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A Bayesian Approach to End-Member Mixing Estimations in a Geological Nuclear Waste Repository in Sweden

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Abstract: The Swedish Nuclear Fuel and Waste Management Co. (SKB) has been searching for a site to construct a deep geological repository for spent nuclear fuel in Sweden. In 2012, Forsmark was selected as the location for the nuclear fuel repository and construction will start in 2027. An understanding of the chemical composition and evolution of the groundwaters at the site is an integral part of the long-term safety case. SKB's traditional approach to describe a site has been to use M3 mixing of end-members as the main process controlling the groundwater composition. We propose a new approach using a Bayesian mixing model. Similarly to the traditional mixing approach, the fraction of each end-member for all samples in the dataset is calculated, with the exception of the deep saline end-member. Given the slow movement of the deep groundwaters, it is likely that they have reached equilibrium with the host rock and fracture minerals. Therefore, we introduce an additional step, consisting of a Phreeqc model to construct the theoretical composition of groundwater with an increasing Cl concentration in equilibrium with the mineralogy of the host rock. This is a way of introducing a geochemical explanation to deep saline waters found in the geosphere of the Forsmark site. The results indicated a higher fraction of glacial meltwater in deep groundwaters in Forsmark compared to previous models. This approach could be directly applied to other groundwater systems, with different mineralogy of the host rock, assuming slow moving groundwater in equilibrium.

Keywords: geochemical characterisation; mixing models; statistical modelling; paleohydrochemistry; Bayesian statistics

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1. Introduction

The Swedish Nuclear Fuel and Waste Management Co. (SKB) has researched and developed technology for the final repository of spent nuclear fuel for more than 40 years in collaboration with experts from universities, research institutes and private companies in Sweden and abroad. The repository will be constructed in the Forsmark area according to the KBS-3 method [1], where the spent nuclear fuel will be placed into copper canisters with a cast iron insert, surrounded by a bentonite clay buffer and deposited in a repository at approximately 500 m b.s.l. in the granitic rock.

In order to characterise the site selected for the repository construction, thorough multidisciplinary site investigations have been ongoing in the Forsmark area (Figure 1) since 2002. These investigations include the geology, hydrogeology, hydrogeochemistry, ecology, and thermal and mechanical properties of the bedrock ([2,3] and references therein). The groundwater monitoring programme includes 66 borehole sections from 24 core- and 42 percussion-drilled boreholes, with average transmissivities of 10^{-6} and 10^{-4} m^2/s, respectively, as well as 62 soil water pipes in the regolith. The biosphere is monitored in streams, lakes, precipitation, and sea sampling locations. The entire Forsmark dataset of hydrogeochemical monitoring includes all major and trace elements, gases, microbes and numerous isotope systems, and it contains approximately 6500 data points.

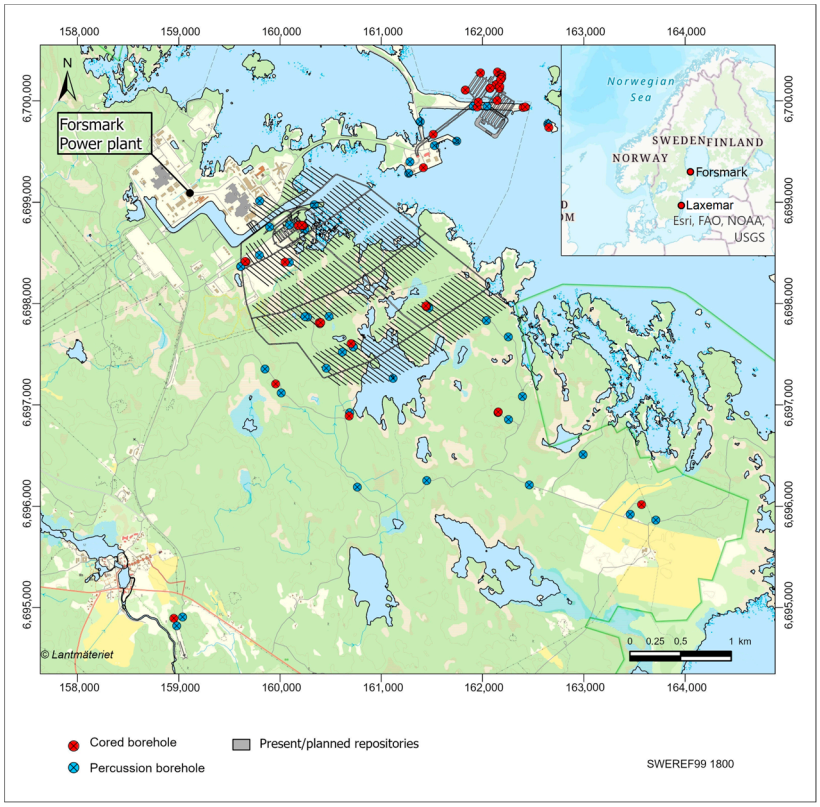


Figure 1. Overview of the Forsmark site, percussion- and core-drilled boreholes as part of the SKB monitoring programme. Shaded outlines represent the planned nuclear fuel repository (500 m b.s.l.) and the current repository for low and intermediate radioactive waste (SFR).

In addition to Forsmark, the Laxemar area was also thoroughly investigated as a possible candidate for the repository construction. The Laxemar area includes several sites, including Laxemar, Ävrö, Simpevarp and the Äspo Hard Rock Laboratory, and the hydrochemical dataset contains roughly 7000 hydrochemistry data points mainly from core-drilled boreholes [4].

The hydrogeochemical evolution, flow paths and groundwater chemistry of the Forsmark and Laxemar sites have varied dramatically over the last 20,000 years and are fairly complex due to their palaeo-hydrogeological history. During the Quaternary, several glacial stages have occurred [5]. Periods of temperate conditions, permafrost and glaciations have occurred repeatedly in the area during the last and most well-studied glacial stage (Weichsel). The Weichselian ice cover reached its maximum some 20,000 years ago and the subsequent deglaciation resulted in the complex evolution of the Baltic Sea ([6] and references therein) (Figure 2). Until approximately 11,000 years ago, large volumes of meltwater filled the Baltic Ice Lake with no open connection to the Atlantic. A short period followed where brackish water entered via the south-central Sweden passage. Approximately 10,000 years ago, the isostatic rebound closed the connection between the Atlantic Sea and the Baltic, resulting in the Baltic becoming a freshwater lake again (the Ancylus lake). This period ended when the global sea level rise resulted in a new opening of the Danish straits, increasing the salinity forming the Littorina Sea. Due to the continuous isostatic rebound, the Danish straits became successively shallower, and the inflow of Atlantic water decreased subsequently. Even if this is a continuous process and there has been a gradual change from the Littorina Sea stage over to the modern Baltic, the limit between the two is usually set to about 4000 years ago. The sea started to regress from the Forsmark area as late as 1000 years ago, exposing it to meteoric recharge. In the case of Laxemar, the coastal area was already exposed to the meteoric recharge 2000 years ago, and even earlier in inland Laxemar.

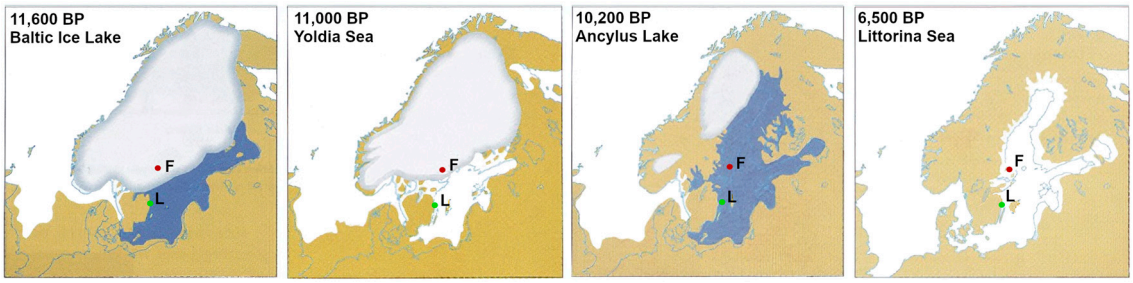


Figure 2. Historic development of the Baltic region from the latest deglaciation period to present conditions. Forsmark and Laxemar are marked with a red and green circle, respectively (modified from [6].

Considering these paleo-events, influences from several end-members are expected to be found in the groundwater: the glacial meltwaters (glacial), the marine waters (Littorina), the modern meteoric recharge (meteoric) and the old non-marine waters present at depth in the geosphere (deep saline).

To study this complex groundwater system, a combination of the multivariate mixing and mass balance modelling technique, M3 (Multivariate Mixing and Mass balance calculations) [7,8], was developed and applied to the site descriptive models in Forsmark and Laxemar [9–12]. However, there are still open questions such as the characterisation of the very old and saline non-marine waters present in the bedrock, for which an explanation based on water rock interactions is proposed here. It is a combined methodology of M3 modelling and Phreeqc [13] calculations and a statistical model utilising Bayesian inferencing in the PCA (principal component analysis) space to interpret the evolution of groundwaters in a crystalline bedrock.

2. Materials and Methods

The dataset used in this study corresponds to the waters with complete set of values for the water chemistry data shown in Table 1, in total including 1400 groundwater samples from Forsmark and 2300 from Laxemar. A detailed and thorough explorative analysis and evaluation of the data used in this study is explained in [14].

Table 1. The end-members traditionally used to explain the paleohydrochemistry of the Forsmark site; in this study, the glacial, Littorina and meteoric end members were the same in the new model approach. The glacial meltwater is a sample taken from a glacier in northern Norway [15]. The Littorina end-member was estimated to closely resemble the Littorina sea [16]. The meteoric end-member corresponds to one of the samples taken in the environmental monitoring program at Forsmark [14]. The deep saline end-member is represented by the most saline sample taken from the investigation programme; the sample was taken from the Laxemar site at a depth of around 1500 m b.s.l. [4]. All the concentrations are given in mg/L and the isotopes are in permil (‰) VSMOW.

End Member	Na	K	Ca	Mg	HCO_3^-	Cl	SO_4^{2-}	Br	δ^2H (‰)	$\delta^{18}O$ (‰)
Glacial	0.17	0.4	0.18	0.1	0.12	0.5	0.5	0.001	−158	−21
Littorina	3674	134	151	448	93	6500	890	22.2	−38	−4.7
Meteoric	13.2	4.52	136	10	355.8	56.3	13.2	0.299	−80.9	−11.43
Deep Saline	8500	45.5	19,300	2.12	14.1	47,200	10	323.6	−44.9	−8.9

The traditional way of calculating mixing proportions using the M3 methodology is summarised in [12]. The methodology is based on transformation of the major constituents of the water samples into PCA space using standard covariance–eigenvalue decomposition transform with normalised data (z-scaling). The mixing fractions are then calculated based on the end-members listed in Table 1. The loadings calculated are on the complete Forsmark data set, and the variability explained on PC1 and PC2 are hence the variability explained in the Forsmark data set. In the case where Laxemar data are shown, the data are projected

on top of the Forsmark data using the Forsmark transformation. In all calculations, the end-members were not part of the PCA transform due to not being in the same data set.

The end-members need to encompass all possible linear combinations of the samples in a mixing model. Figure 3 shows the Forsmark samples with the traditional end-members plotted and marked. The glacial end-member is a sample taken from a glacier in northern Norway. The meteoric end-member is a sample taken from the SKB monitoring programme and the Littorina end-member is an estimated concentration based on the assumed highest salinity of the Littorina sea stage. The deep saline end-member is represented by the most saline sample taken from the investigation programme at the Laxemar site. The sample was taken from a depth of 1500 m b.s.l. and had a salinity of 47 g/L. The deepest groundwaters sampled in Forsmark so far have been taken at 1000 m depth and the highest salinity measured is 15 g/L. This large difference in salinity between the Forsmark waters and the deep saline end-member has caused some issues when evaluating the mixing results for the Forsmark site. As a result, the M3 mixing model needs a large degree of meteoric dilution to compensate for the concentrated values of the deep saline end-member. This is in discrepancy with the oxygen and hydrogen isotopes that show more of a glacial influence.

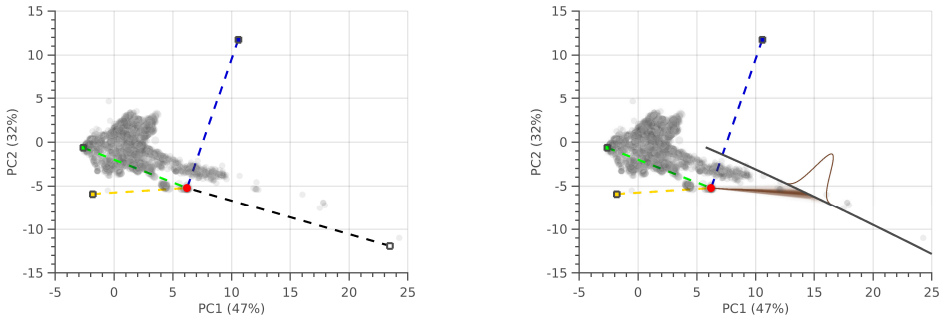


Figure 3. PCA space of SKB samples (grey dots). The variability explained on PC1 and PC2 are for the Forsmark samples and not for the end-members, as they are projected on top of the Forsmark data. (**a**) An example of traditional mixing calculations of one sample (red) using static end-members (yellow, green, blue and white). (**b**) The bedrock equilibrium line replaces the deep saline end-member (white) from Figure 3a. The brown line indicates the most credible position of the deep saline end-member along an equilibrium line based on the samples.

The new method proposed here is based on the assumption that the chemical composition of the old deep groundwater in crystalline bedrock aquifers is primarily determined by the reactivity and mineral composition of the bedrock. Michard [17] presented a model where major water constituents could be calculated by knowing the mineral composition in contact with the water, given any Cl concentration. Similar models have previously been applied to SKB data by Grimaud et al. [18] and Trotignon et al. [19], and also to other deep boreholes [20]. Using similar models, the water composition in equilibrium with the rock-forming and fracture-filling minerals in the Forsmark granitoids was calculated by Phreeqc [13] for a range of Cl concentrations from 4000 to 50,000 mg/L. The mineralogical phases representing the Forsmark granite used in the Phreeqc model included quartz, An29Ab71 (plagioclase with 29% anorthite and 71% albite), microcline, laumontite, chlorite, biotite and calcite (SKB code 101057 in [1]). There was also a sensitivity analysis performed on the mineral phases, performed by sequentially adding other observed mineral phases at the Forsmark site, such as gibbsite, kaolinite, phlogopite and pyrite, which yielded quite unreasonable results compared to water measurements in the deep groundwater. This resulted in using the common granite representation (101057 in [1]) with the addition of calcite. The thermodynamic database used was WATEQ4F [21], with the modifications reported in Auqué et al. [22].

The water chemistry compositions resulting from the equilibrium calculations are then introduced into the PCA space using the same transformation as the measured groundwater samples. Since Phreeqc did not calculate δ^2H and $\delta^{18}O$, these were estimated at around −45‰ and −9‰, respectively, the same as the deep saline end-member in Table 1.

Mixing calculations were based on linear combination of the end-members. Figure 3a shows the traditional way of estimating mixing fractions from the set end-members from Table 1. The new approach solves the problem of end-member selection as the samples will select the most credible position of the end-member based on a semi-weak a priori. The a priori for the deep-saline end-member is any position on the calculated granite equilibrium line shown in Figure 3b set as a uniform distribution along the line. The other end-members were set as small distribution with the average taken from Table 1 with small standard deviations.

The Bayesian inferencing model was written using STAN coupled to Matlab via CMD-STAN [23]. The model structure is visualised in Figure 4. The model follows standard mixing calculations in PCA space, with the exception that all individual samples have a variance in its position, given using analytical uncertainties (σ(u)). The end-members are treated in similar ways to the samples in that they are sampled from a normal distribution with a small variance. The deep saline non-marine water end-member was treated differently, as the concentration was calculated from Phreeqc and then approximated into a linear equation. The end-member distributions were sampled from a standard mixing formula with fraction multiplied with the position of the end-member in PCA space. The prior distributions for the end-members were broad uniform distributions and the fraction parameter was set as a simplex matrix with a uniform prior between 0 and 1.

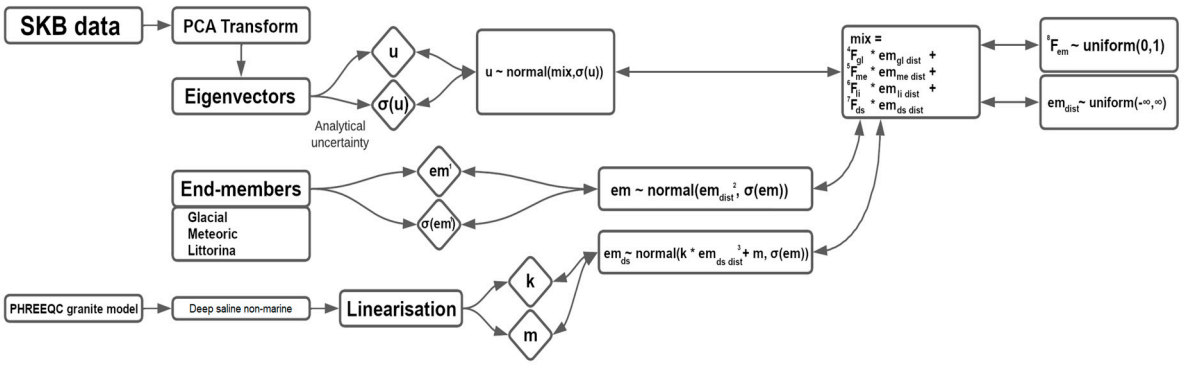


Figure 4. Model structure of the Bayesian model. The SKB samples are transformed using PCA transform described in the Material and Methods section. This gives the scores which are denoted u and their variance in PCA space is calculated via analytical uncertainty, denoted as σ(u). The end-members use the PCA transform from the measured samples and transformed into PCA space using the same transformation. In the case of deep saline end-member, the concentrations for the major water constituents are obtained from the Phreeqc model, which is a linear function in PCA space. The fractions of each end-member, which represent the measured water sample, are then calculated via a simple mixing calculation denoted mix in the figure. [1] End-member, [2] distribution of end-members (glacial, meteoric and Littorina), [3] distribution of deep saline non-marine water, [4] fraction glacial meltwater, [5] fraction meteoric water, [6] fraction Littorina water, [7] fraction deep saline non-marine water, [8] fraction of combined end-members. Sums to 1.

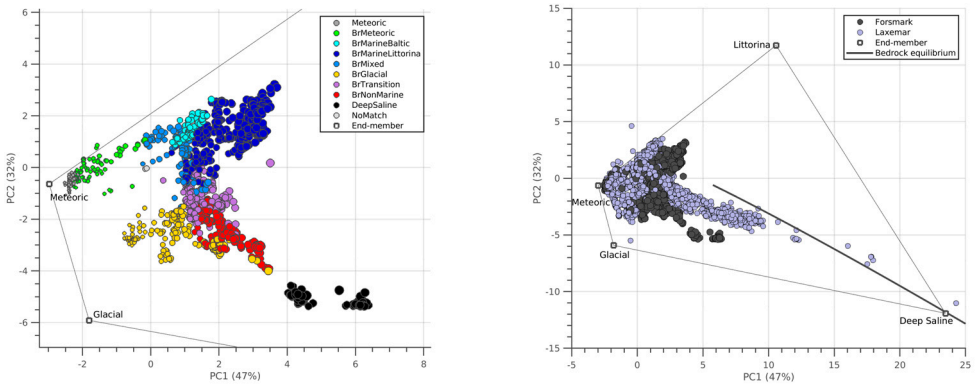
The posterior distributions from the model are the mixture, the fractions and the end-member position in PCA space. The mixture (mix in Figure 4) is the position per dimension of the sample, which has the likelihood function of the measured concentration (and as such the position of the sample in PCA space). This results in a model which samples the position of the old saline non-marine end-member based on the measured samples and creates a posterior distribution of the most credible position of the end-member.

A potential error in the presented methodology is that the PCA transform is not linear with the introduction of analytical uncertainties, as a change in concentration would affect the covariance–eigenvalue decomposition slightly. This effect was tested prior to the model and gave a <1% difference in the PCA transform, which was most likely due to the large amount of data used in this study (<1400 samples for Forsmark and >2300 samples for Laxemar), but might be relevant to consider when using smaller data sets.

The main advantage of the method proposed here is that by using a Bayesian statistical approach it makes it possible to consider the calculated bedrock equilibrium line as an end-member instead of just the single point represented by the deep saline end-member reported in Table 1.

3. Results and Discussion

The PCA plot (scores plot) with the Forsmark waters and the end-members listed in Table 1 is shown in Figure 5a. Figure 5b shows the same data but includes the data from Laxermar as lilac scatter points. The thick grey line represents the equilibrium line calculated with the Phreeqc model as the theoretical groundwaters with different salinities (Cl concentrations) in equilibrium with the Forsmark bedrock. As it can be seen in the plot, this equilibrium line directly intersects the measured deep saline end-member, both in the PCA space and in the calculated concentrations. The calculated loadings from the Forsmark and Laxemar samples are shown in Table 2.



(**a**) (**b**)

Figure 5. PCA figures with the major elements represented (Na, Ca, Mg, K, Cl, Br, HCO_3^-, SO_4^{2-}, δ^2H and $\delta^{18}O$). The variability explained on PC1 and PC2 are for the Forsmark data and not for Laxemar data or the end-members, which are only projected on top of Forsmark data. (**a**) Forsmark samples coloured according to the water types defined by Gimeno et al. [14]. The NoMatch values are samples that could not be categorised into the presented categories. The glacial and meteoric end-members are represented as white squares and the Littorina and deep saline end-members are outside the figure and can be seen in Figure 5b. (**b**) The Forsmark dataset from 5a, in dark grey, together with Laxemar dataset as lilac circles. The four presented end-members from Table 1 are marked with white squares, and the bedrock equilibrium line from varying Cl concentrations between 4000 and 50,000 mg/L are shown as a thick grey line.

Table 2. Loadings from the PCA calculations. Na, SO_4^{2-}, Cl, Br and $\delta^{18}O$ are dominant on PC1; and K, Ca and HCO_3^- are dominant on PC2.

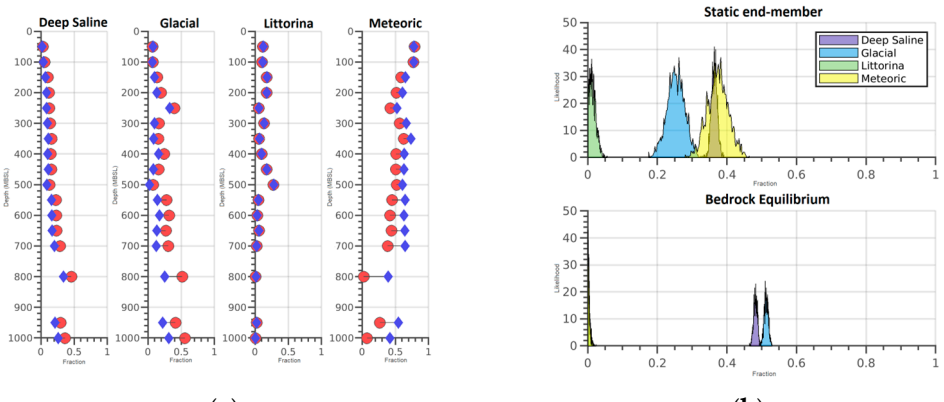
	Na	K	Ca	Mg	HCO_3^-	Cl	SO_4^{2-}	Br	δ^2H (‰)	$\delta^{18}O$ (‰)
PC1	0.46	−0.02	−0.07	−0.01	−0.07	−0.40	0.49	−0.49	0.16	−0.34
PC2	0.25	−0.36	−0.26	0.17	0.82	0.03	0.03	0.12	−0.17	0.00

There are a few characteristic differences between the Laxemar and the Forsmark data. The scatter points on the right side of the figure were generally sampled from a

greater depth with an increasing non-marine saline signature, trending towards a Ca-Na-Cl groundwater signature and approaching the bedrock equilibrium line. This is in line with the assumed slow movement of deep groundwater in low-transmissivity bedrock. Despite the concentration differences between the two data sets, Figure 5b shows that both were trending towards the equilibrium line with increasing Cl concentrations. However, the main difference was that the Laxemar dataset follows the equilibrium line while the Forsmark dataset deviates towards an area of more influence from the glacial end-member.

The Bayesian mixing model used the entire bedrock equilibrium line as an end-member, implicitly stating that the actual position on the line is simply a function of the original Cl concentration of the infiltrating waters. When inferencing the end-member composition of the samples, the most credible position on the equilibrium line will be based on the samples for the model, as the end-member is set to be the same for all samples.

Similarly to the M3 code, the Bayesian mixing model gives the fraction of each end-member for each individual sample. Figure 6a shows depth-averaged mixing fractions in 50 m intervals. The red circles are the Bayesian model and the blue diamonds are the static end-member model obtained with M3. As shown in the figure, the results obtained with the previous approach show a high degree of meteoric dilution; however, due to the depth these samples were taken from, and the paleohydrochemical history of the site, it is unlikely to have a high influence of meteoric dilution. The low δ2H and δ18O values in the deep groundwater in Forsmark also support glacial dilution. As expected, by using the bedrock equilibrium line as an end-member instead of the static model, there was almost no difference in Littorina signatures. The meteoric component was unaffected in the shallow parts of the geosphere, but showed a smaller contribution in the deeper parts of the geosphere, starting at around 300 m b.s.l. The glacial and meteoric influence had an inverse correlation with depth, which is expected in a natural system in Sweden, and the relative dilution observed in the deep groundwaters at Forsmark was due to the influence of glacial waters. This is in agreement with the observed isotopic signatures in the deep groundwater of Forsmark.



(**a**) (**b**)

Figure 6. Estimated mixing proportions for the Bayesian model and the static end-member model. (**a**) Depth-averaged mixing fractions in 50 m intervals. The red circles are the Bayesian model and the blue diamonds are the static end-member model. Bedrock equilibrium model estimates less meteoric and more glacial influence below 300 m. (**b**) Difference in mixing proportions for one individual sample between the two models. The bedrock equilibrium model estimates the dilution glacial instead of meteoric in this individual sample; note that the variance for the end-member fractions are lower in the bedrock equilibrium model.

Figure 6b visualises the difference in mixing proportions for one individual sample between the two models. The sample had a saline non-marine signature with a Cl concentration of around 10,000 mg/L. The Bayesian model estimated a mixing process between the deep groundwater in equilibrium with the rock and the infiltrated glacial waters, while the Littorina proportions were the same in both models. Interestingly, the Bayesian model

introduced uncertainty in the form of analytical uncertainty compared to the static end-member model, but the estimated end-member fractions had a smaller confidence interval in the Bayesian model.

During testing between the traditional M3 methodology and the work presented here, it was discovered that even though there was an introduction of analytical uncertainty in all samples, the results obtained had much less variance than the traditional methodology using direct four-way mixing.

4. Conclusions

In this study we have presented a methodology for calculating mixing proportions in a crystalline bedrock groundwater system. We estimated the mixing fractions between three known, as well as one relatively unknown, end-members. The unknown end-member was most likely water in equilibrium with the bedrock, and the presented methodology worked well with such weakly defined end-members. The bedrock equilibrium line used showed that there was a geochemical interpretation of the old non-marine waters found deep in the geosphere at the Forsmark and Laxemar sites.

The model showed that the groundwaters at the Forsmark site, the planned site for the Swedish deep geological nuclear fuel waste repository, could be well-described using the four proposed end-members. Furthermore, the mixing fractions showed that the injection of glacial meltwater possibly reached as far down as 1000 m b.s.l. in Forsmark. The influence of the glacial meltwater seems to be smaller in the deepest samples from Laxemar (between 1000 and 1500 m depth), which showed a high degree of equilibrium with the bedrock.

Further model development could focus on introducing non-static variations in the other end-members. The glacial end-member was taken from a glacier in northern Norway. A dataset taken from SKB boreholes in Greenland was tested and showed small variations in the PCA plot, even though the waters were of a very similar composition and mainly the stable water isotopes varied. The meteoric composition could similarly be varied due to variations in HCO_3^-, $\delta^{18}O$ and δ^2H in both the short and long term. In theory, all groundwater should trend towards equilibrium with the surrounding host rock. Therefore, a static end-member approach in mixing calculations can be changed to the approach shown in this study, a more process-based model. This also removes the potential bias introduced when selecting a static end-member. It is important to take water movement and time scales into consideration when evaluating which static end-members can be replaced, since far from all minerals are in equilibrium.

The SKB groundwater samples shown in this study were taken from water conducting fractures, with a transmissivity above 10^{-8} m^2/s. The bedrock equilibrium could potentially be present in the rock matrix porewater and subsequently diffuse out into the water conducting fractures, increasing the salinity in fracture water over time. From a post-closure safety assessment perspective, it is important to investigate the glacial influence in the Forsmark groundwaters, and the potential effects on the long-term safety functions of a deep geological repository. One major question is if the glacial dilution we calculated in this study was from the last deglaciation period, which was around 10,000 years ago, or if the glacial meltwater was from a previous deglaciation. This would give an insight into the long-term hydrogeological conditions at the site. In future studies, SKB plans on using various dating methods for very old waters, such as ^{36}Cl and ^{81}Kr.

The model proposed in this study works well for the assessment and characterisation of the Swedish deep geological waste repository, though there are a number of requirements in terms of geological, hydrogeological and transport properties needed to fully utilise the models results. The model could most likely be directly applied to other crystalline systems with a similar paleohydrochemical history as Sweden, but also to other groundwater systems, even with a different mineralogy of the host rock, assuming slow moving ground water being in equilibrium with the host rock.

Author Contributions: Conceptualization, L.N., S.P. and M.J.G.; methodology, L.N.; validation, L.N.; writing—original draft preparation, L.N. and S.P.; writing—review and editing, L.N., S.P. and M.J.G.; visualization, L.N. and S.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: A majority of the SKB data is available on https://skb.com/publications/ accessed on 13 January 2024. And is available in public reports which are published contiously as we gather data.

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Conflicts of Interest: Author Lino Nilsson and Simon Pontér were employed by the Swedish Nuclear Fuel and Waste Management Company. The remaining author declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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