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Interactive comment on “Modeling the impact of soil aggregate size on selenium immobilization”

by M. F. Kausch and C. E. Pallud

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The Authors thank the referee for her/his insightful comments and for the recommendation to accept the manuscript with minor revisions. Below we have included our response to every specific comment of the referee. The original referee comments are included in *italics* for reference.

1. *p12054, In 8-9: You state that the individual soil aggregates were placed in the center of the reaction cell and then a constant flow rate was applied. Was anything else packed in the cell or was the soil aggregate allowed to move around during the experiment? Based on the larger cell dimensions and the spherical nature of the aggregate, I would imagine that the aggregate would not remain stationary while under flow conditions. Do you think this could affect your modeling results?*

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The aggregates were in fact placed on small stands (hollow plastic cylinders), which supported them in a stable position without inhibiting flow. Once the reactors were sealed the aggregates remained immobile throughout the experiment (which could be visually confirmed, since the reactors were transparent). We added the following words to the manuscript:

“...on hollow plastic stands, which supported them in a stable position without inhibiting flow, . . .”

2. p12054, In 20-22: Is 15min sufficient for sparging oxygen from the input solutions? This seems a little too short.

We agree with the referee that the sparging time used was on the lower end of what is customary. However we'd like to point out that the batch volumes were also low (0.5 L) and that the experimental results showed a large, systematic difference in selenite production, solid phase selenium concentrations, and final bacterial cell densities, between aeration conditions. Furthermore the difference in selenate reduction kinetics of *E. cloaca* was consistent with the response to oxic versus anoxic conditions determined by Losi and Frankenberger (see Appendix A). This agreement would have been unlikely if there had been significant amounts of oxygen present in the experimentally defined "anoxic" conditions. We added a figure showing the fit to Losi and Frankenberger's oxygen response data used in the model to the Supplementary Material. In addition, we conducted a test of our sparging procedure using the redox indicator die resazurin. Three batches of the artificial groundwater medium used for experiments were placed in the same 0.5 L Pyrex bottles we used for flow-through experiments and degassed following the same procedure, but for different times (15, 30, and 60 minutes). Each bottle was moved to the glove bag immediately after sparging (as we did for anoxic input solutions). We observed that all three batches changed color at the same rate and were indistinguishable in color throughout. We thus conclude that 15 minutes of sparging were sufficient to remove oxygen from input solutions. In response to the referees concern, we added the following sentence to the manuscript:

"The efficacy of the chosen sparging procedure and time was ascertained through tests with the redox indicator die resazurin (0.5 mg/L)."

3. p12055, ln4-10: It would have been useful to measure both total Se and selenite in the effluent. Since selenite is an intermediate in the reduction of selenate it's difficult to assess how well the treatment is working. Also, digestion of the aggregate (as you stated) can only give the total fraction of reduced selenium (assuming no absorption of selenate by the aggregate). Although it would not be possible for the current dataset, perhaps application of an X-ray technique such as XPS or XANES would be more useful for determining the oxidation state of Se present in different sections of the aggregate.

We did in fact measure total Se in addition to Se(IV) in the outflow. Differences between input and outflow total Se concentrations were within the analytical error range, which is why we did not report the total Se measurements. We added a sentence to section 2.4 to clarify this, it reads:

"Outflow samples were analyzed for selenite and total selenium, with selenate concentrations compute as the difference between the two measurements. Selenate outflow concentrations did not differ significantly from input concentrations and are thus not reported."

Furthermore, we agree with the referee that digestion is not the ideal method for investigating Se speciation in the solid phase. While planning and conducting the experiments we submitted several proposals for beam time at the ALS to conduct XAS and XANES measurements, but unfortunately these weren't approved. It is the authors' hope that we will be able to conduct such measurements for similar experiments in the future: we are particularly excited about the possibility to investigate aggregate scale gradients in Se species at a finer resolution with micro-XANES.

4. p12056, ln 3: I didn't notice this in the current explanation of the model, but did you account for permeability changes within the aggregate during selenate reduction

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to elemental selenium?

For the purpose of our model we regarded porosity (and permeability) as a constant. While the precipitation of solid phases has the potential to significantly affect permeability under certain circumstances, this is unlikely to have been the case in our systems since Se represented a negligible volume fraction of the solid phase. Selenium accounted for less than 5 $\mu\text{g/g}$ at the conclusion of experiments, which at a solid density of 4.8 kg/L for elemental Se and 1.2kg/L for the bulk aggregate material would correspond to a volume fraction under 1.25E-6. We consequently did not model porosity/permeability changes.

5. p12058, In 1: Regarding the predictive simulations, would it be useful to have experimental data at the endpoints (i.e., at 1cm and 2.5cm) and interpolate between the known data, rather than extrapolating all the simulations from the single 2.5cm diameter size?

The referee is correct in suggesting that experimental results with aggregates of different sizes would serve to strengthen the model results, however we'd like to emphasize that our model is mechanistic and not statistical. The question is whether it captures the relevant biogeochemical and physical mechanisms operating in simulated scenarios, which we believe it does: the reaction kinetics as well as hydrodynamic and transport equations should apply to 1cm aggregates as they do to a 2.5cm aggregates. While it would still be worthwhile to conduct experiments with smaller aggregates, this would not be possible with the current experimental set-up. A 1 cm aggregate would have 6.4

6. p12062, In 9-10: You state that concentrations of reactants (pyruvate, selenate, and oxygen) decreased towards the core. However, movie S3 shows that selenate concentrations increase in the aggregate and reach equilibrium with the reaction cell. Can you explain this? Wouldn't selenate rapidly reduce to selenite and elemental selenium within the aggregate?

It is indeed correct that the concentrations of all reactants decrease with increasing

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distance from the aggregate-free fluid boundary. However, in the case of selenate this spatial concentration decrease is minor compared to the large increase in concentrations over time as selenate diffuses into the aggregate (which contains no selenate at t=0) and saturates it. Overall the intra-aggregate gradient for selenate is very small at equilibrium, due to the high selenate concentrations in the input solution: the simulated selenate concentrations at the aggregate core are only about 10

7. *p12068, In 14-15: Although elemental selenium is not affected by diffusive transport by virtue of being insoluble and immobile, would precipitation of elemental selenium within the pore space of the soil aggregate affect the diffusive flux of selenite? Presumably the permeability would decrease during selenite reduction. Did you model permeability/porosity changes during the experiment?*

We did not model permeability/porosity changes during the experiments as they are negligible. Please refer to the response to comment 4 above.

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