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Reviewer 1:

This manuscript provides a nice extension of our understanding of Ra sorption to common minerals. As the authors point out a number of times, the very low environmental levels of Ra preclude spectroscopic measurements. It is certainly a weakness of the paper that none of the models are particularly satisfactory or applicable across all mineral types tested. However, the results of this study provide a substantial extension of our understanding of controls on Ra mobility in aquatic systems. I support publication of this manuscript in its current form. Two minor comments are included below.

Lines 91-100. This section states the finding of the study and should be moved to the conclusions or omitted.

[RESPONSE]: Since we already discuss these findings in the conclusion, we will omit these statements.

In Table S1, what do the reported uncertainties represent? Replicate measurements or analytical uncertainty?

[RESPONSE]: We originally discussed the uncertainties reported in 79-84 of the supporting information, however, information about the pH uncertainties was not reported. We have updated that section with the appropriate information.

Reviewer 2:

This paper describes the results of radium adsorption experiment using different mineral matrix and solutions with different salinity in order to quantify radium adsorption equilibrium. The results show differential adsorption capacity of the different solid minerals and decrease of adsorption magnitude with increasing ionic strength/salinity. These results are consistent with previous studies and therefore there are no new breakthrough discoveries presented in this paper. Perhaps the most important contribution of this paper is that it provides systematic characterization of the adsorption capacity of the different minerals and the possible changes of Ra adsorption capacity with diagenetic modification and weathering of minerals. There is nothing wrong with this paper but in order to make it more attractive and relevant to ES&T readers I suggest some modifications that could improve the paper.

First, the paper addresses the changes in adsorption capacity between “brackish” and “seawater” salinities and the role of divalent cations over monovalent cations in completion of adsorption sites; yet there is no quantitative evaluation of the role of the chemistry on Ra adsorption. For example, the authors should include the Ca/Na ratios in the solutions to demonstrate the specific role and the thresholds from which Ca over Na affects Ra adsorption. Since there are no pure Na- or Ca-rich water in nature, quantification of the Ca/Na ratios on Ra adsorption is important for the ability to predict Ra retention to solids. It might require additional experimental work but this would provide a much better assessment of the role of the water chemistry on Ra adsorption, which is the major objective of this study.

[RESPONSE]: We agree that it would be insightful to examine how changing ratios of divalent to monovalent cations would affect Ra sorption to these different minerals, however, for this work, there is insufficient time to complete such a study and submit the revised manuscript. For this manuscript, we will expand the discussion to further probe these competitive effects. For example, when considering Ra sorption to the montmorillonite, we observe much larger decreases in Ra sorption with a mix of cations (artificial groundwater) as compared to a single cation alone, even for one that is anticipated to compete significantly, such as strontium. The use of a SCM was meant to enable these comparisons, however gaps in the data for relevant sorption constants (selectivity coefficients for Sr and K, for example) made it difficult to make any definitive statement. The work here, and the reviewer’s suggestions point clearly at further work that is needed to better constrain Ra transport in the environment, a fact we will highlight in the manuscript.

Second, although the paper has a section on “Implications of radium mobility in soils, sediments and aquifers” – this section needs a major lift. It lacks a systematic literature review that would demonstrate actual cases of Ra occurrence and distribution in soils, sediments, and aquifers. For examples, several studies have shown elevated levels of radium in anoxic aquifers, which contradicts the high surface area and the claim that sulfur minerals like pyrite can adsorb Ra – how the authors reconcile this contradiction? Also the reference to hydraulic fracturing is misleading since hydraulic fracturing water is typically low-saline and Ra is not adsorb during hydraulic fracturing process. In short, there are many case studies that report Ra occurrence and distribution in soils and aquifers, and the authors should relate the results of their experiments to these studies. It is conducted in a very general way in the paper – it should be much more specific with actual case studies data.

[Response]: This is an excellent suggestion. The subject of hydraulic fracturing, for example, is of key importance, as while the injected waters are often very low salinity, the formation waters are typically of higher salinity than sea water, and contain natural amounts of Ra that are elevated with respect to both regulatory standard, and near-surface conditions due to the presence of the relevant parent isotopes in the formation solids. Additionally, the injected waters are typically oxic, while formation brines are anoxic, which will drive mineralogical shifts in Ra sorption upon injection, which in turn will impact Ra concentrations in the produced water and flowback water. We have updated the implications section to further discuss our results in context of environmental studies of Ra in natural aquifers.

The third point is related to the Introduction; the introduction section does not include detailed information on previous adsorption studies that have examined the retention of Ra to different minerals. It is important to specify the results and outcome of these experiments and to show how the new study is different from these previous experimental works. In particular, several studies have demonstrated the role of salinity and exchangeable cations on radium adsorption and thus it’s important to demonstrate how the experimental design of this current paper is different from previous studies.

[Response]: We address the previous work done on Ra sorption, and compare our results in the discussion, see lines 173-178, 185-197, as well as table S3, which compares Kd values found for various studies. To our knowledge, no work has clearly demonstrated the ion-specific impacts of Ra sorption for the ions considered here, nor has any work studied Ra sorption to a reduced mineral. Beck and Cochran’s 2013 manuscript on Ra sorption to marine sands illustrated the impacts of salinity, but did not make any evaluation of the how specific ions would compete. Sajih, et al., 2014 demonstrated competition due to the presence of Ca and Ba, but did not use water systems that mimic natural waters (ie, elevated Ra concentrations, and no competing cations). We have added a survey of the literature in the introduction to broadly outline relevant results others have found to further delineate our rationale for this study, as we found no study compared these minerals while also systematically varying specific geochemical parameters (pH, cation, salinity).

In addition, the authors do not include all possible processes and mechanisms that control Ra occurrence in aquatic systems (e.g., adsorption-desorption, recoil, dissolution, co-precipitation, decay). It is important to emphasis that dissolved Ra in water reflects complex processes, and adsorption is not the only mechanism of Ra retention.

[Response]: To our knowledge, we have included the relevant processes. In lines 40-44 we discuss alpha recoil being the dominant process sourcing Ra from aquifer solids to groundwater, while in lines 62-64, we discuss that how co-precipitation exerts some control on Ra fate, but depends on systems having elevated Ba, Sr, and SO42- concentrations to proceed. We primarily have focused on 226-Ra, whose half-life is long enough that decay is typically negligible, hence why we have not discussed decay. We have updated the manuscript to make the discussion of the various processes clearer, as well as briefly discuss the role of the different Ra isotopes’ decay as a competitor for removal of Ra from solution.

Finally, there is some confusion in the literature review; some of the previous studies address Ra occurrence in saline oil produced waters while other show results from low-saline groundwater in the Middle East. Many of the other studies that show the correlation of with on groundwater salinity are not cited. In short, a better and much wider literature review is needed.

[Response]: The reviewer is correct, we had misinterpreted Vengosh et al.’s paper on Ra in the middle east. Overall, we will expand the literature review with respect to Ra as discussed above.

Finally, some comments on the analytical section; most common Ra measurements in environmental samples are conducted by gamma spectrophotometry. The authors need to provide more information on the scintillation counting method, what nuclides were measured, the precision and detection limit of the method. Is there any a cross-method comparison that can demonstrate the capability of this method?

[INTERNAL Response]: When measuring environmental samples of Ra, it is typical to use gamma or alpha spectroscopy, as it allows for energy discrimination which allows for the determination of different Ra isotopes, often without any pre-concentration or chemical separation, and very low detection limits. However, we use only 226-Ra in our experiments, which was confirmed through gamma spectroscopy of our Ra stock. Therefore, we do not need to make these separations or pre-concentrations, so we directly count the sealed samples mixed with scintillation cocktail containing 226-Ra after the ingrowth of the daughter products. Additionally, liquid scintillation counting allowed us to process samples at a much faster rate than if we had use gamma counting. We have provided a key reference from the literature in the manuscript to support the use of this method, and do not think it is necessary to report the details in the manuscript.1

As for the limit of detection, we have already provided one developed from multiple measurements (N=47) of blank samples and calculated using a standard EPA method (see lines 72-75 in the supporting information). As for the precision, multiple measurements of individual samples were made, and the results of all these measurements averaged (minimum of 3 separate measurements). The standard error of the calibration curve (from an excel linear regression) was larger than the standard deviation of the samples’ measurements. The error of the calibration curve was also generally less than the standard deviation of the triplicates, thus we report the standard deviation of each samples’ triplicate measurement as the error.

Reviewer 3:

Sorry, but I'm still not convinced of the section on surface complexation modeling.

The first paragraph (line 248-258) starts with "good visual fits were achieved...", but I can't find any such plots from which to evaluate this good visual match. In principle, SCM fit quality can visually be evaluated from % adsorbed vs. pH value plots together with the model curves. Fig. 1 provides the data points, but no any model curves (altough denoted "fits" in figure caption) to evaluate visually the good matching.

[Response]: While we state the fits are good, we did not wish to encourage use of this model due to the issues we highlight in line 298. We have provided figures of the visual fits in the supplementary information.

RMSE values for log K prediction is not representative for a SCM fit quality, but for a fixed experimental condition data set (fixed pH, solid/solution ratio, etc.) only.

[Response]: There was not an easy way to represent the impact of differing background solutions on Ra sorption, as compared to the simple fit of solution pH vs % sorbed. Therefore, we use the RMSE of the simulation result vs the corresponding experimental data point to evaluate the goodness of fit. We also plotted the % sorbed found experimentally vs % sorbed determined by the model, which allowed us to identify weaknesses in the model for predicting specific experimental conditions. We initially excluded these figures for the same reason stated for the pH vs % sorbed figures. We will provide examples of those plots in the supporting information, alongside the visually fitted pH vs % sorbed figures.

In the second paragraph (line259-274), the SCM approach is mixed up with ion exchange. Both processes are quite different with respect to clay minerals as can be read in any related textbook. SCM relies on the varying (pH dependent) charging on frayed edge sites, while ion exchange is due to pH independent negative charging in interlayer sites due to cation substitution in the clay lattice. Therefore, the flawed statement "Surface complexation modeling of Ra sorption to montmorillonite was achieved through inclusion of an inter-layer exchange reaction..." by which this paragraph starts, and further discussion thereafter, are highly misleading and definitely not on an EST state-of-the-art level of sorption modeling.

[Response]: The reviewer’s interpretation of the Montmorillonite Ra sorption modeling is correct; the model features both pH dependent surface sites, and pH independent ion-exchange styled sites. The reviewer highlights an important point: the montmorillonite model is not just a surface complexation model, but rather, the 2 site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model previously described.2 We have updated the text to reflect this difference.

We disagree with the reviewer, however, about their judgement on how appropriate the model is for this study. We have very clearly stated, both in review comments, and in the main text, that this model is drawn, as is, from Baeyens and Bradbury’s model of metal sorption to clay minerals first published in 1997. Our reasoning for this is two-fold: first, we wished to obtain a model that would be simple to implement for a larger scale reactive transport model, intentionally limiting the complexity (ie, the number of fitting parameters). Second, because we wished to test the veracity of these models against our different experimental sets, we needed to select a model that had many readily available thermodynamic constants for the sorption of cations other than Ra to the clay surface. Exclusion of those sorption constants for the other cations would result in the model that assumes that background cations would have no effect, clearly contradicting our experimental results. The 2SPNE SC/CE model fits both criteria handily. Additionally, to our knowledge, this model is still considered current, as evidenced by its inclusion in a review of montmorillonite sorption modeling techniques,3 as well as recent studies of metal ion sorption to illite, another 2:1 layer clay.4 We share the reviewer’s frustration with this model, and with the other minerals’ models, in that they are not able to reproduce the sorption behavior over all of the experimental conditions we have studied, but this highlights a major point made in our paper: fitting any one of these mineral specific models to experimental data does not guarantee the prediction of other data.

(1) Jia, G.; Jia, J. Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology. *J. Environ. Radioact.* **2012**, *106*, 98–119 DOI: 10.1016/j.jenvrad.2011.12.003.

(2) Bradbury, M. H.; Baeyens, B. A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part II: modelling. *J. Contam. Hydrol.* **1997**, *27* (3–4), 223–248 DOI: 10.1016/S0169-7722(97)00007-7.

(3) Tournassat, C.; Grangeon, S.; Leroy, P.; Giffaut, E. Modeling specific ph dependent sorption of divalent metals on montmorillonite surfaces. a review of pitfalls, recent achievements and current challenges. *Am. J. Sci.* **2013**, *313* (5), 395–451 DOI: 10.2475/05.2013.01.

(4) Marques Fernandes, M.; Vér, N.; Baeyens, B. Predicting the uptake of Cs, Co, Ni, Eu, Th and U on argillaceous rocks using sorption models for illite. *Appl. Geochemistry* **2015**, *59*, 189–199 DOI: 10.1016/j.apgeochem.2015.05.006.