**Reviewer Comments to Author:**

**Reviewer 1:**

**Reviewer Summary:** This is a nice manuscript detailing some experimental work to model Ra sorption to several common minerals. The manuscript is well-written, clear, and succinct. Overall, I recommend publication in essentially its current form. A few specific comments are below that the authors might consider.  
  
**Reviewer comment:** Line 106 and elsewhere. Suggest using “anoxic” instead of “anaerobic”.

**Response:** This is an appropriate substitution to make in the manuscript, since no microbes are used.

**Reviewer comment:** It’s interesting that pyrite showed higher sorption per unit surface area. Given the method of preparation (crushing), it’s likely that the experimental conditions resulted in far lower surface area than would result from authigenic formation in natural systems. It might be worth mentioning that all else being equal, sorption to sulfide vs. oxide minerals could result in pulses of Ra mobilization/sequestration during changes in aquifer redox conditions.

**Response:** Measurements of natural pyrite surfaces suggest higher surface area than found here (~1 m2/g as reported by Naveau et al., 2007).1 We agree that in natural systems that experience shifts in redox condition, there is potential for differential sorption that could drive pulses of Ra release. However, shifts in redox typically are also accompanied with shifts in solution geochemistry, which will make it difficult to anticipate Ra fate without knowledge of the specific shifts in solution geochemistry, as our work also demonstrates changes in common geochemical parameters (pH, major cations, etc.) will also impact sorption.

**Reviewer comment:** Line 244. Competitive sorption, see also: Koulouris, G., 1996. Sorption and distribution of 226Ra in an electrolytic manganese dioxide column in the presence of other ions. J. Radioanal. Nucl. Chem. Lett. 212 (2), 131–141.

**Response:** Based on this comment, and other comments from other reviewers, we’ve performed additional experimental work that quantifies the impact of different competing cations and ionic strength on the Ra sorption initially presented in this work. We find, as Koulouris did, that there are significant competitive effects between differing cations, though the particular mineral affected the amount of competition observed.

**Reviewer: 2**

**Reviewer summary:** This study attempts to evaluate the retention of radium to different mineral phases using experimental adsorption tests of reacting synthetic water (NaCl 10 mM ) with known amounts of Ra solution and different minerals under constant liquid: mineral ratios. The results of these adsorption simulations show Ra uptake to the different minerals phases, including ferrihydrite, goethite, pyrite and sodium-saturated montmorillonite. In addition to the experiments, surface complexation modeling was conducted to evaluate the mechanism of the Ra uptake.

Although this is an important study that can provide some understanding on the fate of radium in aquatic systems and interaction with minerals, there are several fundamental issues that need to be resolved before accepting this paper for publication in EST. I therefore recommend a major revision.  
  
**Reviewer comment:** The first critical issue is the quality of data as are presented in Figure 1. The experiments were based in some cases on 2 data points, and in others on 3 data points from which regression lines of sorption isotherms and thus the Kd values were obtained.  This obviously raises a question on the validity of these experiments. The authors need to show for a least one experiment that the sorption isotherms values are statistically valid when extrapolation to only 2-data points regression.

**Response:** The reviewer raises a valid concern regarding the validity of our fits. We have added additional experimental points to improve the available data for fitting, such that there are at least 3 points for each isotherm, as well as provided the standard error of regression associated with the fitted Kd values.

**Reviewer comment:** The authors show that the Kd values obtained in their experiments are NOT consistent with values reported in previous studies and try to suggest different explanations. Yet there is no testing of the validity of the experimental results. The quality of Figure 1 surely does not help in evaluating this.

**Response:** We see a mix of agreement and disagreement between the results found here and results for isotherms previously published in the literature. Except for the case of sodium montmorillonite, we see roughly similar values as compared to previous work, if experimental conditions are roughly similar. For the montmorillonite it is not clear to us why there would be a difference, given the similarities in the experiments (which also includes the radium activity used). Given the linearity of the extended isotherms, we are confident in our experimental results, with the only possible explanation deriving from the specific clay used (STx-1 here, vs SWy-2).2 This suggests to us then that the bulk parameters (Kd) measured here may not be sufficient to elucidate Ra sorption behavior in natural environments.

**Reviewer comment:** The second issue is the experimental design. In the experiments, 10 mM NaCl solution for the aqueous medium of the adsorption experiments.  The problem is that such water does not exist in nature and the lack of other competing cations in the solution makes the Ra adsorption experiment disconnected from actual conditions in aquifer systems. Yes, the objective of this study was to show if there is any Ra adsorption but that has been done before for all minerals except for pyrite, which is really the first time.  So there is not much novelty here. A better experimental design could address the water chemistry and the role of competing cations on the Ra adsorption on and/or exchange with the different minerals. I strongly suggest to conduct such experiments to increase the importance of this paper. The third point is that the paper does not provide any in-depth evaluation of the implications of the experimental adsorption results to actual aquifer conditions. In Line 269 the authors state “Radium adsorbed extensively to every mineral examined, albeit maximum adsorption varied”. This statement is incorrect.  The data show large differential adsorption to the different mineral phases at typical groundwater pH range (5-8) in which sodium-saturated montmorillonite adsorption is several orders of magnitude higher than the adsorption on to the other minerals phases (maybe ferrihydrite has also higher Kd values at that pH range).

**Response:** The reviewer raises excellent points here. While we originally used 10 mM NaCl to provide an experimental medium to make comparisons to other experimental work (which typically used NaClO4 or NaCl as here) and reduce competitive effects due to cations present in solution, it is necessary to expand the geochemical conditions under examination to make comments on Ra transport in natural systems. To that end, we have expanded the experimental dataset to include experiments that address the role of a mixed cation solution at differing ionic strengths, representing typical groundwater, seawater, and mixed brackish water, as well as experiments using 10 mM of different cations (K, Ca, Mg, Sr). This is provided a wealth of new insights, which are a major focus of the updated manuscript. We clearly see differential sorption to these different minerals, and have updated statements to reflect this, as well as incorporate the significant impacts of competing cations.

**Reviewer comment:** The section “Implications for radium mobility in soils and aquifers” needs therefore to be revised and providing a rigorous and in-depth analysis of the differential update of Ra into the different mineral phases. It looks like that montmorillonite would have the highest Ra adsorption capacity relative to the other minerals and yet a systematic modeling of this differential uptake is not provided in this paper. I suggest to the authors to provide a detailed modeling of the differential Ra uptake and taking into account also the possible ambient conditions (pH, redox state), water chemistry and the competing cations that could affect the Kd values obtained in the solute-less (only Na) experiments. Without this the paper is not really relevant and suitable for EST level.

**Response:** We have also incorporated the experimental work in modeling efforts, as is reflected by the SCM section in the updated manuscript, which we also discuss in the updated section “Implications for Ra mobility in soils and aquifers.” While we think it would have been instructive to model the effects of multiple mineral phases in a single experiment, we elected not to because the models we used could not accurately predict the impact of the different geochemical conditions we considered. While good fits could typically be made to account for the impact of pH or the impact of different cations, the two could not converge on a similar result to describe Ra binding these mineral surfaces, especially for the montmorillonite. Additionally, a very careful experimental design would be needed to test any model that examines competition between mineral phases, as our methodology here does not allow for discrimination between Ra sorption to one mineral phase vs another. We also hesitated to include more “complex” models in this updated manuscript, as we did not have spectroscopic measurements of Ra surface complexes to support their usage. These limitations are discussed in the updated manuscript.  
  
    In addition there are several other issues that need to be corrected:  
**Reviewer Comment:**  Line 28: should be Rn (not Rd)

**Response:** We have fixed the typo.

**Reviewer comment:** Line 52: Ra is NOT a conservative element in any aquifer systems. Only at high salinity and high levels of cations, Ra may not be retained by the solid phase.

**Response:** We certainly agree that Ra is certainly not a conservative element in aquifer systems, however, established methods that leverage Ra as a tracer do not necessarily make considerations for this non-conservative transport, an idea we wished to highlight in the introduction as false. We have clarified the updated manuscript to prevent this confusion.

**Reviewer comment:** Line 157: I thought the ionic strength of the experiments was constant, how come it varies?

**Response:** The wording here was meant to indicate that there are differences between the ionic strength of our experiments and those performed by others, which may be a driver for the observed sorption differences. We have clarified the wording here.

**Reviewer comment:** Line 178-181: Pyrite may has the largest sorption of all of the minerals considered as normalized to surface area but the absolute adsorption as shown in Fig. 1 is very low compared to montmorillonite. This should be discussed and explained.

**Response:** While the total amount of radium sorbed to pyrite is minimal compared to montmorillonite, the amount of radium that is sorbed per unit surface area is very large because of how small the measured surface area of pyrite was. This is also evident when examining table S1 in the original manuscript, where you can simply divide the fitted Kd by the measured surface area to find the Ksa reported. We discuss this, but in the absence of more detailed studies of Ra surface complexes with any of the mineral surfaces considered here, it is difficult to explain these differences without further experimental study.

**Reviewer comment:** Line 203: For readers outside the field, the authors should explain what is “tetradentate reactions” relative to "simple adsorption" model.

**Response:**  We have reworked the surface complexation modeling in response to comments by another reviewer, as the tetradentate models we drew from the literature have notable flaws, and were not easily extended to account for sorption of competing ions. Thus, the discussion of “tetradentate” vs “simple” models has been removed.

**Reviewer: 3**  
  
   **Reviewer Summary:** The paper by Chen and Kocar on “radium sorption to iron (hydr)oxide, pyrite, and montmorillonite” reports on an evaluation of capacity and sorption processes for a radionuclide important in underground repository, hydrofracking, as well as deep geothermal resources formation water management. This paper addresses therefore an important topic, and is clearly an actual issue of intense debate and appropriate subject matter for this journal. However, most results and conclusions are not based on a thorough understanding and state-of-the-art approaches in that research field. Therefore, I cannot help but to recommend rejection of the paper.  
  
**Reviewer comment:**  Line 56 “rather than precipitation (or co-precipitation)”: It is well known that dissolved radium concentrations are strongly affected by co-precipitation with barium and strontium sulphate minerals, c.f. (e.g.) the textbook on aqueous environmental geochemistry by Langmuir. There are numerous papers reporting on solid-solution aqueous-solution equilibrium modeling of this process immobilizing the Ra in underground repositories. The authors must show by an exemplary equilibrium modeling scenario or other Arguments, that this process is less important than adsorption to Fe hydroxides or pyrite.

**Response:** The reviewer raises a valid concern, as barite and celestine have readily been demonstrated to scavenge radium from solution (see Zhang et al., 2014, Co-precipitation of radium with barium and strontium sulfate and its impact on the fate of radium during treatment of produced water from unconventional gas extraction), which we acknowledge is not made clear in the original manuscript. However, outside of highly saline waters or engineered systems, there are not sufficient concentrations of barium, strontium, and sulfate to support the precipitation of these minerals (log Ksp = -6.64, -9.99 from the Zhang et al., 2014) in the long term for natural groundwater systems. Additionally, the precipitation of these mineral phases is rapid on the time scale of groundwater flow and do not completely sequester Ra. Thus, even if co-precipitation does occur, as may happen during hydraulic fracturing, Ra will remain available to sorb to mineral surfaces, and can be released into solution.

**Reviewer comment:** Line 215 „simplified reactions (table S3)“: First of all, Ra is dissolved as a cation which means that minimum one proton is released during adsorption reaction, otherwise you wouldn’t get the usual cation behavior of no sorption in the acidic pH range, and full sorption in the alkaline pH range, with an adsorption edge somewhere at circumneutral conditions (line 88-89). A simplified reaction must then read: FhyOH + Ra = FhyORa + H, or GoeOH + Ra = GoeORa + H, or ClayOH + Ra = ClayORa + H. All respective adsorption reactions in Table S3 are not simplified, but simply wrong from a complexation chemistry base point of view.

**Response:** We agree with the reviewer’s valuation of the models presented in the original manuscript. For the iron oxides, we have reviewed the original work detailing the “tetradentate” model originally used, and have dropped it in favor of the Dzombak and Morel model for ferrihydrite, and the Mathur and Dzombak single site model for goethite.3,4 For montmorillonite, we restored the original reactions fit by Baeyens and Bradbury’s original paper, but note that the fits are poor, and also do not compare favorably when examining the impact of competing cations. Ultimately, we find that these models do not possess sufficient predictive power for Ra sorption to mineral surfaces.

**Reviewer comment:** Line 235 „The number of fitted sites in this model were significantly lower than reported in the literature“: Well, it is a matter of arbitrary choice whether to fit the data by an enhanced number of strong sites or by an enhanced number of sorbent molecules in the stoichiometry.

**Response:** The reviewer highlights a major weakness of any surface complexation model, namely, that there are many parameters that can be fit, which include surface area and number of surface sites. Since we have adjusted the type of models used, we also took this opportunity to use the same number of sites that were used in the original models referenced, thereby reducing the number of fittable parameters. As has been stated though, the arbitrary nature of these models helps explain why they lack predictive power when modeling Ra sorption over the range of conditions examined in the updated manuscript. We note however, that these models are often used to make predictions in natural environments, and find the exercise of rigorously proving them against experimental data instructive in their limitations.

**Reviewer comment:** Actually, the „tertradentate“ equation 4=FhyOH + Ra = (FhyOH)3FhyORa + H (Table 1) is conceptually equal with the respective equation mentioned above, except that three inactive FhyOH moeities are added. This is neither a tetradentate nor a tetranuclear surface complexation formulation. Even more flawed is a stoichiometric formulation like 4=FhyOH + Ra + 2H = (FhyOH2)2(FhyOH)2Ra, which would mean to reverse the adsorption behavior of an cation in such one of an anion. From a purely fitting point of view, all these reaction equations might have provided good fitting results by trial and error (vs, by chance), but from a chemical surface complexation point of view, they are all nonsense. I guess it is a wise policy by ES&T to accept adsorption modeling papers only if supported by spectroscopic data to avoid such arbitrary modeling results.

**Response:** We would like to highlight that we used the exact formulation that Sajih et al. used in a previously published work, as it allowed us to compare directly with their fitted results in a manner that is supposed to be more nuanced than simple partition coefficients and try to explain differences between those differences.3 However, we also agree that the conceptual errors in the model make it unsuitable, which was one of the major driving factors for using the Dzombak and Morel model, as we discussed both in the comments here and in the updated supporting information. We wholeheartedly agree with the reviewer that much of SCM can be arbitrary and lack predictive power as we discuss above and in the main revised text. However, it is not enough to only consider the sorption using averaged approaches such as Kd. We wished to test to see if these published models of Ra surface complexes had sufficient predictive power for the experimental system we have considered. Unfortunately, it seems to not be the case here.

As for the comments on not including spectroscopic evidence, natural radium concentrations are too dilute to enable spectroscopic measurements of radium binding to these surfaces, as clearly stated in line 194 of the original manuscript. Additionally, there is a significant radiological hazard associated with using concentrations of radium that would be detectable using x-ray spectroscopy, which have historically precluded it from analysis. It is also unclear if spectroscopic measurements at elevated Ra concentrations would necessarily match the sorption mechanisms at play in our study here. These combined difficulties precluded taking such measurements.

It is clear from this particular reviewer’s comments that our overarching purpose in this work was not well understood. To make clear our intentions for using surface complexation modeling, we have updated the manuscript in a few ways: 1) We expand the experimental work performed as recommended by the other reviewers and 2) Use our expanded experimental data set to test well established surface complexation models for predictive capabilities for varying geochemical conditions, and 3) Make clear our objectives with SCM at the start of the manuscript  
  
**Reviewer comment:** Line 257 „The fitted reaction constant is also the lowest of all“: It becomes not clear why the authors used a 1-pK model for pyrite, but changed arbitrarily to a 2-pK model for the other adsorbents.

**Response:** The change here was not arbitrary. As clearly discussed in lines 254-255 of the original manuscript, this model of pyrite SCM is based on the only available SCM of the pyrite, which demonstrated through potentiometric titration that an unoxidized pyrite surface functionally has a single pK, with the second acidity coefficient being too strong to determine through potentiometric titration.5 In the original text, we were able to obtain reasonable fits to pyrite data by significantly changing the available surface sites of this previously published model. We have purposefully chosen to not alter those surface sites concentrations in this revised manuscript, but that model cannot fit the experimental data collected here. Therefore, we do not report the use of any pyrite SCM, as it defeats our stated purpose of using our experimental data to validate a few established SCMs of the minerals studied.  
  
**Reviewer comment:**  Line 78: Na-montmorillonite

**Response:** A typo.

**Reviewer comment:** Line 110 “kinetic study of Ra adsorption to montmorillonite”: these data should be depicted in the Supporting Information. Usually, exchange reactions are not as fast as pure adsorption reactions on outer surfaces. It becomes not clear how the authors differentiate between both in their kinetics study.  
 **Response:** We have included the requested figure in the supporting information. The large amount of sorption at low pH suggest that protonated surface sites cannot be the only factor contributing to sorption of Ra to the montmorillonite.

**Reviewer comment:** Line 32 “bicarbonate solution”: no ternary Ra-carbonate surface complexation has been considered.

**Response:** The mineral in question, goethite, was synthesized using a bicarbonate solution, but then washed multiple times to remove excess ions on the surface. It is well established, however, that strong carbonate complexes form when synthesizing goethite through our selected method.6 That said, it is also well established that radium only weakly complexes with carbonate ions, and there is minimal data on the formation of Ra-Carbonate surface complexes in the literature. Because we do not have spectroscopic measurements of the system, we will not presume to include a Ra-carbonate complex unless there is support for such a surface complex in the literature. We have also included competition from carbonate complexes in models of sorption specifically to goethite.

**Reviewer comment:** Table S1 “50.162”: I doubt that precision and accuracy of your BET measurement is as high. Please give numbers with +/- precision.

**Response:** The lab which performed our analysis did not provide us with a +/- precision, and we originally provided the reported numbers as is. We have updated those values’ accuracy to match the masses used.