

This interesting manuscript follows a relatively large scale experiment in which contaminated water (perchlorate) is pumped, and the shallow subsurface acts as a reactor for the remediation. The presented work include experimental work (some of it already presented, but its extent is not clear from the presentation), and a numerical model using the HYDRUS platform. Overall the manuscript is easy to follow, presents an interesting approach (even if somewhat questionable), and is of value. Most of the conclusions make sense. However, too many aspects need to be improved before the manuscript can be accepted for publication. Primarily, the authors need to convince that their model is reliable - I was not convinced and therefore I could not evaluate the model results and the conclusions drawn by these results

1. While the idea is certainly interesting, one should wonder why use the shallow vadose zone, where it is far from being trivial to control pH and oxygen levels, instead using a controlled reactor and let clean water percolate. After all, the water is pumped anyway. The authors should at the very least discuss their alternative vs. more classic pump & treat approach.

Reply to comment 1: The concept of using soil as a bioreactor is primarily aimed at reducing costs and eliminating the need for large, expensive, and complex reactors. Soil naturally contains the bacteria necessary for the process, and pH levels can be monitored and controlled through the addition of buffer solutions. Oxygen penetration can also be regulated by covering the area with polyethylene sheets. These two factors - pH and oxygen - can be managed in a relatively straightforward way, as opposed to the complexities involved in constructing new bioreactors.

In addition, we revised the introduction with an overview of more classic approaches for perchlorate treatment. (lines 55-65).

2. overall the text is "slopy", especially the introduction and materials and methods - see too many examples below - and should be polished.

Reply to comment 2: The introduction was revised accordingly. See the examples below.

3. acronyms should be defined, even if the authors believe they are common (they are not).

Reply to comment 3: The comment is accepted. All acronyms were defined. See lines 9,16,18,92,122.

4. L19 and on This part of the abstract lacks clarity. 70 days or additional 200 days?

Reply to comment 4: The comment is accepted, and the abstract was revised accordingly. Line 21-22: " **According to modeling simulations, in order to achieve complete removal of contaminants from the groundwater as well, the implementation of the in-situ bioremediation should be continued for an additional 200 days.**"

5. L33 There are so many "conventional methods", that accuracy is needed. The most conventional method is pump and treat, but it is not trivial to call it in-situ method.

Reply to comment 5: The comment is accepted, the sentence was revised. Line 32-33:

" **Among the in-situ treatment approaches, bioremediation is becoming an increasingly popular alternative.**"

6. L45 if the final product is water, the chemical equations should contain hydrogen and its source (and the consequence of its use - pH change) should be discussed.

Reply to comment 6: As mentioned in the text: the process continued and the oxygen is also reduced. This part is not presented in an equation (not relevant). Nevertheless, the consequences of the pH were added, lines 51-53: " **Several factors can affect the pH level, such as the mineralization of ethanol, oxygen reduction, and different competitive electron acceptors. Previous conclusions have shown the acidification process during the treatment (Levakov et al., 2019) which required buffering and frequent monitoring.** "

7. L59 what further treatment? If further treatment is needed, why bother with in-situ remediation?

Reply to comment 7: The full sentences: "For deep unsaturated zone environments, clean water is injected to displace the pollution to the groundwater from inaccessible layers (Evans et al., 2011; L. Liu et al., 2018; Luciano et al., 2013). Subsequently, the groundwater is pumped for further treatment (Guo et al., 2013; Høisæter et al., 2021)."

As mentioned, further treatment refers to common treatment from the literature, aiming to solve deep unsaturated zone contamination. In this method, clean water is flushed through the deep pore water into the groundwater, and then the groundwater is treated ex-situ (pump and treat). The flushing process is necessary in order to extract the contamination from the unsaturated zone.

We try to clarify this point, lines 67-68: " Usually, the subsequent treatment includes ex-situ methods outside the contaminated site (Guo et al., 2013; Høisæter et al., 2021)."

8. L62 by using "the contaminated site" the authors assume that the reader is familiar with the site, which is questionable

Reply to comment 8: the introduction was revised. Lines 62-64

As opposed to those methods, the current research site is characterized by a deep unsaturated cross-section (40m) while the major mass of perchlorate is located in the deep layers (17-36 m) (Dahan et al., 2017; Gal et al., 2009; Levakov et al., 2019).

Next, the research area is well described in the methods chapter. Lines 86-98.

9. L85 the more appropriate term would be variably saturated zone. e.g., it is more than likely that the clay layer (or the soil just above it) gets saturated at least occasionally

Reply to comment 9: the term unsaturated zone is appropriate and acceptable. No evidence for saturation was observed.

10. L119 for how long?

Reply to comment 10: the methods chapter was revised. Line 130: "(up to 10 days)"

11. L129 m³ or m⁻³? not clear

Reply to comment 11: the text was corrected. Line 146: "5 m³ "

12. L129 and elsewhere the term injection is used throughout the manuscript. Is that the right term? my understanding of the system is that it is mostly gravity driven

Reply to comment 12: injection is the right term since the water from the storage tank is being injected using a booster pump (in order to increase the pressure in the drip irrigation system).

13. L140 raise power

Reply to comment 13: we correct the units. Line 155: 0.1 mg l⁻¹

14. L163 is the use of first order reaction, for reaction that (as the authors claim) depends on the lack of oxygen and the availability of oxygen donor, justified? Can the authors show that the oxygen levels, pH and ORP are in the desired ranges. One can speculate that the experiment is simply diluting the contaminants (to be

clear, I do believe that the experiment is performing as planned, but the text does not support it well neither by measurements (many of which unreliable, as the authors indicate, nor by the model that lacks the complexity and the supporting measurements

Reply to comment 14: The comment is accepted and an analysis of oxygen level and pH were added to the supporting information. (see supporting information). Reference in the manuscript: line 367-368: "(pH values in the supporting information-Figure S4)"

Lines 401-402: "Oxygen levels were measured during the experiment using a biogas analyzer. According to the measurements, no evidence for oxygen was observed below a depth of 0.5m during the degradation state."

In addition, a general clarification on the degradation process was added to the discussion in order to clarify the speculation of dilution instead of degradation. Lines 379-383:

Previous laboratory and field experiments dealing with the current contaminated site have proven that the decrease in perchlorate concentrations is attributed to microbial degradation in the soil (Avishai et al., 2017; Levakov et al., 2021, 2019; Itamar Sikron, 2013). Those experiments examined the assumption using measurements of different products along the process, changes in the microbial population abundance and relevant genes, and organic materials mineralization.

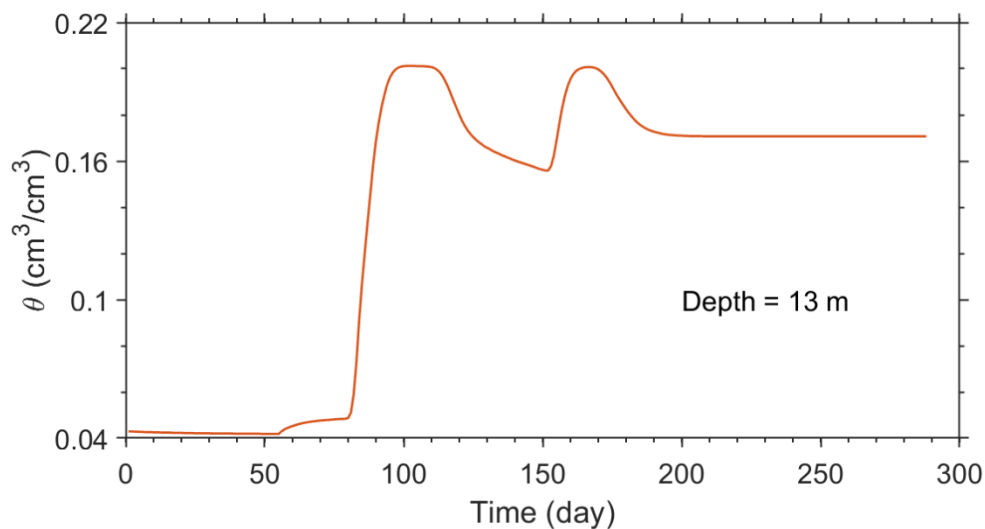
15. L167 a word about model heterogeneity would be in place. The subsurface seem to be highly heterogeneous (Fig. 1) and therefore some heterogeneity, physical (VG parameters, porosity) and chemical (reaction rates) should be considered.

Reply to comment 15: We agree with the reviewer's comment regarding the vertical variability of the lithology. Essentially, the decision of the parameterization of the model domain is according to the sensitivity analysis (which now added to the manuscript; lines 217-234) and the calibration process (which now improved and more organized; lines 235-248). Therefore, the prescribed and optimal VGM and reaction rates parameters are shown in the 'Results and discussion' section (Table 1, 2 and 3).

16. the use of a one-dimensional model should be justified. Clay layers tend to induce lateral flow

Reply to comment 16: no evidence for saturation in the clay layer was observed thus we don't expect lateral flow during the treatment. Moreover, we don't have any information to support a 3D model, and no significant benefit from such a model. Below we provide simulated water content at the at the bottom of layer 3, and close to layer 4 (the clay layer). The saturated water content (θ_s) of layer 3

and layer 4 are 0.37 and 0.38, respectively (Tables 1 and 2 in the manuscript). The simulation results illustrate that only unsaturated conditions prevail during the time of the experiment.



17. L185 why atmospheric BC? there is no runoff, true, but there is also no rainfall and almost no evaporation is the site is covered by plastic, as mentioned above

Reply to comment 17: We agree with the reviewer's comment that using atmospheric boundary conditions (BC) under non-atmospheric conditions might be misleading and wrong. However, these boundary conditions were used for technical reasons, since it is easier to implement fluxes and concentrations (zero or non-zero). The default of Hydrus is to switch between flux and head (i.e., h_{crit} is a value that is predefined). We provided this explanation in the text (lines 203-204).

18. L186 Where is the lower boundary condition? still in the vadose zone or in groundwater (and why so)?

Reply to comment 18: The lower BC at 40 m depth is prescribed as constant head since water table fluctuations are small (lines 204-205)

19. L190 again. those are HYDRUS terms. What are the BCs? For the contaminant, the concentration changes over time - making the BC non-linear and state dependent. How was that taken into account?

Reply to comment 19: For the upper boundary condition, a third-type (Cauchy) boundary was imposed. The main advantage of this BC is that there is a full control over the mass balance and how much solute enters into the transport domain by prescribing the solute flux. In the lower boundary we imposed zero concentration gradient (a second-type boundary condition; Neumann type). We added this information to the text (lines 209-210).

20. L198 trial and error is fine, but still - some 15-20 parameters are involved. Any details about the process and its convergence would be nice

Reply to comment 20: Both reviewers showed concern regarding the application of the trial and error approach for such large parameter space. Therefore we improve our calibration method by first applying a sensitivity analysis to reduce the number of parameters that go through calibration. Subsequently, a calibration method that includes an uncertainty analysis was implemented (lines 214-250).

21. L217 it is really funny to see equations written in formal mathematical notation, and then others that make use of asterisk ... or others that include unit conversion as part of the equation

Reply to comment 21: all the equations were fixed.

22. Fig. 3 clearly the model calibration is problematic beyond 2 m. Is that an issue? The authors mostly bame the measurements, possibly rightfully, but they do not discuss the consequence of a less-calibrated model. Are the model results and the conclusions drawn reliable?

Reply to comment 22: We acknowledge the reviewer's comment and elaborate the discussion concerning the modeling results (lines 307-316). The calibrated water flow and bromide transport succeeded in simulating the first arrival time and peak bromide concentrations for most depths. However, the model simulations display a longer tailing compared to bromide observations. Note that the objective of the modelling approach is to predict the time which requires to operate the treatment method in order to assess accurately the operation requirements. Furthermore, the treatment time scale is expected to extend over number of years (900 days). Thus, the error in decrease of bromide concentrations is acceptable. We added this clarification in lines 525-528:

"It is important to mention that modelling the unsaturated zone can present significant challenges due to the high complexity of the vadose zone and multiple variables that require for the calculation. Nevertheless, the primary objective of the model is predicting the required treatment duration and therefore minor deviations from the ultimate outcome may be acceptable"

23. L263 an alternative explanation may be that the water bypasses this region, that is beneath the clay. Here the question of 1D vs 3D comes to mind

Reply to comment 23: Obviously preferential flow in the unsaturated zone is expected. Nevertheless, the vadose zone monitoring technology that was implemented in this study enables measures water flow and solute transport in multiple points located under independent profiles of the unsaturated zone (practically multiple 1D profiles). Accordingly the Heterogeneity is also expressed through the data. Nevertheless except of the isolated point in depth of 17 m all the other 14 measurement point enabled us to assume that the general

flow direction is vertical and the degree of heterogeneity is "small enough" to enable a 1D model. Moreover we don't have any information to support a 3D model and no significant benefit from such a model (see comment 22 – the aim of the model).

24. Fig. 4 for 17 m the model is really off. For 36 m the model captures the general trend, but not the details. Any reason other than easurements?

Reply to comment 24: Following the implementation of the uncertainty approach, it seems that most of the observed perchlorate observations at 36 m depth fall within the uncertainty boundaries (new figure 5). Therefore, the model captures both the general trend and the perchlorate concentrations. The observed perchlorate concentrations at 17m depth were presented in order to illustrate the challenges in acknowledging the spatial heterogeneity of texture and concentrations in models. Yet we believe that this point is relatively isolated and do not well present the general flow process and transport across this domain. As was flagged by both reviewers, the number of parameters or the parameter space of the suggested 1D model is vary large. The parameterization of a 3D model requires even larger space. Ultimately, the heterogeneity can challenge the in-situ cleaning approach, and therefore both Continuous monitoring and simulating the expected results are necessary for control purposes.

25. location of tables should be re-thought

Reply to comment 25: table #1 was relocated, Line 317.

26. Table 1 quality of the calibration, per layer, would be nice here

Reply to comment 26: We now have implemented a sensitivity analysis and a calibration approach that includes uncertainty estimations (lines 235-250). Note that Table 1 has been modified.

27. Fig. 6 I do not see this figure as being useful by any means

Reply to comment 27: Figure 6 has been removed.

28. Fig 7 horizontal axes is missing

Reply to comment 28: Figure 7 has been revised accordingly.

29. L391 other than nitrate (that is related in a way to the degradation of the main contaminant), the value of the other co-contaminants is not clear. For nitrate, it ill be useful if the authors can show that its degradation is actually related, and not just assumed so

Reply to comment 29: the degradation of all three co-contaminants is important to the rehabilitation of the soil as often Perchlorate is produced and disposed with other explosives. The degradation is shown in figure 8 and discussed in chapter 3.4. for example, nitrate, lines 477-487:

" In addition, denitrification was observed in the reactive shallow soil, which decreased the nitrate concentration to below the detection limit in the upper 1.5 m (**Error! Reference source not found.**). Several perchlorate-reducing bacteria were found to be capable of using nitrate as electron acceptors (Youngblut et al., 2016). The process of denitrification is considered thermodynamically preferable to (per)chlorate reduction (Xu et al., 2003) and, therefore, was observed sooner. Nitrite, as a by-product of the process of denitrification, was not detected throughout the experiment at any depth (data not shown). The increase of chlorate and nitrate at depths of 2.6 to 13 m was due to the initial application of the polluted groundwater when the microbial population was not yet adapted. The initial pollution front that progressed along the unsaturated zone was partially degraded by the developed microbial populations until 13 m, where no evidence of chlorate and nitrate was observed due to biodegradation and dilution. During the rest of the experiment, while applying high concentrations of chlorate and nitrate to the shallow soil layers, continuous bioreduction was responsible for maintaining the low concentrations of the co-contaminants."

Nevertheless, we clarified the point in lines 487-489:

Evidence for conjugated nitrate and perchlorate degradation was observed in different in-situ treatment sites (Evans et al., 2011b; Höhener and Ponsin, 2014; Lorah et al., 2022; Zhao et al., 2022). Moreover, the correlated trends of those two components can also demonstrate the mutual source of the processes.