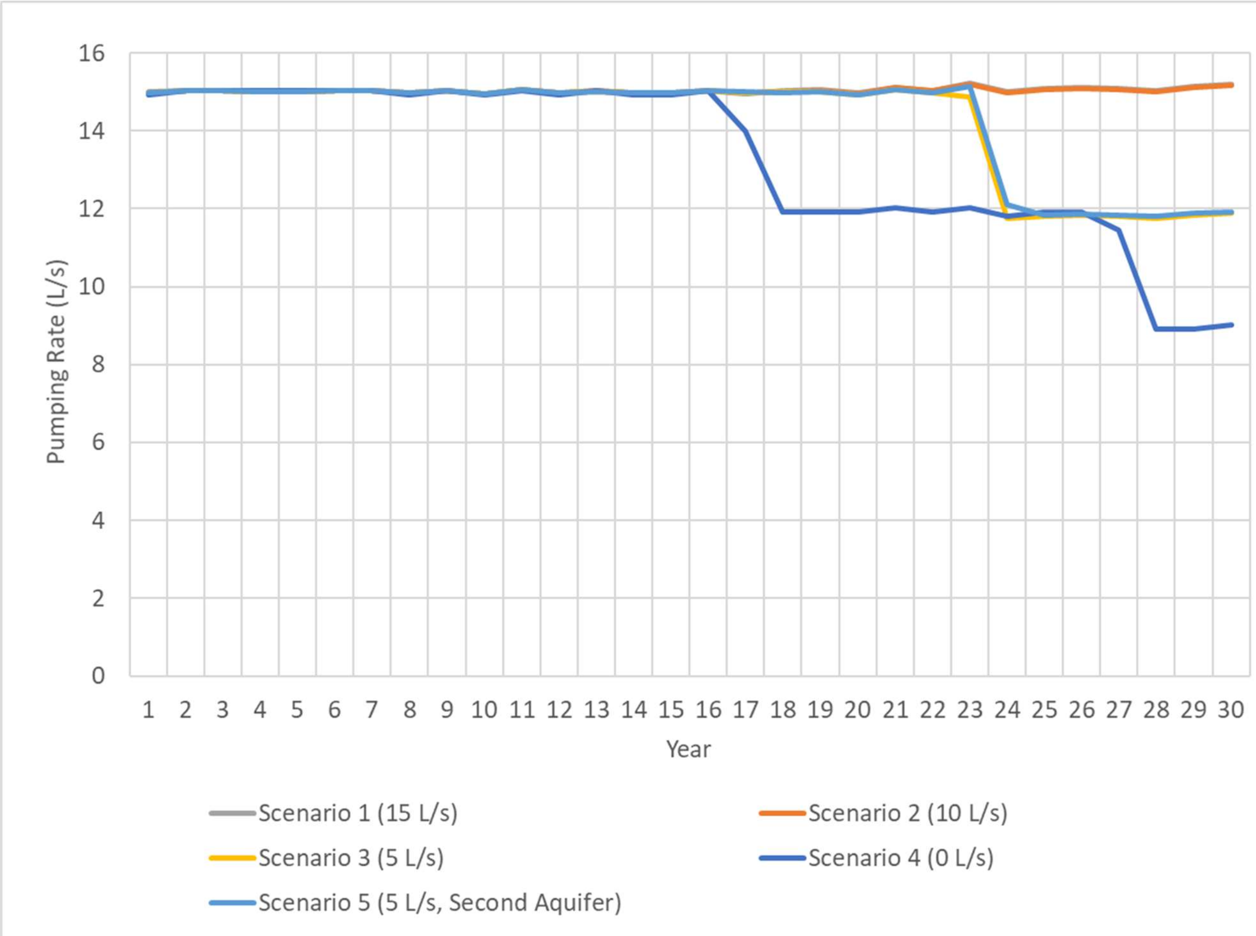

Figure 2 Production Well Pumping Rate

The average pumping rates achieved in scenarios 3 to 5 (0 to 5 L/s injection) were reduced 11% and 5% lower than the prescribed pumping rate as a result of groundwater level reduction. These results suggest that re-injection of brine fluids may support maintaining groundwater levels in the production.

2.3.2 Lithium Concentrations at Production Well

For all scenarios, the average concentration of lithium at the production wells over the 30-year simulation period is presented in Figure 3.

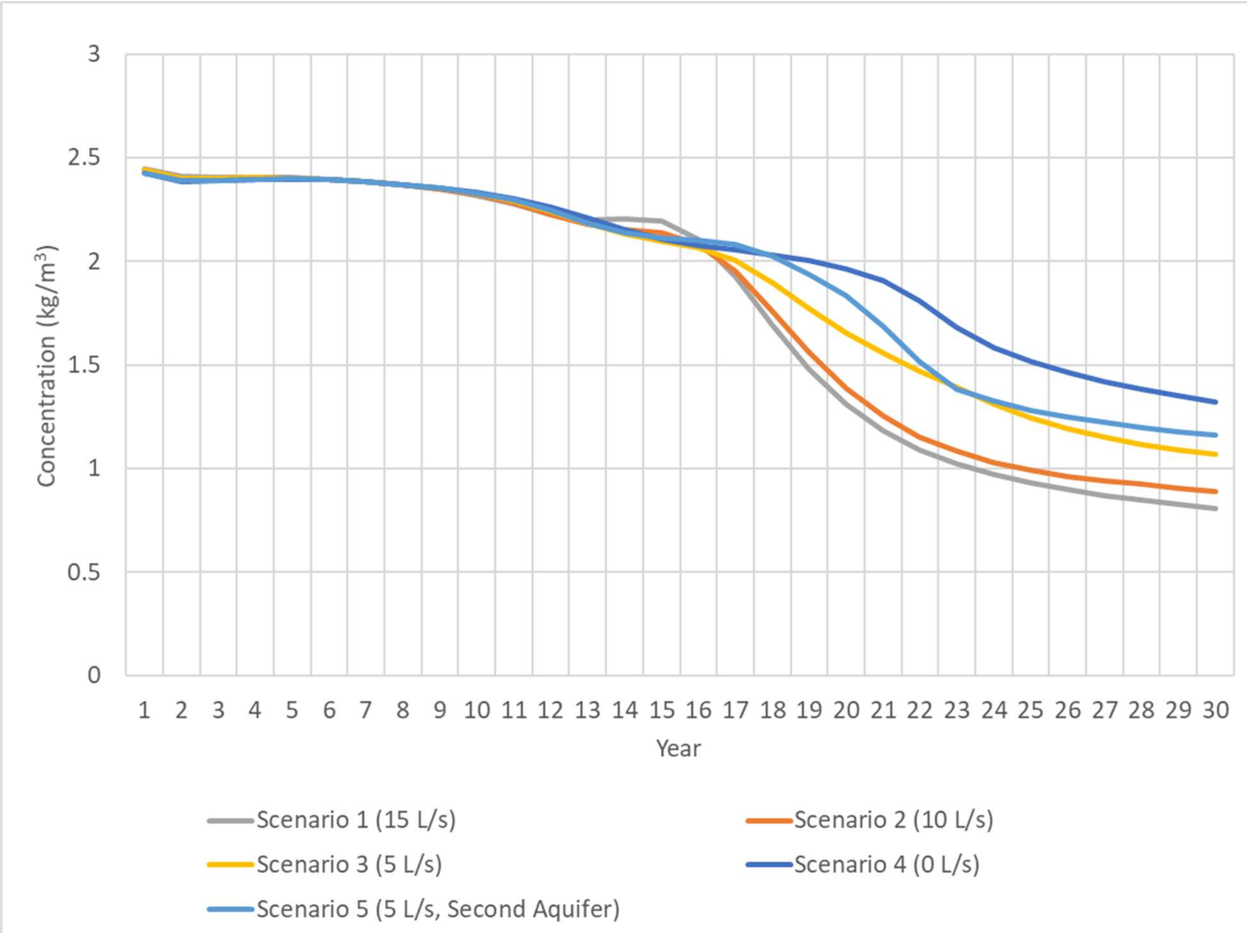

Figure 3 Production Well Concentration

Concentrations of lithium at the production well for the different scenarios are similar for the first 10-12 years but begin to deviate approximately halfway through the simulation period. The highest concentrations observed at the production well through time are associated with scenarios that have the lower re-injection rates. The average concentrations at the production well and the concentrations as a fraction of the No Re-injection scenario are presented in Table 5. Overall average lithium concentrations at the production well vary within approximately 10% of one another.

Table 5 Production Well Lithium Concentration

	Scenario 4 (0 L/s Injection)	Scenario 1 (15 L/s Injection)	Scenario 2 (10 L/s Injection)	Scenario 3 (5 L/s Injection)	Scenario 5 (5 L/s at Injection at Depth)
Average Lithium Concentration (kg/m^3)	2.01	1.79	1.89	1.77	1.93
Average Concentration as Fraction of No Re-injection Scenario (Number 4).	N/A	0.89	0.94	0.88	0.96

The reduction in concentrations associated with increasing re-injection rates is likely the result of a recirculation of brine fluid occurring in the first aquifer. The upper aquifer represents the highest hydraulic conductivity layer and offers the easiest flow path between the injection well and the production well. As the reinjected brine is lithium poor, having only 10% of the background lithium concentration (0.2 kg/m^3), the re-injection of this fluid into the first aquifer would be expected to reduce overall concentrations in the unit over the long term. The recirculation theory is supported by the fact that when we inject at depth in the 2nd aquifer unit at 5 L/s we maintain higher average concentrations at the production well. It is important note these results are highly influenced by the conceptual model (e.g. geologic layer structure, boundary conditions) and the scenario specification (e.g. well placement, pumping rates).

2.3.3 Lithium Mass Recovery

The cumulative mass of lithium recovered at the production well through the 30-year simulation period is presented in Figure 4.

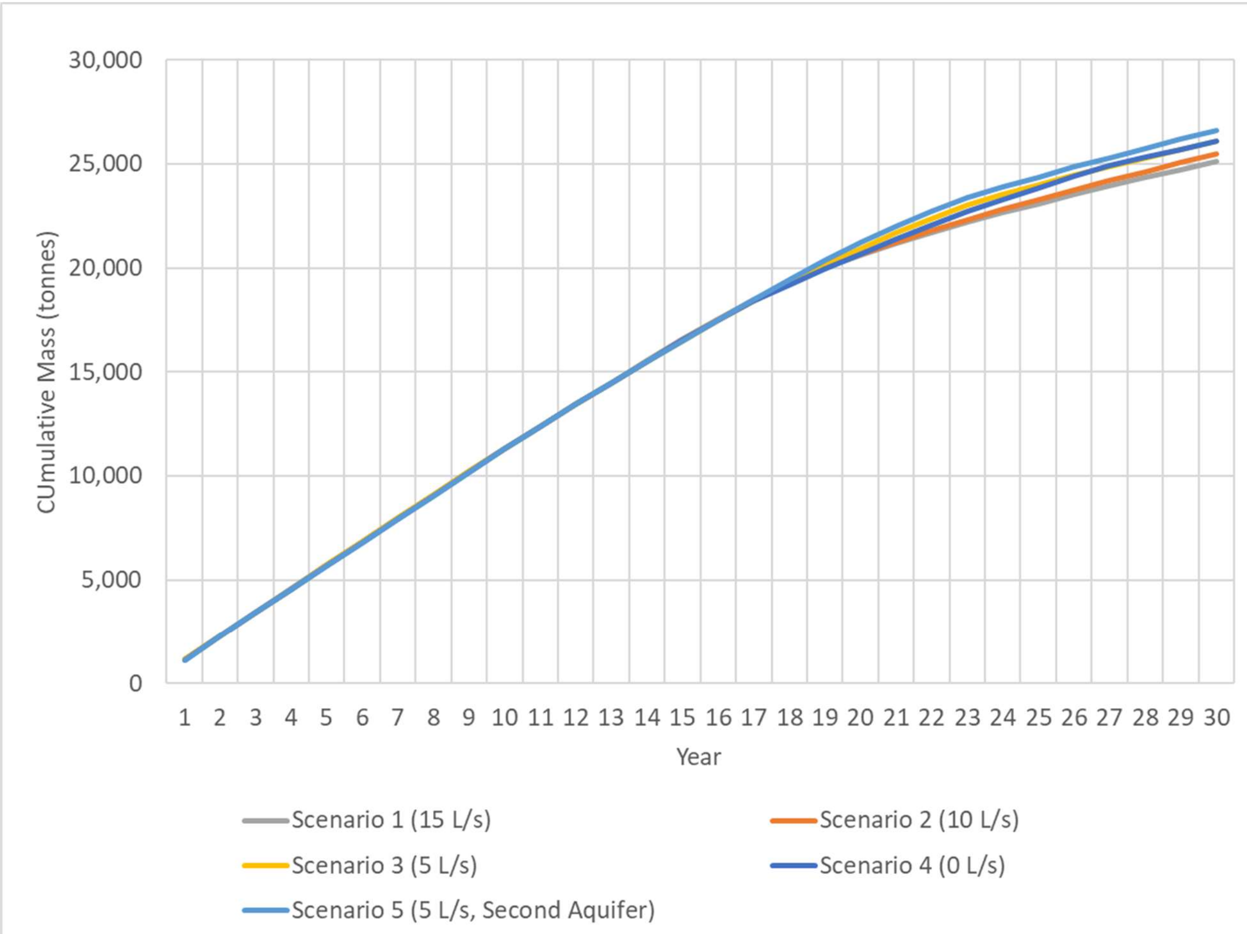

Figure 4 Lithium Mass Recovery at Production Well

The cumulative lithium mass recovery achieved at the production wells for all scenarios demonstrate that while higher rates of re-injection support higher pumping rates at the production well, the reduced concentrations of lithium at the production well offset these gains in those scenarios. Ultimately the mass recovery in each scenario is very similar through the 30-year simulation period.

2.3.4 Lithium Mass Distribution

The distribution of lithium mass within the model is presented for the initial (0 years) and final (30 years) of the model in Figure 5 and Figure 6 respectively. The primary changes observed are a depletion of lithium concentrations in the salar nucleus within the first aquifer and a portion of the aquitard as well as a plume of low concentration lithium associated with the injection well.

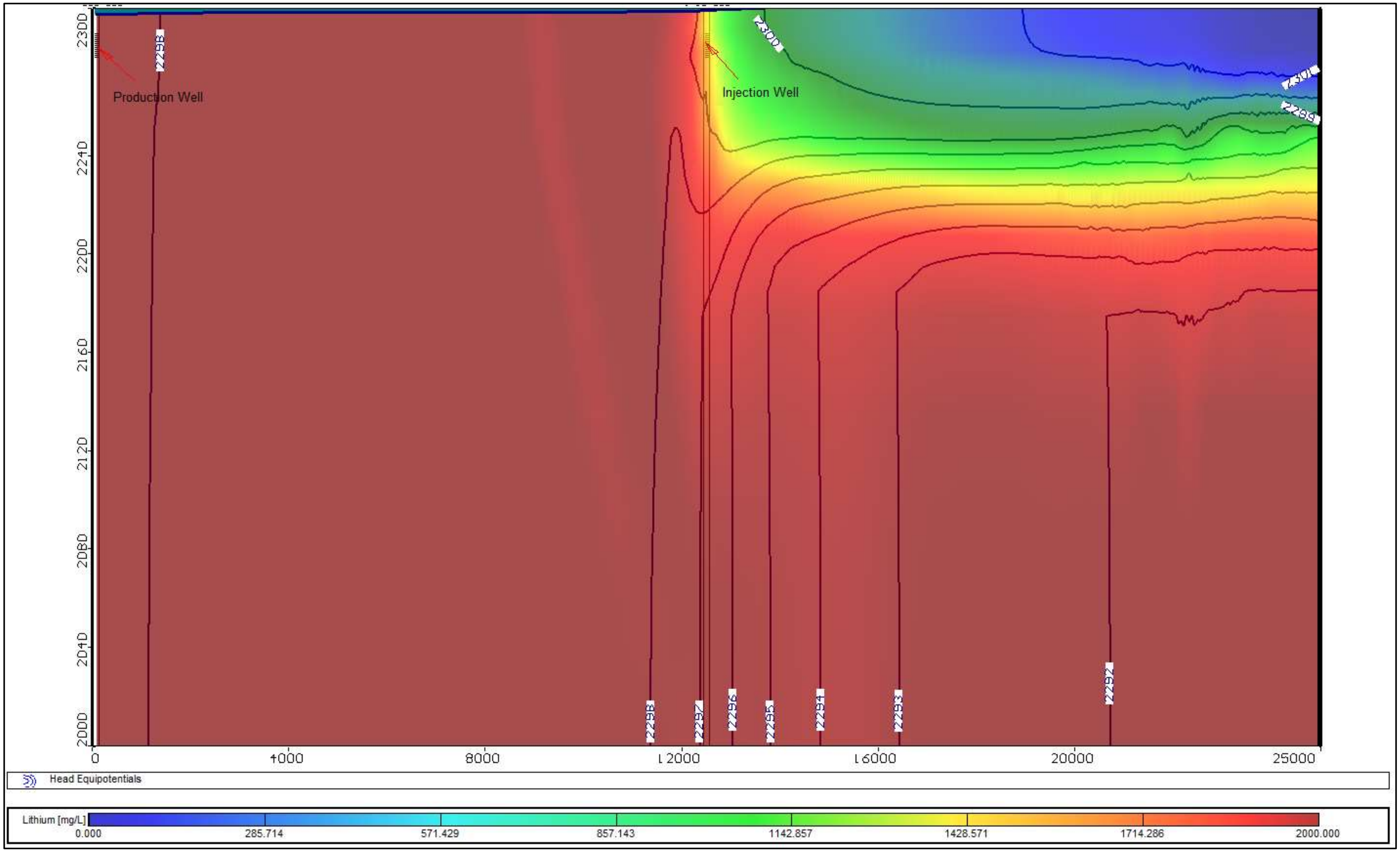

Figure 5 Initial Lithium Distribution (0 Years) 50x Vertical Exaggeration

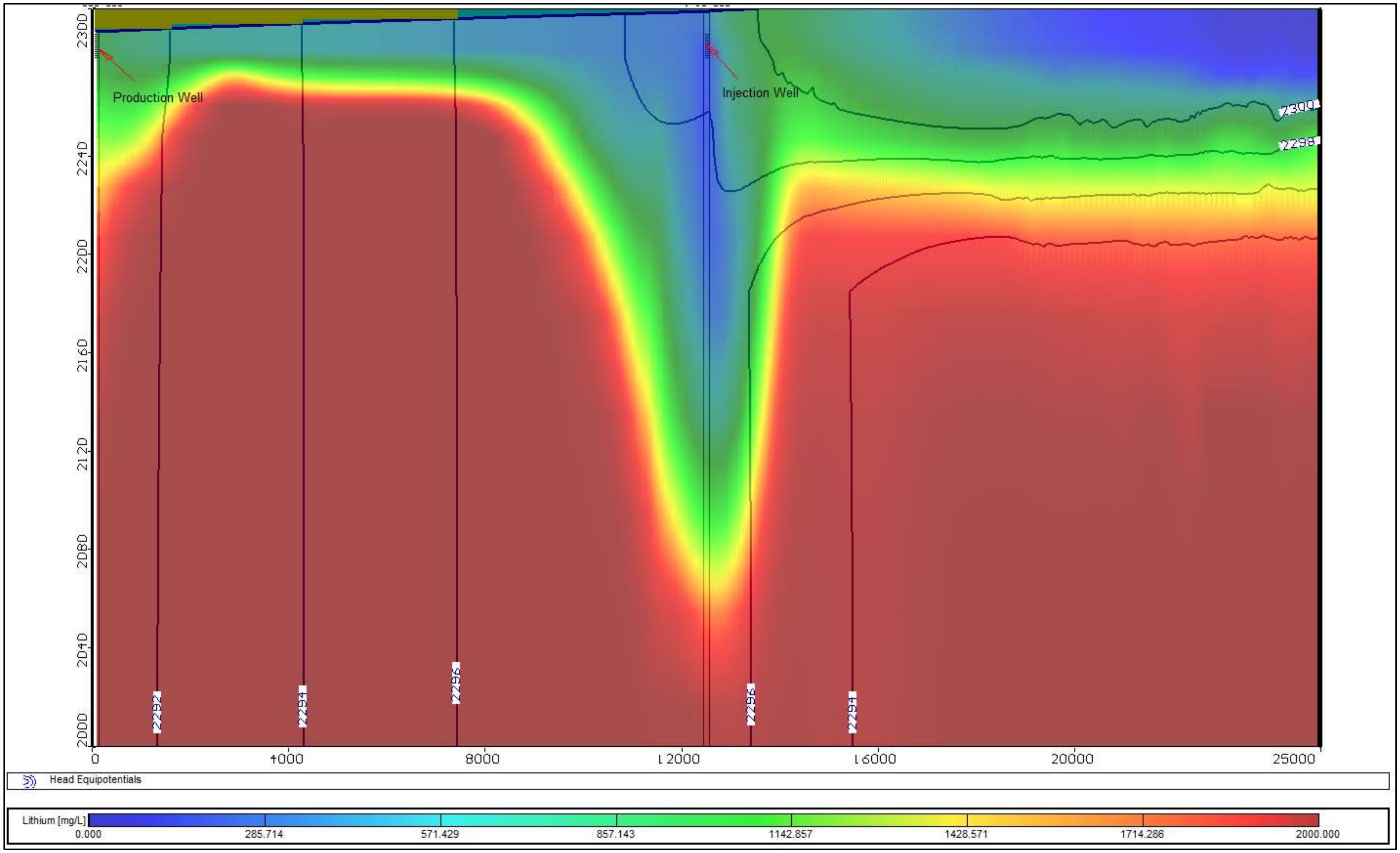

Figure 6 Final Lithium Distribution (30 Years) 50x Vertical Exaggeration

2.3.5 Scenario Interpretation

The scenario results indicate that re-injection of brine within the salar system is possible at injection rates that match production well pumping rates (15 L/s) and does not appear to alter lithium recovery rates at a production well substantially in this conceptual examination. Further the re-injection of brine fluids at depth within the lower aquifer layer (Layer 3) was shown to be possible as well and produces similar lithium recovery rates to no re-injection at rates of up to 5 L/s.

3 SUMMARY AND NEXT STEPS

Using a two-dimensional cross-section model of a salar, the impacts of re-injecting spent brine within the salar system were evaluated. The objective has been to determine if the re-injection of spent brine will have an adverse affect on the lithium production rates in the salar nucleus. Re-injection of brine within the mixing zone of the salar was demonstrated to be supported at rates of up to 15 L/s. Re-injection within the mixing zone within the deeper second aquifer system was also evaluated and supported at rates of 5 L/s. In all scenarios examined, the recovery of lithium mass at the production well was very similar.

Within the simplified context of the model these results of these scenarios suggest that it may be possible to re-inject lithium brine in a salar system with limited effect on lithium production within the system.

To further this work and expand the applicability of the findings reported here further investigation is required. Extension of this work might involve a similar investigation of lithium production and brine re-injection scenarios but applied to a site specific salar model which features a detailed representation of local hydrogeologic and hydrologic conditions, considers time varying model inputs and boundary conditions and is calibrated to observational data.

4 ASSUMPTIONS AND LIMITATIONS

This model represents an idealised conceptualisation of a salar basin system behavior under average conditions and the governing hydrology and hydrogeology are simplified relative to the complexity of actual salar system. Further, there are physical processes not represented in the model which may influence the subsurface flow and transport of lithium in a salar basin system (e.g. salt dissolution and precipitation) and the system is represented in two-dimensions rather than three. As a result of the assumptions and simplifications employed in the model the results obtained here should not be applied outside of the context in which they were derived. The impacts of brine re-injection in a salar system must be evaluated in the site-specific conditions for which they are being considered using a non-idealised, well calibrated numerical model which represents all relevant physical processes for the system in question.

5 REFERENCES

Grilli, A. and F. Vidal (1986). Evaporación desde salares: metodología para evaluar los recursos hídricos renovables. Aplicación en las regiones I y II. In: Revista de la Sociedad Chilena de Ingeniería Hidráulica, 1(2).

Houston, J. et al. (2011). The Evaluation of Brine Prospects and the Requirement for Modifications to Filing Standards". In: Economic Geology 106.7, pp. 1225{1239. doi: 10.2113/econgeo.106.7.1225.

Marazuela, M.A. et al. (2018). \3D Mapping, Hydrodynamics and Modelling of the Freshwater-Brine Mixing Zone in Salt Flats Similar to the Salar de Atacama (Chile)". In: Journal of Hydrology 561, pp. 223{235. doi: 10.1016/j.jhydrol.2018.04.010.

Marazuela, M.A. et al. (2019). \Hydrodynamics of Salt Flat Basins: The Salar de Atacama Example". In: Science of The Total Environment 651, pp. 668{683. doi: 10 . 1016 / j .citotenv.2018.09.190.

Zourek, Leonard 2020. Modelling scenarios for re-injection of spent brine from Direct Lithium Extraction. ETH Zurich Institute of Biogeochemstry and Pollutant Dynamics. Masters Thesis, July 2020.

Langevin, C.D., Thorne, D.T., Jr., Dausman, A.M., Sukop, M.C., and Guo, Weixing,. (2007)._ SEAWAT Version 4: A Computer Program for Simulation of Multi-Species Solute and Heat Transport. United States Geological Survey.