**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”.

**[Internal] Response:** This is an appropriate substitution to make in the manuscript. We may also consider the use of “sub-oxic” phrasing, as we can cannot definitively prove that there is no oxygen at all, only <1 ppm.  
  
**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.

**[Internal] Response:** Measurements of natural pyrites and iron sulfides typically still show very low surface area (CITATION), but we agree that it is possible that naturally formed pyrites, particularly in systems that see cycles of redox (ie estuarine systems) may have iron sulfide mineralogy that has larger surface areas than are depicted here, thus resulting in enhanced sorption due to higher surface site availability. Another reviewer comments on wanting us to expand the environmental implications of this work (ie through examining further the differential sorption). We could address this comment there, discussing the potential impact this differential sorption would have.  
  
**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.

**[Internal] Response:** I read through some of this paper, where the author examines competitive sorption to MnOxides by Ra2+ by Fe(III) and Ba2+. Ultimately, I think the broad consensus is that radium will competitively sorb compared to other ions, but I think we should clarify in the manuscript that based on the posed surface complexation models, it is not clear which ions will dominate in a natural system. This is particularly important for clay minerals where multiple types of sites (ie exchange vs surface) are involved.

Aside: While an interesting paper, I’m not entirely confident in their methodology with iron, since they work at high pHs that should drive the precipitation of iron solids (I will note that they believe they work with low enough concentrations that this doesn’t happen)

I think this comment is mostly a suggestion as to what other works to look at, and I think we can include some additional references to address it.

I’ve been talking with Neha about her competitive sorption type work, which has been showing some… unexpected results, but this may not be the venue in which to publish those.

**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.

**[Internal] Response:** The reviewer poses a valid critique here; some of our regressions only have 3 data points, which brings into question how valid these fits are. This is primarily driven by detection limit issues in the experiments, which result in fewer reported data points. It is important to note that no isotherm fit has only 2 data points, we are not making the extrapolations the reviewer suggests. I propose a few means to fix this misunderstanding: **1) We improve the clarity of the figures such that it is obvious how many data points inform the fit line. 2) We additionally publish the standard error of the regression for each of the Kd values in the supplementary information, which will also enable comparisons between the different isotherms.** This is a simple, clear measure that can help us understand the validity of the numbers we publish, and will also allow us more rigorous comparison of our Kd values, while not attempting to use statistical measures that may or may not be appropriate. **3) Due to our issues with our control experiments, we will be rerunning the isotherms anyway in plastic bottles, which presents us with an opportunity to “expand” our isotherms such that each one has at least 4 data points.**

**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.

**[Internal] Response: The results of the re-run isotherms will inform whether or not our discrepancies are true or not.** If they still persist, I think that the expansion of our dataset outlined above (inclusion of error, clarification of figures) will help us assert our validity, given that these experiments are run in triplicate. When discrepancies arise between our measurements and others’, there is always a significant difference in solution chemistry and experimental setup (solid solution ratio for example); this highlights why we discuss the limitations of Kd as a means of comparing experimental results. Further, when our solution conditions are similar to others (ie with the Sajih work) we find similar results which I think reinforces the validity of this work.  
  
**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.

**[Internal] Response:** The reviewer raises a valid concern: very few natural systems are composed of only one cation/anion pair, instead containing a multitude of different cations and anions. We chose this system for two reasons: we wanted to be able to make direct comparison between sorption to different minerals with very close geochemical condition, and we also wanted to be able to compare to the work previously done using these minerals given the limitations of using Kd (see line 162 in the original manuscript). **We accept however, that additional work needs to be done to make the work more relevant to natural systems. We propose a comparable experiment, using an artificial groundwater consisting of a subsampling multiple cations found commonly in the groundwater, but with the same total ionic strength, at a single, environmentally relevant pH. We wish to avoid using a “location specific” composition, rather we wish to address the role variable cation composition has on the sorption process vs a single cation.**

**Reviewer comment:** 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).

**[Internal] Response:** The reviewer raises, correctly, that there are issues with the statement in line 269**. We first will need to re-run the isotherms before addressing these comments, as the results may alter these statements.**

**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.

**[Internal] Response: We accept the reviewer’s suggestion for additional modeling looking at competitive sorption between multiple phases.** Given though that our models are not rigorously based on spectroscopic data of Radium specific sorption to these surfaces, however, we should be careful not to over-state the accuracy of the models. Additionally, we may consider the addition of a subset of experimental work (maximum 10 bottles) that uses a combination of minerals (for example, Na Montmorillonite and FHY) to assess the combined effect multiple mineral phases would have in the same pore space and confirm the modeling result. The combination of the additional modeling and a mineral competition study enable the discussion the author requests.  
  
    In addition there are several other issues that need to be corrected:  
**Reviewer Comment:**  Line 28: should be Rn (not Rd)

**[Internal] Response:** A typo on our part.

**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.

**[Internal] Response:** We agree with the reviewer that Ra is not a conservative element in aquifer systems, however this fact has only recently become apparent in the literature, particularly in the fields studying submarine groundwater discharge (see Moore, 2010, The Effect of Submarine Groundwater Discharge on the Ocean). Additionally, some very recent methods using Radium isotopes to trace contamination related to oil and gas extraction do not consider this differential sorption, essentially assuming that Radium is not readily desorbed from contaminated soils (see Lauer and Vengosh, 2016, Age dating oil and gas wastewater spills using radium isotopes and their decay products in impacted soil and sediment). We wished to highlight that this type of thinking still persists, in spite of the clear evidence both here, and in the literature more broadly, that environmental radium transport is rarely conservative. **We will update the statement to better illustrate this.**

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

**[Internal] Response:** The experiments presented in the original manuscript do not have variable ionic strength. The statement is intended to mean that the ionic strength and mineral surface area of our experiment differs from other studies in the literature using the same mineral, which may explain some of the discrepancies in our measured Kd values for goethite. See Table S2 for specific solution conditions. **We will clarify 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.

**[Internal] Response: We will clarify this.** 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.

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

**[Internal] Response:**  We discuss this difference in more detail in the originally submitted supporting information (line 80-86). **However, we will properly define “tetradentate” reactions in the main text for clarification.**

**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.

**[Internal] 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 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), where typical barium and strontium concentrations are in the uM to nM range CITATION AND NUMBER NEEDED, ALSO FOR SULFATE. Additionally, the precipitation of these mineral phases is rapid on the time scale of groundwater flow (CITATION NEEDED), thus while they do play a role in constraining the concentration of radium in natural groundwaters, they are not wholly dominant as the reviewer seems to suggest. **We will update the manuscript with this information to avoid confusion, co-precipitation is certainly important in high salinity systems, such as those tapped for natural gas extraction, but are less important for groundwater systems.**  
  
**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.

**[Internal] Response:** We explicitly state in lines 83-85 of the original supporting information of the manuscript that these simplified reactions do not attempt to accurately represent actual surface complexation chemistry. We use them in this work because they allow us to compare our modeling results with the modeling results using the exact same system of equations used by others in the literature (See Sajih, 2014, Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study, supporting information). It is worth noting that this is a major driver for most of the decisions regarding what formulations we use for our surface complexation models. Secondly, reviewer suggests that we would not observe the pH dependent behavior observed in the experiments using the system of reactions posed in table S3 of the original manuscript. The simulation results (not included) clearly show the pH dependent behavior, which is a result of changing site availability**. That said, the reviewer correctly states that this reaction is fundamentally flawed from a surface complexation point of view, thus we will update this simplified model using correctly formulated models.**   
  
**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.

**[Internal] Response:** The section this line is pulled from discusses the surface complexation modeling results for clay minerals, which did not feature the tetradentate model formulation the reviewer takes issue with below featuring an “enhanced number of sorbent molecules.” The number of sorbent molecules in the stoichiometry for clays clearly matches that of those used by others (see for example, Bradbury and Baeyens, 2004, Modelling the sorption of Mn (II), Co (II), Ni (II), Zn (II), Cd (II), Eu (III), Am (III), Sn (IV), Th (IV), Np (V) and U (VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides), where one site binds a single sorbate molecule. Therefore, that the number of fitted sites is lower than those found in other work suggests at some differences in the geochemistry of radium with respect to the montmorillonite surface compared to the chemistries discussed in this referenced, and other, works.

We acknowledge that the reviewer is highlighting a major weakness of surface complexation modeling; that without any kind of spectroscopic evidence, there is limited utility in a model that correctly fits an experimental data set. This underscores the fact that we use these models not as a mechanistic statement on radium sorption, but rather a more geochemically enlightened means by which we can compare our experimental results to those of others, especially when experimental conditions differ. Additionally, we highlight this weakness in surface complexation modeling in lines 220-225 of the original manuscript, referring to a recent editorial (Duster, 2016, An integrated approach to standard methods, materials, and databases for the measurements used to develop surface complexation models.) **We will make explicit in the text of the paper what our aims are and are not in the use of these surface complexation models to avoid this confusion.**

**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.

**[Internal] Response:** The reviewer’s comment here is false. The presence of these so called “inactive” moieties is a reflection of the fact that multiple sites are occupied with the coordination of radium with the surface, making it fundamentally different from a reaction in which a single site is involved.As the reviewer stated previously, one could argue that the use of this formulation is simply a means by which to artificially inflate the fitted number of sites. We again reiterate here that because we wish to use these models to compare against other groups’ work, we choose to match the surface complexation model formulations posed previously by those other groups, rather than attempt to formulate our own model without direct spectroscopic evidence.

**Reviewer comment:** 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.

**[Internal] Response:** We originally use the same reaction formulations for ferrihydrite and goethite that are used by another study (Sajih et al., 2014). Since our primary goal was to enable comparisons between the relevant surface complexation constants. We agree that the behavior described, in particular, by this equation, does not match general understanding of ion sorption to surfaces, thus **we propose to examine alternative model formulations (still based in the literature) that are more sound from a surface complexation standpoint.**

**Reviewer comment:** 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.

**[Internal] Response:** We wholeheartedly agree with the reviewer that much of SCM can be arbitrary as we discussed earlier (see Duster, 2016 referred to above). However, it is not enough to only consider the sorption using averaged approaches such as Kd. Some attempt at representing the chemical system must be made, hence the usage of these potentially flawed surface complexation models. As to the issue with spectroscopic data, Line 194 of the original manuscript clearly highlights the reason that such spectroscopic data is not available, followed by a discussion of where we choose to draw our surface complexation modeling formulations from. We must re-emphasize that we choose these modeling formulations not because we believe that they are true to life representations of surface geochemistry, but because, in spite of their weaknesses, they are able to provide additional insight into actual surface behaviors beyond a Kd value. (e.g. that montmorillonite modeling did not work without the inclusion of an exchange reaction).

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. Additionally, there is a significant radiological hazard associated with using concentrations of radium that would be detectable using x-ray spectroscopy**. We will more explicitly indicate throughout the SCM discussion that the purpose of this modeling is not make statements on the actual coordination of radium with these surfaces.** Instead, the purpose is to use literature published models to make more enlightened comparisons between the minerals and conditions studied here, as well as make comparisons to other sorption work using radium. These models are grounded in a combination of spectroscopic study of similar elements, so we expect that they will likely be more accurate as compared to a naïve model (=SOH+Ra = =SORa +H+).

I can understand, however, the reviewer’s confusion as to the purpose of this paper, which does include a significant component discussion surface complexation modeling as means to compare the results of our experimental work. To this end, **I propose the inclusion of additional experimental work, particularly using competing cations, which can then be included as we rework the surface complexation modeling as described above.** This will give us some sense on how robust these models are with respect to changing solution conditions, as well as give us the opportunity to highlight some of the weaknesses that these models possess (or lack if they are robust).  
  
**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.

**[Internal] Response:** **This change is not arbitrary.** As clearly discussed in lines 254-255, 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 (Naveau et al., 2005, Sorption of Sr(II) and Eu(III) onto pyrite under different redox potential conditions). We therefore expect that the second acidity constant will not be relevant under the conditions we’ve studied.  
  
**Reviewer comment:**  Line 78: Na-montmorillonite

**[Internal] 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.  
 **[Internal] Response: We will provide the results of this kinetic study (which will need to be rerun because it was in glass).**  This study found that for a 24 hour period, total sorption of Radium was very stable. We would expect that if there were slow exchange, this would be observable by changing rates of radium sorption.

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

**[Internal] Response:** The mineral in question, goethite, was synthesized using a bicarbonate solution, but then washed multiple times to remove excess ions on the surface. However, we recognize that bicarbonate is in the experimental systems generally by exposure to atmospheric CO2. It is 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.

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

**[Internal] Response:** We will have to contact the lab that performed these measurements to get information on the accuracy and precision. **We will update the manuscript numbers with a measurement of their accuracy as appropriate.**