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Responses to Reviewer 2

This manuscript presents results from a study designed to develop predictive maps of the Li concentration in soil or Australia. The calibration data set used was the Li data generated during the National Geochemical Survey of Australia. In addition, several environmental covariates were used such as annual precipitation, annual evaporation, airborne radiometric data, etc. The predictive Li maps were then compared to a validation data set from the northern Australia Geochemical Survey. The paper is relatively well-written and well organized. Unfortunately, the results of the study were disappointing in that the correlation between observed Li in the validation data ser and the predicted Li values from the model was relatively poor. The authors have recognized several limitations from their study, but have neglected to discuss what I think is an important issue—the nature of the Li data from the NGSA.

We thank the reviewer for the constructive comments. We have clarified within the revised manuscript that the Lithium concentration mentioned in the text are aqua regia extractable Li.

The authors should emphasize that they are using aqua-regia extractable Li data from the NGSA in this study. Aqua-regia digestion only extracts a portion of the total Li found in soil. I am not sure what the fraction of the total that may be, but it depends on the extraction parameters (e.g., temperature of extraction, length of time the soil material is left in contact with the aqua regia) as well as soil mineralogy. Lithium in clay minerals may be extracted, but I am not sure that Li in spodumene will be released by aqua regia extraction. The national-scale soil geochemical survey of the conterminous United States (Smith et al., 2019, complete reference given below) used a 4-acid extraction that is a much more vigorous extraction than aqua regia and should give a good estimate of the total Li content in soil For this US study, three samples were collected at each site (4,857 sites): soil from a depth of 0-5 cm. a composite of the soil A horizon, and a sample of the top 20 cm of the soil C horizon. The results shows a range of <1-300 mg/kg (median 20 mg/kg) for the 0-5 cm sample; a range of <1-315 mg/kg (median 20 mg/kg) for the soil A horizon; and a range of <1-280 mg/kg (median 24 mg/kg) for the soil C horizon. These concentrations are considerably higher than the aqua regia extraction data for Australia. So one might ask if the results of the current study would be different if total Li data were used instead of the aqua-regia-extractable data? Another question is whether a weaker extraction that only released "plant available" Li might be more likely to give better results.

We thank the reviewer for the constructive comments and pointed out the nature of the NGSA sample and the possibility of better results if Total Li was measured. We have included this in comparison with the NGSA data in our revised paper.

Despite the somewhat disappointing results of this study, I feel the paper should be published to demonstrate a step forward in the development of machine learning in generating predictive geochemical maps. The authors should also perhaps do a better job of recognizing the importance of the National Geochemical Survey of Australia whose data gave them the opportunity to conduct the current study. Perhaps a recommendation might be to recognize the need to conduct higher density national- and international-scale geochemical surveys and to add additional parameters to these studies (e.g., quantitative mineralogy) that would aid in future studies such as these authors have conducted.

Reference for Smith et al. (2019):

Smith, D.B., Solano, F., Woodruff, L.G., Cannon, W.F. and Ellefsen, K.J. (2019). Geochemical and Mineralogical Maps, with Interpretation, for Soils of the Conterminous United States. *United States Geological Survey Scientific Investigations Report, 2017-5118,* https://pubs.usgs.gov/sir/2017/5118/index.html.

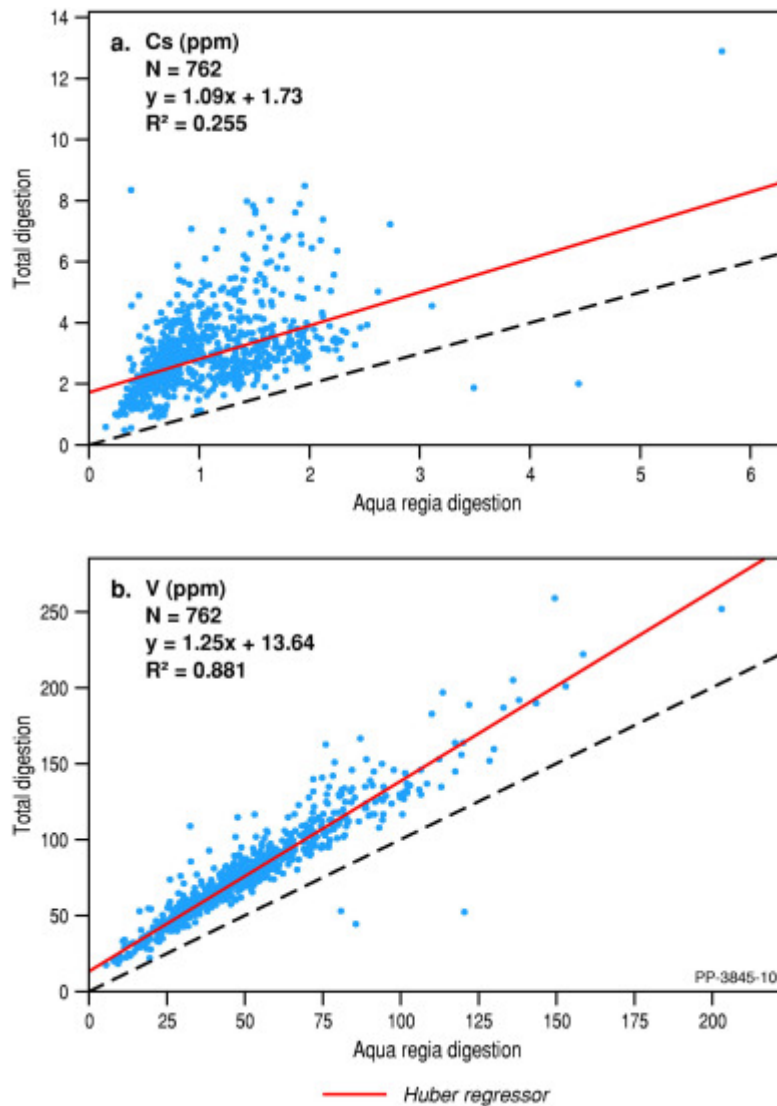
We thank the reviewer for the comments and added this in our discussion.

Prior to ICP-MS analysis, the samples underwent the following digestion process:

A 0.50 ± 0.02 g aliquot of the sample was digested with an aqua regia solution (1.8 mL concentrated hydrochloric acid added first followed by 0.6 mL concentrated nitric acid) at 90 ± 3 °C for 2 hours to leach the acid-soluble components (the leach only partially dissolves silicates and oxides). Once the sample had cooled to room temperature, 17.5 mL of diluent was added and the bottle was capped and inverted 10 times to completely homogenise the content. The sample was then allowed to settle over a 6 hour period or longer. The sample was exposed to light for as little time as possible to prevent reduction of silver. The sample was diluted a further 50 times with 18 MΩ/cm water.

We have added this information within the manuscript. We also mentioned within the text (Li measurement section) the any reference to Li refers to aqua regia extractable Li. The reason total Li was not measured in the NGSA (or NAGS) samples is simply that all total analyses were done on XRF fused beads made using Li-borate flux.

We are not sure how much the aqua-regia extractable portion accounts for in comparison to the total Li because the geochemical survey data for Lithium was only conducted on the aqua regia extractable portion. Depending on the element, the concentration of aqua regia digestion could vary significantly in comparison to those from total digestion. (see Figure below from Main and Champion (2022)).

Main, P. T. and Champion, D. C.: Levelling of multi-generational and spatially isolated geochemical surveys, Journal of Geochemical Exploration, 240, doi::1016/j.gexplo.2022.107028, 2022.

The results could potentially be improved if the total Li was measured (this would require a completely new analytical process). Most of the observations collected had relatively low concentration; having more representative samples at higher concentration might improve the prediction accuracy.

Thank you for the suggestions. We have added those in the conclusion section.

I have made a few specific suggestions and editorial comments below:

1. Lines 16-17: The authors begin this sentence by stating that "soil samples were collected." Then later in the sentence, they refer to "catchment outlet sediments." Are they saying that all the catchment outlet sediments sampled during the National Geochemical Survey of Australia can also be considered

to be "soils?" This is explained later in the text (lines 121-124); however, it probably deserves a sentence in the abstract to clarify this issue. An alternative would be to avoid the use of "catchment outlet sediments" in the abstract.

We have corrected it into catchment outlet sediments samples.

2. Lines 24-25. Note this sentence: "The map shows high Li concentration around existing mines and other potentially anomalous Li areas." It seems a bit strange to this reviewer to say there are high Li concentrations around potentially anomalous Li areas. If there are high Li values, then the area is, by definition, anomalous. Perhaps the sentence is constructed in this manner because the map to which the authors refer is predictive and it would require collecting physical samples from the "potentially anomalous" areas to confirm if they were actually anomalous.

We have corrected the sentence into:

The predicted maps show high Li concentration around existing mines and other potentially anomalous Li areas that have yet to be verified.

3. Line 43: Change "was the second" to "is second"; change "the first" to "first"

We have corrected the words.

4. Line 44: Change "economic resource" to "economic resources." Change "According to recent survey" to "According to a recent survey"

We have corrected the words.

5. Line 47: Change "Li is hosted mainly spodumene" to "Li is hosted mainly in spodumene" Change "while" to "whereas"

We have corrected the words.

6. Line 142: Note this sentence: "Furthermore, these samples were collected at different times and /or laboratories." Do you mean that multiple laboratories were used to analyze the samples? It is unclear what exactly is meant here.

Samples from NAGS dataset were collected and analysed at different laboratories to those samples from NGSA dataset. We have clarified the sentence.

7. Lines 142-145. In my opinion, there should be a more specific discussion about the leveling of these two data sets. What Certified Reference Material was used? Was it Till-1 as mentioned previously for the NGSA data? How

about a simple plot of NGSA Li concentration versus NAGS Li concentrations to give the reader a better idea of data comparability. I just do not think there is sufficient information given here.

The TILL-1 CRM is used. We clarified the process taken to level the dataset in the manuscript. We cannot compare the NGSA and NAGS concentration directly as the measurements were taken at different locations.

8. Lines 148-149. Change ", that contributes" to "that contribute"

We have corrected the word to "that contribute".

9. Line 178. Change "map" to "mapping" or just omit the word "map"

We have removed the word "map".

10. Line 179-180. I think there is a word missing between "measurements" and "soil" in line 179. Perhaps it should be "measurements on soil?"

We have corrected the sentence.

11. Line 238. I would suggest using "aqua-regia-extractable Li concentrations" instead of just saying "Li concentrations" here and anywhere else in the text. This lets the reader know that you are using data derived from a partial extraction (aqua regia) and not the total Li content of the soil. Another option would be to have a sentence early in the text to state that for the remainder of the paper, any reference to Li concentrations is understood to mean aqua-regia-extractable Li unless otherwise noted.

We have already mentioned that the Li concentration is derived from the aqua-regia digestion method (Line 137-138). We re-emphasised it again later on within the same paragraph.

12. Line 242. Here, again, I would suggest using "aqua-regia extractable Li concentrations" when referring to the Negrel et al. (2019) publication. The European study also used an aqua regia extraction in the determination of Li concentrations, so their data should be comparable to the Australian data.

We have updated the sentence

13. Line 243. I do not know what data Schrauzer (2002) used for obtaining the estimated range of 7-200 mg/kg for a world background Li concentration. If you have that information, I would suggest including it in the manuscript. However, Hu and Gao (2008, complete reference given below) estimated the average concentration of Li in the upper continental crust is 41 mg/kg. This is

higher than even the US study where the median Li content was about 20 mg/kg using a total extraction method. I think a brief discussion about reported Li concentration being totally dependent on the extraction used would be useful in the text.

Reference for Hu and Gao (2008):

Hu, Z., and Gao, S., 2008. Upper crustal abundances of trace elements—A revision and update. Chemical Geology 253 (3-4), 205–221.

No details on what specific Li were reported by Schrauzer. Hence, we removed them to avoid confusion. We have added reference from Teng et al., which analysed the Lithium concentration using HF+HNO$_3$ extractable.

Discussion about dependency of Li concentration on the extraction method used is beyond the scope of this paper because we did not measure the samples using various method to be able to document this.

14. Lines 250-254. The concentration ranges of the various sized circles in Figure 1 make it difficult for the reader to see where the higher concentrations of Li occur. I suggest that you show a range and median for the samples in each of the areas discussed in the text (i.e., Cape York, Goldfields-Esperance, etc.).

    We have added descriptive statistics showing the range and median concentration of Li in the areas mentioned.

15. Lines 55, 265, and 380. The authors cite "Foregs (2006)". However, there is no Foregs (2006) in the References. I think the authors have this listed as "Geochemical Atlas of Europe" in the References. The correct citation in the text should be "De Vos, Tarvainen, et al. (2006)." Then the complete reference should be as follows:

    De Vos, W., Tarvainen, T., Salminen, R., Reeder, S., De Vivo, B., Demetriades, A., Pirc, S., Batista, M.J., Marsina, K., Ottesen, R.T., O'Connor, P.J., Bidovec, M., Lima, A., Siewers, U., Smith, B., Taylor, H., Shaw, R., Salpeteur, I., Gregorauskiene, V., Halamic, J., Slaninka, I., Lax, K., Gravesen, P., Birke, M., Breward, N., Ander, E.L., Jordan, G., Duris, M., Klein, P., Locutura, J., Bel-lan, A., Pasieczna, A., Lis, J., Mazreku, A., Gilucis, A., Heitzmann, P., Klaver, G. and Petersell, V. (2006). *Geochemical Atlas of Europe. Part 2 – Interpretation of geochemical maps, Additional Tables, Figures, Maps and related publications*. Geological Survey of Finland, Espoo, Finland, p. 225-228. http://weppi.gtk.fi/publ/foregsatlas/text/Li.pdf

    We have updated the references accordingly.

16. Line 315. Here again the authors refer to "releveling" the NAGS data sets. As stated in comment #7, it would be useful to discuss this leveling process in a bit more detail.

    We have added more detail in section 2.1.

17. Line 423. Delete "with anomalous Li concentration" at the end of this sentence.

    We have removed the words "anomalous Li concentration.