Solid Earth Discuss., 6, C1608–C1613, 2015
www.solid-earth-discuss.net/6/C1608/2015/

Solid Earth
Discussions
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Interactive comment on "Adsorption, desorption and fractionation of As(V) on untreated and mussel shell-treated granitic material" *by* N. Seco-Reigosa et al.

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Received and published: 26 February 2015

Reviewer 2 The paper submitted by Seco-Reigosa is interesting and under the scope of Solid Earth. However some speculations of the authors, beyond the scope of the paper should be consider carefully. I think that they should show the implications, but also show evidences or data that can prove it. I think that the paper needs a minor revision previous to be accepted to publication in Solid Earth.

Page 2 Abstract Line 17-19: This is a very strong affirmation. Despite As be a toxic element classify, say that granite material (which is natural and abundant in NW Spain) is a potential risk to water pollution and food chain is too strong. Please rephrase this

or delete it. ANSWER: Thank you for your comment. We have changed the phrase (red fonts) in order to make it more clear, giving: "The granitic material did not show high As(V) retention capacity, which could facilitate As(V) transfer to water courses and to the food chain in case of As(V) compounds being applied on this material; however, the mussel shell amendment increased As(V) retention, making this practice recommendable."

Introduction Line 1-2: If granite has low As, how can be considered a problem to environment? ANSWER: Thank you for your comment. In that sentence we do not mean that granite is a problem for the environment due to its As content. However, we investigate As retention in the granite material, and, in cases where As is weakly retained, some additional treatment could be useful to increase As retention, then lowering risks of As transfer and further pollution of waters and organisms. At that point, we considered that mussel shell could aid to increase As retention on the granite material, and we tried it, as described latter in the manuscript.

Page 3 Line 2-3: Please show at which levels, As can be considered a risk to environment and human health? ANSWER: Thank you for your comment. We have included a new sentence (red fonts), giving: "...so having the potential to provoke environmental and public health issues. In fact, the recommended threshold level for As in drinking water is 10 μg L-1 (WHO, 2011)."

Line 4-6: In which situation As based products are spread on soil. Please explain clearly with facts and previous works that the usage of As products have a potential risk to environment and human health. ANSWER: Thank you for your comment. We have included a new sentence (red fonts), giving: "... and subsequent transfer to the food chain, must be taken into account. As indicated in previous works, the use of wood preservative compounds including arsenic, or of As-based herbicides, could cause arsenic pollution episodes in forest areas (Smith et al., 1998) and cultivation soils (Gur et al., 1979), in both cases increasing risks of soil and water pollution (Clothier et al., 2006)."

Page 4 Line 2: Here the authors have to show a better justification and novelty of their work. ANSWER: Thank you for your comment. We have included a new sentence (red fonts) at the end of that paragraph, giving: “As long as we know, no equivalent studies were made previously with the combination of materials here used.”

Materials and Methods Line 12: Please show the coordinates and altitude of the place where the material was collected. ANSWER: Thank you for your comment. We have included a new data (red fonts), giving: “a) granitic material from Santa Cristina (Ribadavia, Ourense Province, Spain), (latitude 42° 17′33.81′′ N; longitude 8° 07′ 21.75′′ W; altitude 162 m above sea level)”.

Line 15: Do you have any evidence that the C horizon studied is similar to granitic mine spoils? ANSWER: Thank you for your comment. To clarify what we mean, we have changed the sentence (red fonts), giving: “then needing organic matter and nutrients to be restored, as granitic mine spoils need”. Any case, some similitudes exist when comparing with dumping sites, even when they are not limited to spoils where granite materials dominate. As examples of this, we could refer to the following previous papers by Álvarez et al. (2003): http://www.sciencedirect.com/science/article/pii/S0048969703002614 by Rieuwerts et al. (2014): http://www.sciencedirect.com/science/article/pii/S0048969713013107 and by Silva et al. (2014): http://www.sciencedirect.com/science/article/pii/S0009281913000676

Page 5 Line 2: Show the amount of sample used to measure the pH and all the other studied elements. ANSWER: Thank you for your comment. We have included the data you requested.

Line 22: Change “pollutant” by “element” ANSWER: Thank you for your indication. We have changed it.

Results and discussion Page 8 Line 23-24: Please show the influence of the surface area in As adsorption. ANSWER: Thank you for your comment. We have changed the sentence, adding new words (red fonts), giving: “The different behavior for both mussel

shell materials (higher As adsorption on fine than on coarse mussel shell) can be in relation with the higher surface area of fine shell (1.4 m2 g-1) than that of coarse shell (1 m2 g-1), as previously stated by Peña-Rodríguez et al. (2013)”.

Page 9 Line 10-13: Do you have some explanation for the increase in the adsorption between 0.5 and 5 in in the granitic material and granitic material + 12 t/ha shell. ANSWER: Thank you for your comment. We have changed the paragraph (red fonts) to make clear that here we refer just to percentage adsorption. In fact, when we increased the added As concentration, the absolute amount of adsorbed As also increased, as the As concentration in the equilibrium did (see Fig. 1b to illustrate it). However, expressing adsorption as percentage gives the more variable behavior shown in Fig. 2.

Line 21: Increase to which pH level. ANSWER: Thank you for your comment. We have changed the sentence, adding new words (red fonts), giving: “. . .whereas increased pH values (from above 5 for clay minerals to above 12 for calcite) favor desorption (Golberg and Glaubig 1988).”

Line 22: Can you show some explanation for this irreversibility? ANSWER: Thank you for your comment. We think that probably the high binding energy promoting irreversibility is mostly in relation with the presence of Fe oxides and hydroxides. At this regard it could be also interesting a paper by Zhang et al. (2008): http://www.sciencedirect.com/science/article/pii/S0021979707013331

Line 25: Do you have some explanation for the fact that coarse mussel shell only fits the Freundlich model. ANSWER: Thank you for your comment. In this study, both fine and coarse mussel shell can be fitted only to the Freundlich model (fitting was not possible due to estimation errors being too high). Taking into account that mussel shell is an alkaline material, and bearing in mind that Yolcubal and Akyol (2008) (cited in the present manuscript) obtained better fitting to the Freundlich model using carbonate-rich solid substrates, whereas Maji et al. (2007) (cited in the present manuscript) found satisfactory adjustment to both Freundlich and Langmuir models studying As(V) adsorption on

lateritic substrates, it seems that these alkaline materials could approach the assumptions of multilayer adsorption of the Freundlich model, rather than the adsorption on monolayers postulated by the Langmuir model.

Page 10 Line 20: It is possible to provide some more explanations about the effect of the addition of fine and coarse mussel shell in the natural relation of As(v) with pH. ANSWER: Thank you for your comment. At this regard we added commens on a new reference (red fonts), giving: "...when pH values are higher (Alexandratos et al. 2007). Using another alkaline material, Salameh et al. (2015) found that arsenic was completely removed by charred dolomite samples over a wide range of pH (2 to 11)."

Page11 Line 4-6: In these correlations you did not show the p value, please show it and proof that the correlations are statistical significant. Please do it here and in the other correlation coefficients calculated in the paper. I suggest the authors to describe in the materials and methods the statistical analysis carried out, the correlation coefficients used and if the data followed the normal distribution. ANSWER: Thank you for your comment. We have done all you indicate, including new details in red fonts.

Page 12 Line 18: To identify if there are important changes in the three measurement periods and among the different treatments, it would be important to carry out some statistical tests, in order to know if differences were significant. ANSWER: Thank you for your comment. We have changed the sentence (red fonts), giving: "The increase of incubation time from 24 h to 1 week and to 1 month, as well as the 12 t ha-1 shell amendment of the granitic material, did not cause statistically significant modifications in the percentage content of each fraction of the adsorbed As(V) (Fig. 5)".

Conclusions Line 16-19: Do your data show this evidence? Adsorption capacity of coarse mussel shell is not so high. I suggest the authors to not speculate about these impacts, or present studies in the discussions that confirm this argument. ANSWER: Thank you for your comment. We have removed parts of the sentences to make it less speculative.

Line 24-26: Please see the previous comment. ANSWER: Thank you for your comment. As with the previous comment, we have removed parts of the sentences to make it less speculative.

Tables Tables 1 and 2. Please show the SD. ANSWER: Thank you for your comment. We have now included SD values.

Please also note the supplement to this comment:
http://www.solid-earth-discuss.net/6/C1608/2015/sed-6-C1608-2015-supplement.pdf

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Interactive comment on Solid Earth Discuss., 6, 3419, 2014.