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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 rigorous evaluation of the manuscript and for the recommendation to accept it for publication once comments have been addressed. In response to her/his comments we have made a number of modifications that have improve the quality of the manuscript. Below we have included our response to every specific comment of the referee as well as a description of the proposed changes to the final manuscript (the original referee comments are included in italics for reference).

*1. Based on the model calculations, the differences in Se(0) concentrations between aggregates of different size is caused by differences in diffusive loss of Se(IV). However, the diffusive flux of Se(IV) out of the aggregate is overemphasized in one aggregate systems compared to porous media. In a porous medium with many aggregates,*

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*the concentration gradients are expected to be much shallower because Se(IV) concentrations increase along the convective flow lines in the macropores. In this case, Se retention can be higher in soils with small aggregates, in particular when diffusive supply of electron donor and Se(VI) is limiting Se(VI) reduction rates. Furthermore, the authors should highlight that the obtained trends are only valid when Se(VI) is added in large excess and diffusive flux of Se(VI) into the aggregate is not limiting the overall reduction rates. This also holds for the provision pathway of electron donor. In the experimental study, the electron donor is provided via the inflow solution. In natural environments, the electron donor used for Se(VI) reduction might be generated from the organic matter inside the aggregates. I recommend that the authors revise section 4.3 by paying more attention to the limitations of extrapolating the calculated trends for the one aggregate systems to natural soils.*

We agree with the referee that our single aggregate systems are representative of only certain aspects of a structured soil and do not capture its full complexity. The remark regarding the possibility of increasing Se(VI) concentrations in macropores along the flow path in a natural soil was particularly insightful and we implemented it into our discussion as an example of the additional processes that may impact the aggregate size-selenium reduction relationship on the field scale. Furthermore we followed the referee's recommendation to highlight that the obtained trends are only valid when Se(VI) is added in large excess and diffusive flux of Se(VI) into the aggregate is not limiting the overall reduction rates. Overall, we revised section 4.3 to address the referee's concerns regarding the extrapolation of calculated trends to natural soils by explaining limitations in greater detail and formulating conclusions in a more cautious manner. The following paragraph that has been added to section 4.3 highlights these changes:

“A single, artificial aggregate surrounded by saturated flow cannot capture the full complexity of a structured soil and relevant processes are likely to have been excluded. For example, selenite diffusing from aggregates may build up in macropores along

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the diffusion path, thereby decreasing the concentration gradient at the aggregate-macropore interface and reducing the impact of aggregate size on intra-aggregate selenite concentrations. Furthermore, the trends here discussed were obtained with selenate supplied in excess, while diffusive limitations in selenate supply may reduce selenium reduction in larger aggregates under field conditions. On the other hand, the dynamic saturation conditions in a natural surface soil may serve to increase the impact of aggregate size on selenium reduction through steeper redox gradients, as the macropores surrounding aggregates are expected to be filled with air rather than water part of the time. The advantage of simplified models in studying complex natural systems is that they allow for the isolation of individual processes that may be inextricable in nature. The results here described, point to general reactive transport mechanisms that may lead a soil with a larger mean aggregate size to retain more selenium.”

*2. P 12054 line 6: I assume that selenate and selenite principally can adsorb onto quartz surfaces by a ligand exchange mechanism as onto other metal oxides surfaces although I do not know a study on Se oxyanion adsorption onto quartz. However, I would recommend to modify the statement: Pure quartz sand was chosen as adsorption of selenium oxyanions is negligible under the experimental conditions thus. . .*

The suggested change has been made in the manuscript.

*3. P 12054 line 10: rate instead of rates*

The suggested change has been made in the manuscript.

*4. P 12055 section 2.4: Why did the authors not measure selenate concentrations? Did the authors verified [sic] the selenate concentrations in the inflow solutions? With the given data, the Se mass balance cannot be closed. That is a pity as the mass balance could have been very useful to constrain the parameterization of the model. I presume that Se(VI) concentrations were not measured and / or reported because only a very small fraction of the Se in the inflow was reduced in the reactor. In my opinion, this fact should be explicitly be mentioned in the results. Furthermore it should*

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*be motivated in the method section why Se(VI) concentrations were not monitored.*

Selenate concentrations were in fact monitored, but not reported. The referee is correct in the presumption that only a small fraction of Se(VI) was reduced in the reactor. We measured total Se in addition to Se(IV) in the outflow and Se(VI) was computed as the difference between the two measurements. Difference between input and outflow Se(VI) concentrations were within the analytical error range, which is why we did not report the Se(VI) 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.”

*5. P 12056 line 16 replace ‘cycling’ with ‘consumption or production’ or ‘rates of...’*

The sentence has been modified to remove the word cycling.

*6. P 12057 line 3 I would appreciate if the fitting of the data from Losi and Frankenberger was reported in the supplementary material section. Is it possible to produce figures with the data and the fitted model?*

The figure showing the model fit to Losi and Frankenberger’s data has been added to the supplemental material (see below).

Figure S1. Selenate (red) and selenite (orange) inhibition models (solid lines) fitted to the data collected by Losi and Frankenberger (1997b) for *E. cloacae* reducing selenate (diamonds) and selenite (squares) at various oxygen concentrations. The inhibition of selenate reduction was fitted with a reverse Monod type inhibition term (Van Cappellen and Gaillard, 1996) and that of selenite reduction with an exponential function (see Eqs. A12 A13 in the Appendix of the main manuscript). The R2 of these fits are 0.985 and 0.999 for the inhibition of selenate and selenite reduction respectively.

7. *P 12057 line 15: simply refer to Appendix A. Appendix A is appended to the manuscript and not part of the supplementary material.*

We thank the referee for pointing this out. We now simply refer to Appendix A.

8. *P 12059 line 18: As far as I understand, the same data as presented in Kausch et al. (2012) were used in this study. How is it possible that reduced Se concentrations did not vary significantly between different input solutions in Kausch et al. (2012) but a dependency on pyruvate concentrations was found here. Was the statistical analysis in Kausch et al. (2012) incorrect? Please clarify.*

No, the statistical analysis in Kausch et al. (2012) was correct: the observed differences in reduced solid phase Se concentration between different input solutions are not statistically significant. In the passage the referee is referring to we simply attempted to describe the experimental data set against which model results were being matched. We clarified the passage, which now reads:

“The differences within the oxic and anoxic sets of solid phase concentrations were not statistically significant (Kausch et al., 2012), but are here presented separately for the purpose of showing the fits of individual model scenarios. For example, under oxic conditions the concentrations of reduced solid phase selenium appear systematically higher for pyruvate input concentrations of 1.2 mM as compared to pyruvate input concentrations of 0.3 mM and while this difference in experimental results was not large enough to be statistically significant it was nevertheless reproduced by the simulated results.”

9. *P 12063 line 26: add comma after conditions*

We thank the referee for pointing this out. The comma has been added.

10. *P 12070 line 5: add ‘are’ after conditions*

We thank the referee for pointing this out. It has been corrected.

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11. *P 12073 line 9: change table S1 into table A1*

We thank the referee for pointing this out. It has been corrected.

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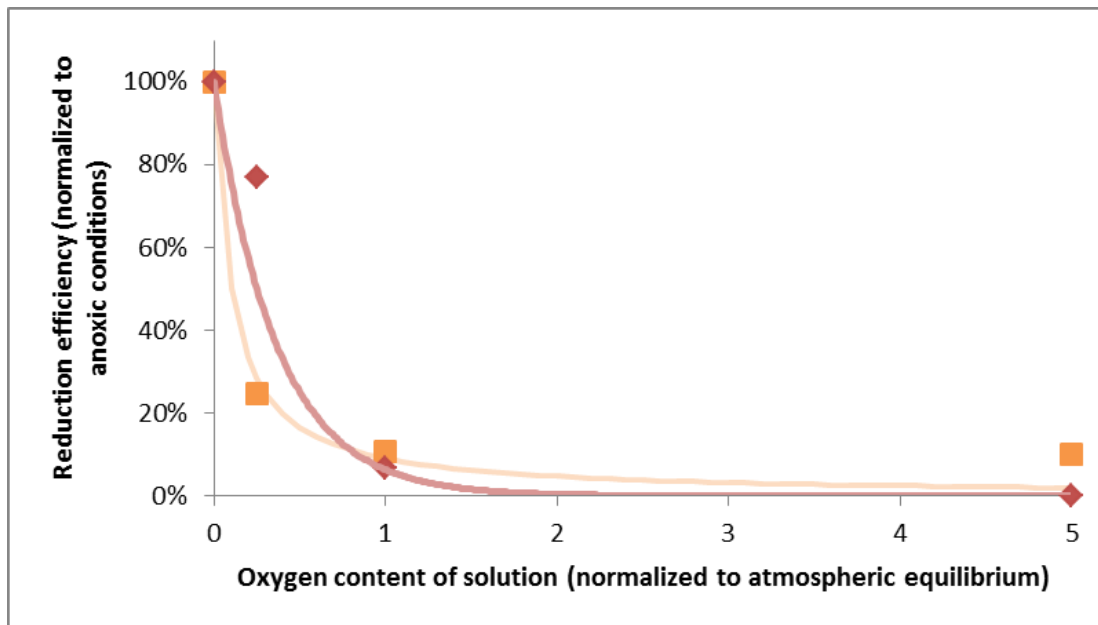


Fig. 1.

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