Reply to the Comments of Reviewer 1.

Keck et al.; Quantitative imaging of the 3-D distribution of cation adsorption sites in undisturbed soil.

Thank you for reading our manuscript carefully and for the time and effort you spend to comment on it.

Comment 1:
p. 5, L. 19--23 and p. 6, L. 22--23: How much of the Ba2+ is likely removed from the CAS with a 0.1 M KCl wash? Although there should be a high proportion of divalent to monovalent cation in the exchanger phase for an equal ratio of aqueous cations, it seems that a 0.1 M KCl wash would remove a significant portion of Ba2+ from the CAS? Perhaps the assumption that all CAS was saturated with Ba2+ after the 0.1 M KCl wash (p. 6, L. 22-23) is not completely valid. An alternative is to call the Ba2+--saturated sites "sites of higher affinity for Ba2+"). Actually, the authors address this possibility in their discussion of CEC relationships (p. 10), but perhaps the possibility could be raised in the methods section also.

Reply to comment 1:
Thank you for this comment. We agree that not all CAS may be completely saturated with Ba2+ after the KCl wash. We also think it is a good idea to address this issue not only in the discussion but also in the material and method section of the revised manuscript and will adapt the term 'Ba2+ saturated sites' accordingly.

Comment 2:
Fig. 5. Is there a "cutoff" difference value to assess what regions of the X--ray images are artifacts? For example, it is not clear in Fig. 5 how it was deduced that the SNO3 sample had a global shift whereas the "very bright" or "very dark" areas in the SNO2 image was apparent. Also, can a brightness scale bar be put on Fig. 5 (and 6) to give an idea of the difference scale of the various grey shades?

Reply to comment 2:
In Fig. 1 we visualised the global gray value (GV) distribution of the soil columns of samples number (SNO) 1, 2 and 3. All difference images show histograms with a small peak around GV -1300 (black vertical line). These correspond to air bubbles that formed after the reference images were taken. A difference between SNO1 with very few artefacts and SNO2 and 3 with more abundant artefacts is also apparent. The histograms of SNO2 and SNO3 have two plateaus in gray value abundance at approx. GV +/-1500 to +/-4500 and GV +/-1500 to +/-3750 respectively (red horizontal lines in Fig. 1). These plateaus represent local particle shifts within the samples that occurred after the reference images were taken (for an example see the highlighted areas in Fig. 2).
This can be assumed following the reasoning that a particle shift will lead to bright areas if high GV are subtracted from low GV and in dark areas, if the reverse is the case. This means that per shifted aggregate there is usually one side that is 'framed' by higher GV and one side that is 'framed' by lower GV. Both in equal proportions. This may be a more objective way to characterise artefacts due to shifts in difference images. Determining and integrating the plateaus could be used to quantify registration errors in future studies. A cut-off value can be determined at the beginning of the plateaus (approximately at a GV +/- 1500), however this might exclude some GV originating from regions of enhanced barium adsorption.
We have included a gray scale bar for Fig. 5 and 6 (see below, Fig. 2 and 3).

Comment 3:
It would be helpful to have more details in the methods on how the artificial sample (SNO9) was prepared.

Reply to comment 3:
Thank you, we will include more details on the preparation of the artificial sample.

Comment 4:
Because the manuscript primarily discusses a new X--ray imaging technique, the conclusions could be expanded to present opportunities for using this technique other than for CAS mapping. For example, I found the discussion of organic--lined biopores to be an interesting observation. Could, for example, the technique presented here be used to study such pores in more detail, e.g., at the original spatial resolution of the data for smaller sample volumes?

Reply to comment 4:
Yes, we believe that it is possible to use this method for mapping organic matter within undisturbed soil cores, especially when it comes to the organic-lined biopores. For this purpose the KCl rinsing process should be somewhat longer and one could consider to increase the KCL concentration. This would make it more likely that most of the Ba2+ bound to clay surfaces and other exchange sites is replaced by K+, whereas the B2+ bound in complexes to organic matter would stay in place.
Heavy anions could be used as contrast agents for imaging the soil organic matter instead of barium (e.g. I^-, Br^- , WO_4^{2-} or MoO_4^{2-}). When used on soils from temperate climate regions these may have the advantage that the CEC is not biasing the results.
It is furthermore possible to improve the resolution. However, an improved resolution mainly depends on the sample size. The smaller the sample the better the resolution. Note that the maximal resolution also depends on the hardware used (X-ray scanner and computer) and its configuration. After some preliminary tests we found that the scanner used in this study (GE Phoenix v|tome|x m) is capable of taking images at a resolution down to 5 µm at a soil column with a diameter of 8 mm. Others have reported resolution down to 1 µm when using X-ray scanner optimized for smaller sample sizes (e.g. Tippkötter et al., 2009). By using a monochromatic X-ray source Voltolini et al. (2017) imaged soil micro-aggregates with a sub-micron resolution.

Tippkötter, R., Eickhorst, T., Taubner, H., Gredner, B., Rademaker, G., 2009. Detection of soil water in macropores of undisturbed soil using microfocus X-ray tube computerized tomography (μCT). Soil Tillage Res. 105, 12–20. doi:10.1016/j.still.2009.05.001

Voltolini, M., Taş, N., Wang, S., Brodie, E.L., Ajo-Franklin, J.B., 2017. Quantitative characterization of soil micro-aggregates: New opportunities from sub-micron resolution synchrotron X-ray microtomography. Geoderma 305, 382–393. doi:10.1016/j.geoderma.2017.06.005

Figures:

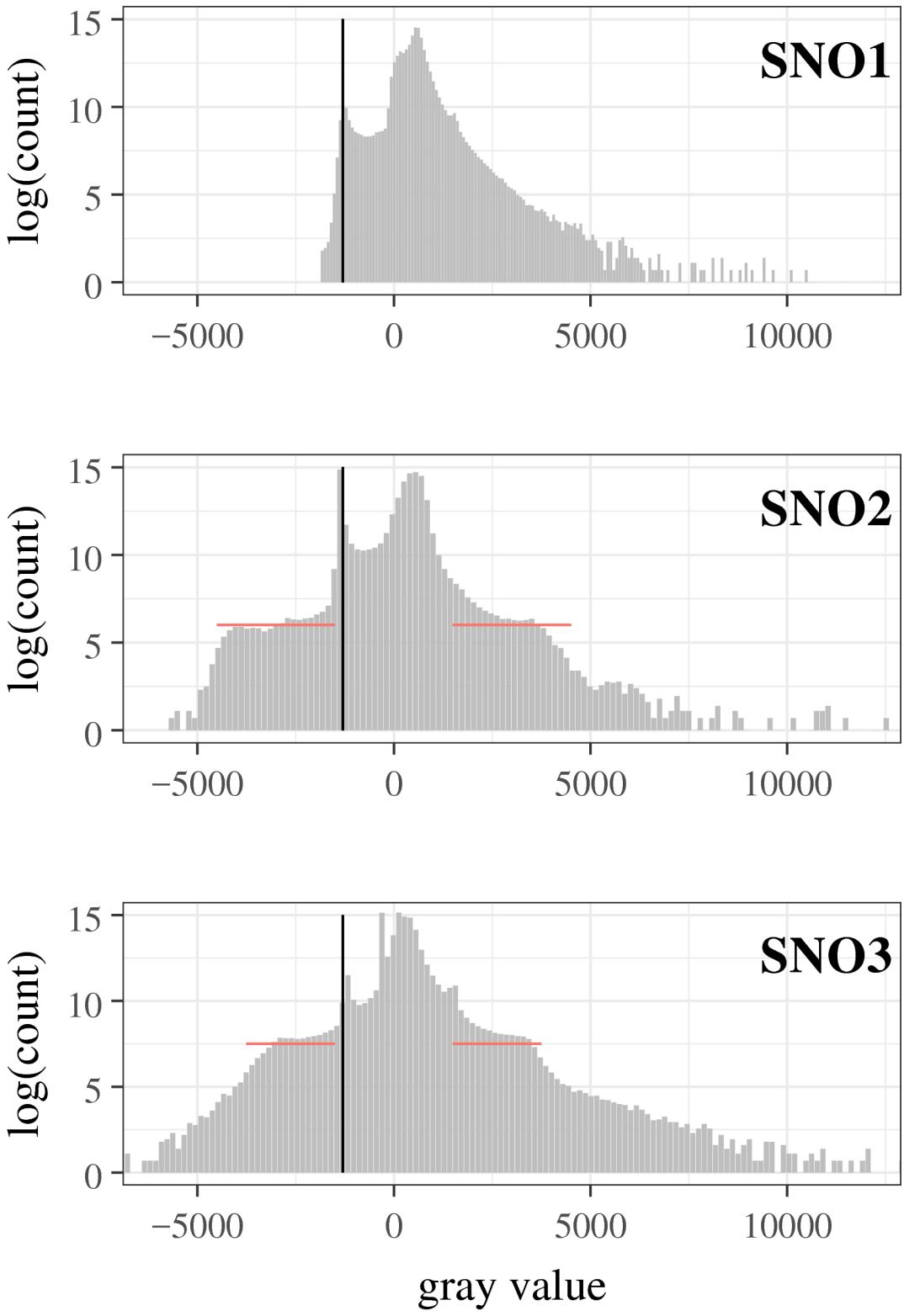

Figure 1: Global gray value distribution for SNO1, SNO2 and SNO3.

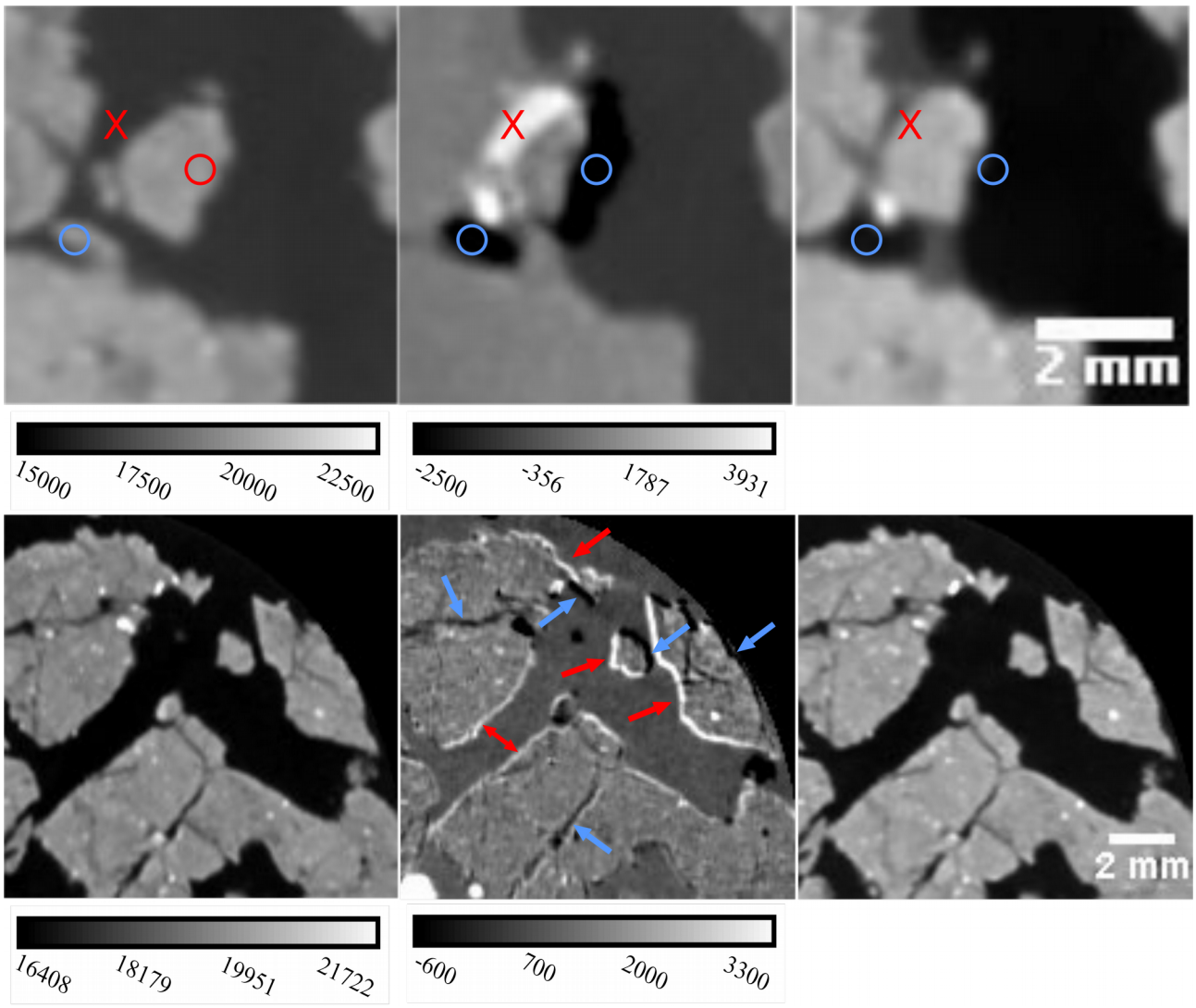

Figure 2: Effect of aggregates movement on the difference image of SNO2 (top) and SNO3 (bottom). Reference image (left), difference image (middle) and the image of Ba^{2+} treated soil (right). The red cross and circle indicate the identical coordinates in all three images. The movement of one soil aggregate resulted in very high gray values (red marks) or very low gray values (blue marks) in the difference image. Note that the reference images and the image of Ba^{2+} treated soil share the same gray value calibration bar.

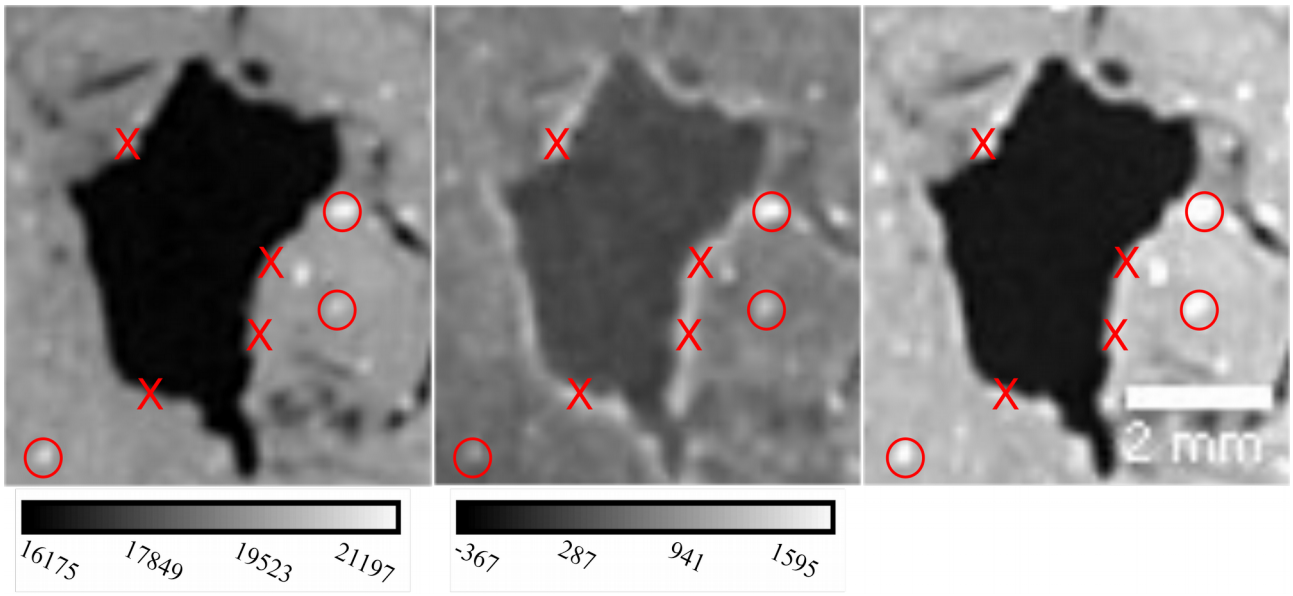

Figure 3: Magnification of a macropore from SNO1. Reference image (left), difference image (middle) and the image of Ba^{2+} treated soil (right) (right). The X and the circle indicate the identical coordinates in the images. Note that the reference image and image of Ba^{2+} treated soil share the same gray value calibration bar.