Interactive comment on “Cr(VI) adsorption/desorption on untreated and mussel shell-treated soil materials: fractionation and effects of pH and chromium concentration” by M. Otero et al.

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Referee #2 General comments This paper describes an experimental approach to the study of Cr sorption/desorption kinetics for different soil materials and acidity. In my opinion, this manuscript falls within the scope of SE. The experiment is well designed, although not well explained. Also, there are some inconsistencies in the text that need deep revision and re-writing. Especially, statistical analysis is very poor. Simple statistics may be applied to the analysis of results, which will improve the interpretation of results and discussion. ANSWER: Thank you for your comment. We have made changes...
(detailed below, in the “Detailed comments” section) to improve the manuscript in that you indicate. When changes are new (not previously indicated by Reviewer-1) we mark it in red fonts.

In the objectives, it is stated that “risks of water pollution and transfer to the food chain” will be analyzed and discussed, but I have not found discussion on this. Just a short paragraph focused on this aspect should help to give the manuscript a wider scope, in agreement with the journal characteristics. I consider that this manuscript should be of interest, but needs a lot of work (then, conclusions should be perhaps modified). It should be reconsidered after major revision. ANSWER: Thank you for your comment. We have changed objective c), as follows (red fonts): “c) to determine the fractions where Cr(VI) is retained in the various solid materials investigated, which affect Cr(VI) release and then to overall risks of pollution.” We have also included a new reference and a new comment at the end of the first paragraph of the Introduction section, as follows (red fonts): “...more easily mobilized. Mobilization of Cr(VI), and then risks of water pollution and even of transfer to the food chain, are strongly related to retention processes affecting the pollutant (Lilli et al. 2015)”.

I have uploaded a separate doc with detailed comments. Please also note the supplement to this comment: http://www.solid-earth-discuss.net/6/C1628/2015/sed-6-C1628-2015-supplement.pdf

Detailed comments Pages and line numbers correspond to the discussion paper published in SED. Page 3394 Line 2 Here in after, I suggest using “sorption” instead of “adsorption”. ANSWER: Thank you for your comment. We have changed it. It was also an indication of Reviewer-1, and we had already marked these changes in blue fonts.

Lines 22-23 You should add a reference supporting this statement. I suggest these: iÇğ Alves et al. (1993), http://dx.doi.org/10.1016/0043-1354(93)90220-C iÇğ Di et al. (2006), http://dx.doi.org/10.1016/j.chemosphere.2004.06.044 ANSWER: Thank you for
your comment. We have included both references (red fonts).

Page 3395 Line 1 Substitute “has” with “have”. ANSWER: Thank you for your comment. We have corrected it (red fonts).

Line 2 Micoorganisms cannot be referred to as Âź materials Âž. Try to re-word this sentence. ANSWER: Thank you for your comment. We have changed the sentence to: “Different bio-adsorbents have been tried to remove Cr(VI) from polluted environments, as was the case for some microorganisms and other natural sorbents . . .”.

Line 5 Re-write: “at pH<2”. ANSWER: Thank you for your comment. We have corrected it (red fonts).

Line 6 Re-write: “when pH increased”. ANSWER: Thank you for your comment. We have done it (red fonts).

Lines 9-10 Re-write: “Globally, it is necessary to increase the knowledge on Cr(VI) retention processes by sorbent materials”. ANSWER: Thank you for your comment. We have corrected it (red fonts).

Line 18 Substitute “In view of that” with “Therefore”. ANSWER: Thank you for your comment. We have corrected it (red fonts).

Lines 18-25 Delete “firstly” and “secondly” (the order is shown by “a” and “b”). Re-write: “and, finally, (c)”. ANSWER: Thank you for your comment. We have corrected it (red fonts).

Page 3396 A “Data analysis” section should be added. This should include: îÇğ Checking the normal distribution of data. îÇğ After the normal distribution hypothesis is accepted/rejected, description of the correlation statistic used (Pearson/Spearman). îÇğ Fitting to Freundlich and Langmuir models. Part of this is included in the first lines of page 3398, and should be moved to the new section. ANSWER: Thank you for your comment. We have made it.
Lines 3-20 I suggest adding a table with materials used and simplify the text. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1. We have included a new Table 1 and changed the text (blue fonts).

Lines 3-7 Was this similar-to-a-C-horizon material sampled as is or were the upper horizons previously removed? ANSWER: Thank you for your comment. The material was sampled as is now. The upper horizons were removed around three years ago by the owner of the land. Lines 17-20 Not clear to me. Was the zig-zag sampled material used to form a composite sample? Please, check this paragraph. ANSWER: Thank you for your comment. Each zone was sampled in a zig-zag manner, then performing each of the composite samples (FS, PM and GM) using 10 subsamples for each one. We have changed the paragraph trying to make it more clear (red fonts).

Line 25 Total or organic C and N? ANSWER: Thank you for your comment. We have added the word “Total” (red fonts).

Even native English speakers have problems with this, but, in the future, “relationship” is for people and “relation” is for things. However, in this case, delete “relationship” or substitute it with “ratio”. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Page 3397 Lines 18-20 Repeated text? Again, I suggest using a table and simply citing it here if necessary. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Page 3398 Line 12 “After the ending...” sounds strange. Please, re-write. ANSWER: Thank you for your comment. We have previously made changes indicated by Reviewer-1 (blue fonts), giving: “Immediately after finalizing each batch experiment...”

Lines 14-15 Here and in page 3399, check: “shaking”, “centrifuging” and “filtering”. Please, re-write. ANSWER: Thank you for your comment. We have corrected it.
Lines 17-19 Repeated again. Check! ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Line 18 Although tonnes (t) and hectares (ha) are not part of the Int. System of Units, they are widely used. But just as a suggestion, much better if you use “Mg” instead of “t” and “m-2” instead of “ha-1”. So, 12 t ha-1 should be written as 1.2 kg m-2. Please, insert a space between t and ha-1. ANSWER: Thank you for your comment. We have included the following in the Abstract section (red fonts): “… amended with 12 t ha-1 (1.2 kg m-2) shell, …”, and in the “Materials” section (red fonts): “The unity t ha-1 is widely used, but note that the dose 12 t ha-1 mussel shell is equivalent to 1.2 kg m-2”.

Page 3399 Lines 15-17 Materials repeated again. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Line 21 Re-write: “acid-soluble” ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Page 3400 Lines 5-6 Re-write: “(60, 17 and 23%, respectively); forest soil (65, 20 and 15%); mussel shell (99.53, 0.34 and 0.13 %); pyritic material (67, 14 and 19 %)”. However, this is not a full characterization of solid materials used. Just texture, so, the head title should be changed. As data ARE INCLUDED in Table 1, I suggest re-writing this paragraph and just describing (not simply listing numbers) textures. ANSWER: Thank you for your comment. We had already changed the paragraph as indicated by Reviewer-1 (blue fonts).

Line 9 No function in the figure. Re-write: “…increased with Cr(VI) concentration…”.

ANSWER: Thank you for your comment. We have changed it (red fonts).

Line 18 The mentioned “slight decrease” is not very clear in absence of statistical analysis. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Line 18 Re-write: “1.2 kg m-2”. ANSWER: Thank you for your comment. We have
included the equivalence (red fonts).

Line 24 and following What does “significant” means? First, you should have included data analysis in methods. Second, tell us what p-values do these correlation coefficients have. ANSWER: Thank you for your comment. We have included a Data analysis section, and we have now indicated that the level of significance is p < 0.005 (red fonts).

Page 3402 Lines 7-13 Not clear at all. I do not know what this means. This discussion needs more detailed description. ANSWER: Thank you for your comment. We changed the paragraph, giving: “Sorption data were satisfactory fitted to the Freundlich model through non-linear regression (Table 3), as other authors found for various biosorbents (Cetinkaya-Donmez et al. 1999; Prakasham et al. 1999). Due to the fact that the Freundlich model considers that, theoretically, sorption could be infinite, the fitting to this equation means that sorption maximum would not be easily predictable for these materials.”

Page 3403 Lines 6-7 Delete “In the present study”. Re-write: “The pyritic material showed the maximum Cr(VI) adsorption”. ANSWER: Thank you for your comment. We have changed it.

99% of what? ANSWER: Thank you for your comment. It was also asked by Reviewer-1, so we had already changed it to include more details (blue fonts).

Lines 9-13 Percentages of what? ANSWER: Thank you for your comment. It was also asked by Reviewer-1, so we had already changed it to include more details (blue fonts).

Page 3404 Line 4 Check these values. ANSWER: Thank you for your comment. We did not find mistakes at this regard.

Line 13 Strongly? In line 8 you wrote “this anion adsorbs strongly both. . .”. This looks correct, but not in line 13. I think you mean that a large amount of Cr(VI) was retained, not “strongly” retained, as you have no evidence to say that. Check also the following
2-3 lines. ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Line 15 Re-write: “indicated”. ANSWER: Thank you for your comment. We have changed it (red fonts).

Line 16 Re-write: “facilitates”. ANSWER: Thank you for your comment. We have changed it (red fonts).

Line 17 Signal? ANSWER: Thank you for your comment. We have changed it (red fonts).

Tables Just as a suggestion, it should be better if you move footlines to captions in tables 1 and 3. ANSWER: Thank you for your comment. We have changed it.

Table 1 Check decimal places! Texture of mussel shell is shown with 2 decimal places, the rest are round values. Also there are some other inconsistencies through the table (eg, Alp, Alop, Alcu...). ANSWER: Thank you for your comment. We have added 2 decimals to all textural data. The reason to have included 2 decimals just for mussel shell was that this material needs that information to difference among its fractions. Regarding the other parameters, in some cases the number of decimals is different considering significant figures.

Table 2 Delete “(dimensionless)”. Add a third decimal place in the third column, second row. Should you add p-value of correlation coefficients or state it in the table caption. ANSWER: Thank you for your comment. We have done it.

Table 3 In the caption: percentage of what? ANSWER: Thank you for your comment. It was also indicated by Reviewer-1, so we had already changed it (blue fonts).

Use the same number of decimal places in all percentages. ANSWER: Thank you for your comment. The number of decimals is different considering significant figures.

Move the footline to the caption (are abbreviations necessary, however? I strongly
suggest using the full forms). ANSWER: Thank you for your comment. We have moved it.

Figures Why not color figures? It will gain dissemination (and citations). ANSWER: Thank you for your comment. We have included color in figures.

Some parts of the discussion and conclusions are not supported by figures. I suggest a more deep statistical analysis of results. ANSWER: Thank you for your comment. We have included new details regarding statistics as indicated in previous comments.

Figures 1-3 I think these figures should gain if displayed as a $2 \times 2$ matrix, instead of one column. Also, font used is too small. ANSWER: Thank you for your comment. We have included higher-size fonts. The $2 \times 2$ matrix would give lower-size figures, then making more difficult to distinguish details.

Figure 1 No curves here! Regression curves should be added, as stated in the caption. If representing only points, why not all (three replicates, according to the main text) and not only mean values (I suppose mean values are displayed, but not explained in the caption). Why granitic material is displayed in b) and c)? Again: why not regression curves in ONE ONLY graph?

ANSWER: Thank you for your comment. Taking into account a previous indication of Reviewer-1, we had already changed the caption (blue fonts) to “Sorption points corresponding to …”. We also indicate (blue fonts) that represented values are means of triplicate samples with coefficients of variation lower than 5%. In b) we include just individual materials, whereas in c) and d) we compare individual granitic material and individual forest soil (respectively) with both materials amended with mussel shell.

Figure 2 See comments above. ANSWER: Thank you for your comment. We had already changed the caption (blue fonts) taking into account previous indications of Reviewer-1.

Figure 3 “As a function”? You should add regression curves or re-write the caption
(“relation between desorbed Cr(VI) (%) and pH for...”). ANSWER: Thank you for your comment. We have changed it (red fonts).

“Fine shell”? ANSWER: Thank you for your comment. We have changed “Fine shell” to “Shell”.

Figure 4 Delete “24 h”, “1 week” and “1 month” in the figure (it is explained in the caption). Check: the same legend is repeated three times. ANSWER: Thank you for your comment. We have changed it.

Please also note the supplement to this comment:

Interactive comment on Solid Earth Discuss., 6, 3393, 2014.