

## **Reply to the Comments of Reviewer #2.**

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

### **Comment 1:**

This is a very interesting study determining the spatial distribution of cation adsorption sites in undisturbed soil columns. Until now, our knowledge about the spatial heterogeneity down to the millimetre scale (and smaller) of this important soil property is very limited and quantitative approaches are strongly needed. The authors compared a 3-D quantitative imaging approach to determine the cation exchange capacity with a conventional method. In general the manuscript is of high quality and well written. I have just a few comments related to the methodological approach including one suggestion for a preliminary test (small amount of work).

### **Reply 1:**

Thank you for your interest in our manuscript and for the time and effort you spend to comment on it.

### **Comment 2:**

Introduction: The list of references on current X-ray CT studies (page 2 line 25 to page 3 line 18) is limited on what seems to be a subjective selection by the authors, but that cannot be held against them as the field is growing quickly and it is neither possible nor desirable to reach a comprehensive overview here. The references are all up to date!

### **Reply 2:**

Thank you.

### **Comment 3:**

Methods: Page 4, line 8: Please add a reference for the ammonium acetate method you used. Page 4, line 14: You referred to the “loss of ignition method” for the analyses of carbon in your soils but you used a CNS analyser. Please check / clarify. page 4 line 23: “inverted” should be replaced by “reconstructed into 3-D tomograms”

### **Reply 3:**

We agree that it is a very valuable information to include and will refer the reader to the description of the ammonium acetate method by (Thomas, 1982). The loss of ignition analysis was done on a TruMac CN analyser from LECO, not as mentioned in the manuscript on a TruMac CNS analyser. We will also change ‘inverted’ (p.4 line 23) to ‘reconstructed into 3-D tomograms’.

### **Comment 4:**

Reference gray values for Al, K and Ba in the contrast image (Fig. 1): What was the motivation to use different concentration for the two solutes (0.1M KCl vs 0.3M BaCl<sub>2</sub>)? Why did you keep the remaining volume inside the soil column air-filled? In a more realistic scenario it should be filled with dry soil at the same or at least the average bulk density of all investigated samples to mimic the X-ray attenuation by the soil matrix. For instance, the reference gray value for KCl will be below

16225 if pure KCl was detected inside soil, because the photon flux will already be attenuated during the passage of the soil matrix, and it is difficult to estimate by how much. I would strongly advise to do such a preliminary test with the same solution columns surrounded by differently packed soil that covers the range of bulk densities reported in Table 2, analyse the effect on the reference gray values of the different materials and add this information as supplementary material. The amount of work to do this is small. If the changes turn out to be small, then you can use this as an asset of your approach to use polychromatic X-rays to measure cation adsorption sites. As this is really the first study in this respect it should lay out the foundations as thoroughly as possible. Additional information about the interplay between attenuation of polychromatic X-rays in water and the soil matrix can be retrieved e.g. in Weller et al. (2017).

**Reply 4:**

Thank you for this very valuable advice!

Concerning your first question, we used the KCl solution to flush out the residual  $Ba^{2+}$  ions and chose to set the concentration lower than that of the  $BaCl_2$  solution. A KCl solution, rather than deionised water was chosen to avoid structural changes of the clay minerals. These changes could be expected if the KCl solution was either too strong or too weak.

Your second question is indeed very interesting to elaborate on. We did some preliminary tests on the effects of higher bulk densities within the aluminium columns of the calibration images. The aluminium columns were filled with differently packed soil, otherwise the procedure was identical to the description in the manuscript. Please see the gray value distributions of the KCl and the  $BaCl_2$  solutions in Fig. 1 and Fig. 2 and corresponding cross-sections in Fig. 3. The average increase in contrast of the three samples with packed soil compared to the sample without soil (air-filled) was 9.99 % (Tab. 1 for more details). Considering that these packed soils exceeded the bulk densities of the samples described in our manuscript this increase in contrast is the maximum expectable increase. Therefore, it would mean that our estimates of the cation exchange capacity (CEC) are underestimated by a maximum of 10 %. Fig. 4 illustrates the implications of such an increase on our estimates of the CEC.

**Comment 5:**

Page 6 line 11: To my knowledge an affine transformation cannot account for local deformations, but only for a change in position and perhaps global distortion of the sample.

**Reply 5:**

Thank you, we will change our wording at the respective position.

**Comment 6:**

Page 6, relationship between gray values and barium mass: It is not clear to me, also after consulting Koestel and Larsbo (2014), how  $C_{max}$  is determined. Is it the hypothetical mass of Ba in one voxel assuming 0.3M  $BaCl_2$  is reached in a pure pore voxel, i.e. no partial filling of that voxel with the solid phase? Also, readers might wonder how changes in background porosity might influence the interpretation of the estimated  $BaCl_2$  mass. Does the same increase in  $m$  ( $BaCl_2$  mass) always result in the same increase in gamma (gray value), no matter whether a voxel is partially filled with pores by, say, 30% or 70%?

**Reply 6:**

In eq. 1  $C_{\max}$  refers to the maximum possible increase in  $Ba^{2+}$  concentration (0.3 m  $Ba^{2+}$  or 41.199 mg  $cm^{-3}$ ) i.e. a voxel filled with  $BaCl_2$  solution (no partial volume voxel).

We are assuming that the increase in  $Ba^{2+}$  mass is linearly related to GV in the difference images, irrespective of the voxel porosity. We are however aware that this assumption is only an approximation (see reply to comment 4). With reference to the results of the additional experiment conducted in connection with comment 4, we suspect that partial volume effects are of subordinate importance. We however agree that such possible effects should be investigated in future experiments.

**Comment 7:**

Page 6-7, Spatial distribution of cation exchange capacity: In order to estimate CEC from m, you need to know the mass of soil in the two regions of interest (soil matrix vs. macropore walls). Do you estimate the (fluctuating) mass of soil per voxel and cumulate this over all voxels in the respective regions?

**Reply 7:**

Thank you for this comment. Actually we did not estimate the CEC within the matrix or the macropore walls itself. Here we estimated the barium mass only. We have realised this is described somewhat misleading (page 6 line 27). We will change the wording from:

*‘In order to test whether the imaged CECs are elevated in macropore sheaths (400  $\mu m$  distance from pore surface) as compared to the CECs in the soil matrix [...]*

to:

*‘To test whether the imaged barium concentrations as proxies for the CECs are elevated in macropore sheaths (400  $\mu m$  distance from pore surface) as compared to the barium concentrations in the soil matrix [...]*

**Comment 8:**

Table 1: Please indicate sampling depths and soil horizons for all soils you used.

**Reply 8:**

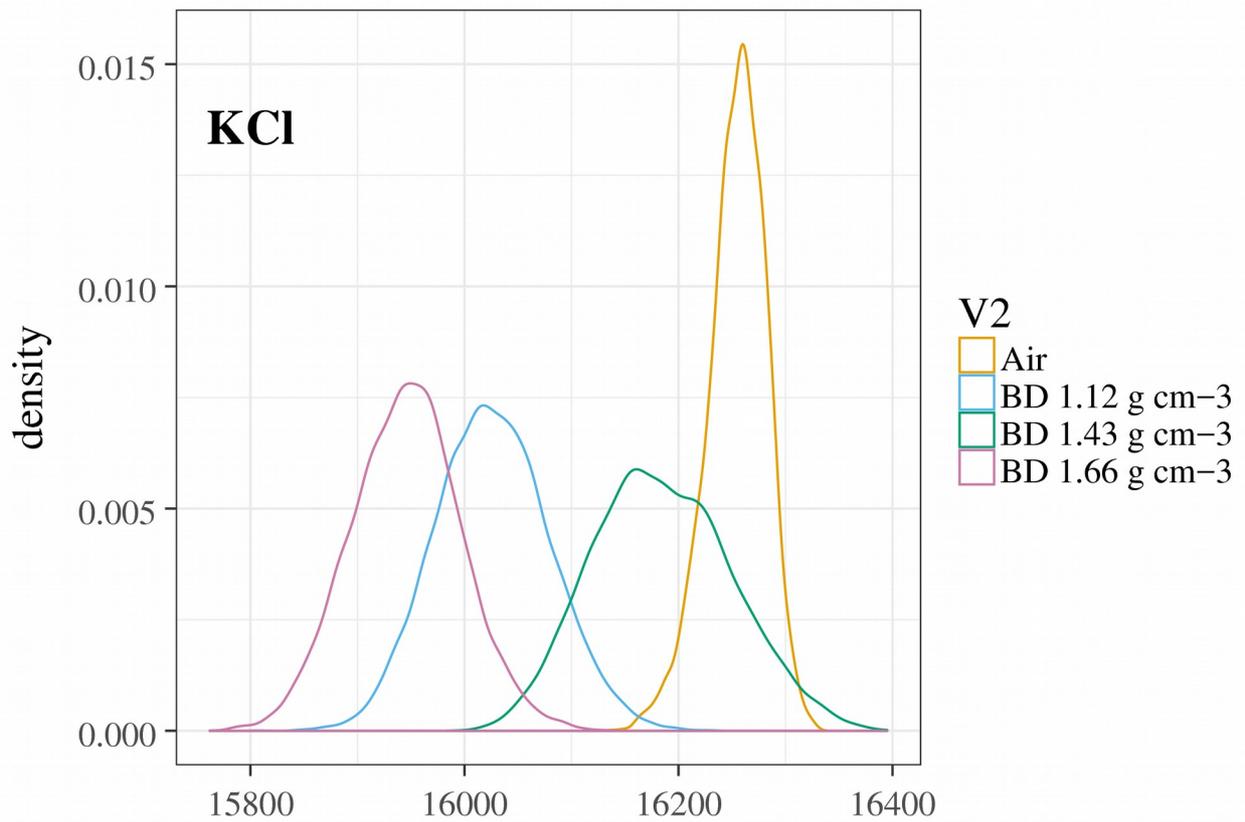
We will add the information on sampling depth to the bog and forest soil in Table 1.

**References:**

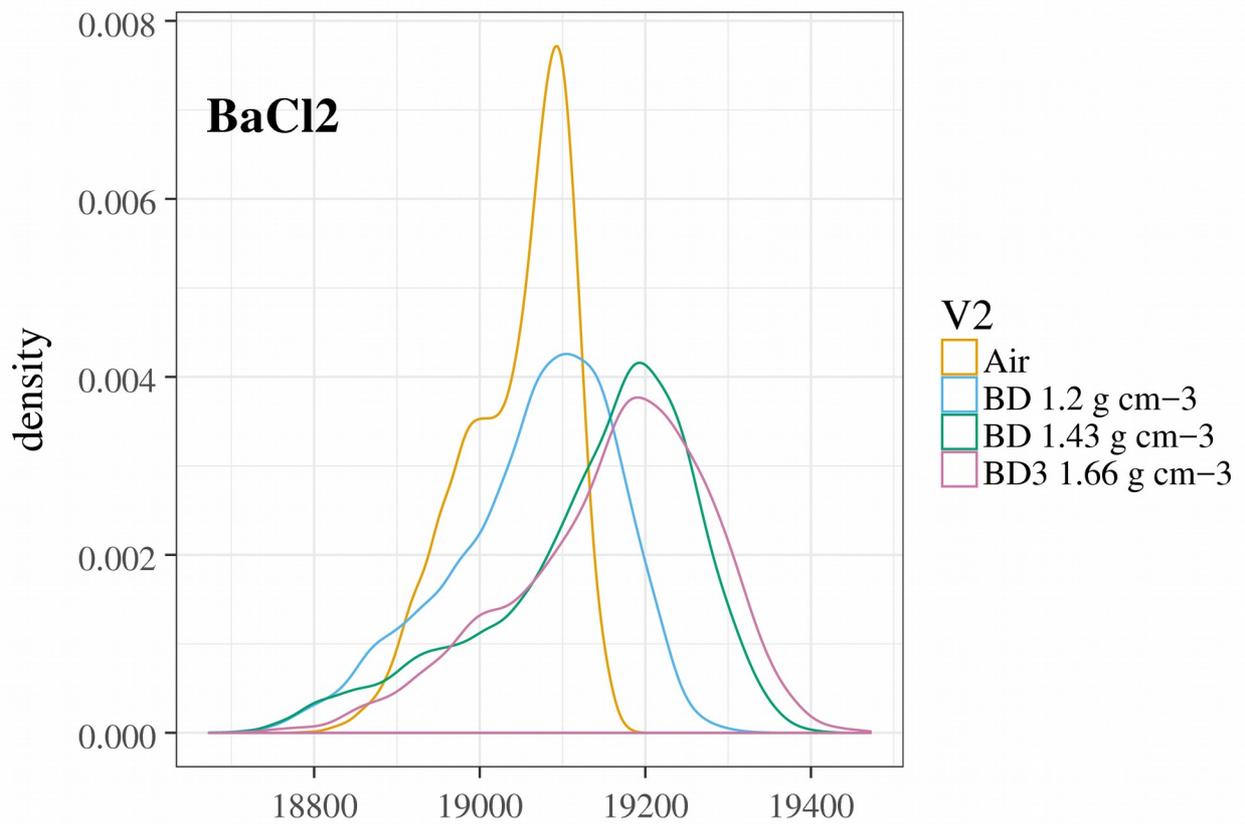
- Koestel, J., Larsbo, M., 2014. Imaging and quantification of preferential solute transport in soil macropores. *Water Resour. Res.* 50, 4357–4378. doi:10.1002/2014WR015351
- Thomas, G.W., 1982. Exchangeable cations, in: *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*. Madison, USA, pp. 154–157.
- Weller, U., F. Leuther, S. Schlüter, H.-J. Vogel: Quantitative analysis of water infiltration in soil cores using x-ray, *Vadose Zone Journal* (in press), url: <https://dl.sciencesocieties.org/publications/vzj/first-look>

**Table 1.** Average gray values (GV) of the KCl and BaCl<sub>2</sub> solutions of contrast images with different bulk densities (BD) and its effect on the resulting contrast between the GV of the BaCl<sub>2</sub> and the KCl solutions.

	<b>Air</b>	<b>BD 1.12 g cm<sup>-3</sup> Silty clay</b>	<b>BD 1.43 g cm<sup>-3</sup> Silty clay</b>	<b>BD 1.66 g cm<sup>-3</sup> Sand</b>	<b>units</b>
KCl solution	16254.30	16026.01	16184.68	15945.33	GV
BaCl <sub>2</sub> solution	19043.46	19063.68	19136.38	19159.73	GV
Resulting contrast	2789.16	3037.68	2951.70	3214.41	GV
Difference in contrast compared to the air sample	0	8.91	5.83	15.25	%

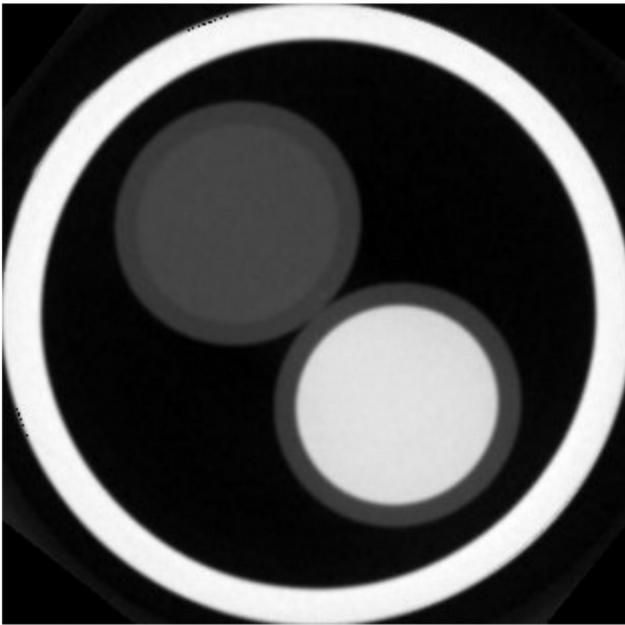


**Figure 1.** Gray value distributions of the KCl solution from four different contrast images. Yellow: with an air-filled aluminium column, blue, green and purple: with packed soil but different bulk densities (BD).

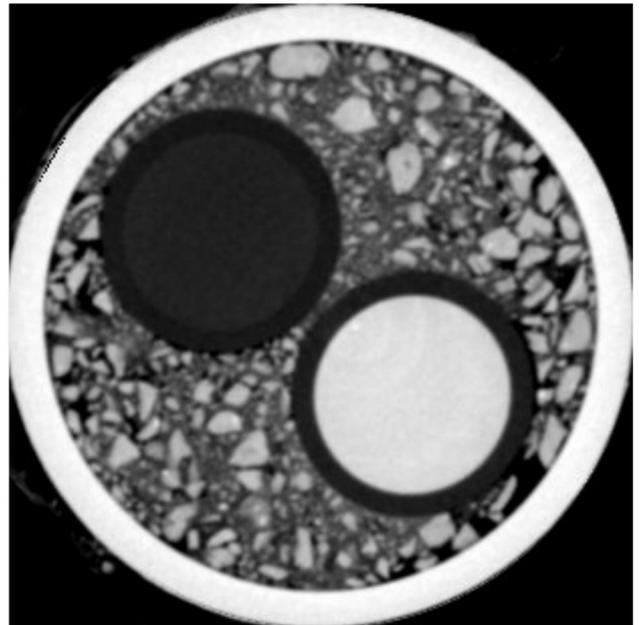


**Figure 2.** Gray value distributions of the BaCl<sub>2</sub> solution from four different contrast images. Yellow: with an air-filled aluminium column, blue, green and purple: with packed soil but different bulk densities (BD).

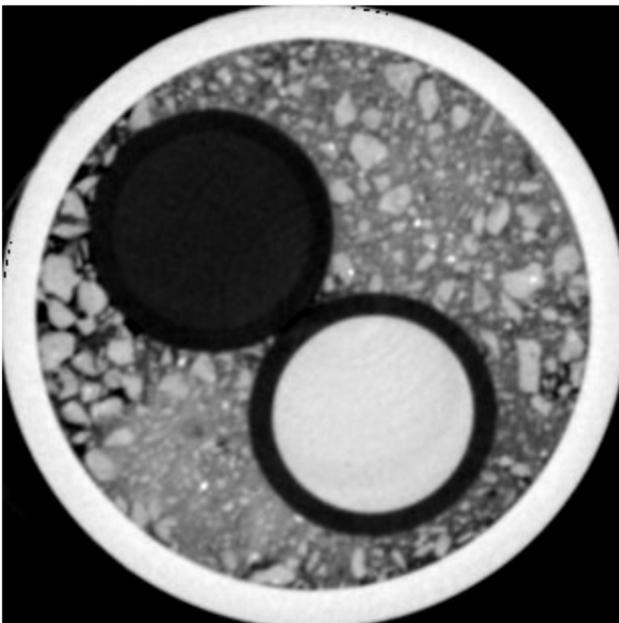
Air



BD  $1.12 \text{ g cm}^{-3}$



BD  $1.43 \text{ g cm}^{-3}$



BD  $1.66 \text{ g cm}^{-3}$

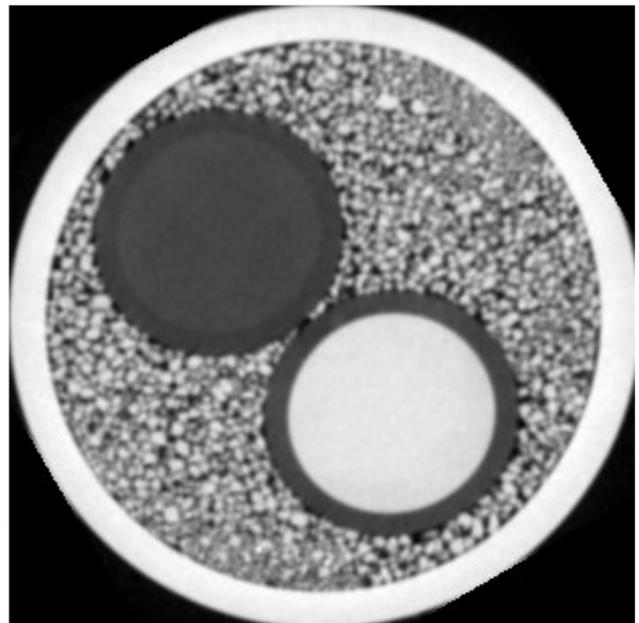
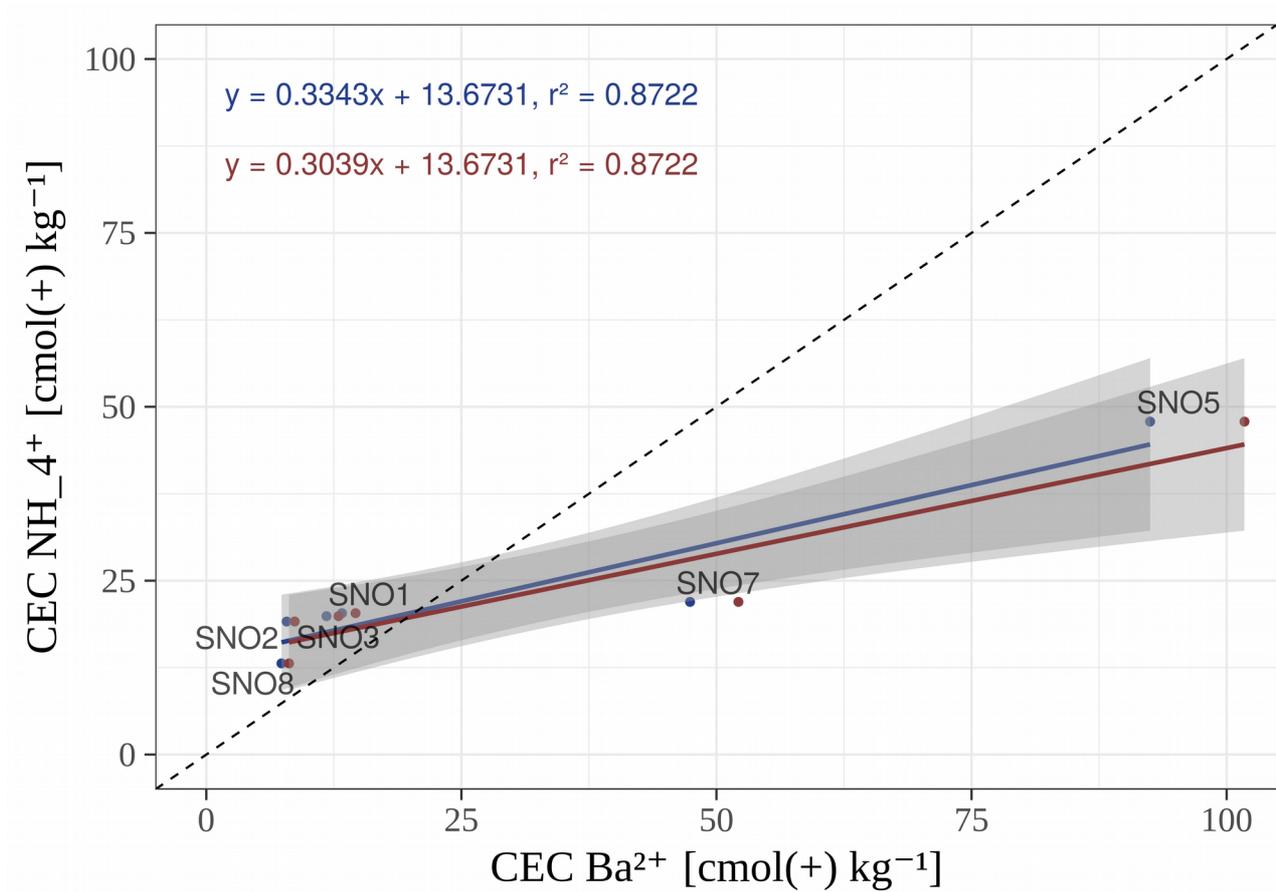


Figure 3. Cross-sections of four different contrast images.



**Figure 4.** Relation between the cation exchange capacity (cmol(+) kg<sup>-1</sup>) measured with NH<sub>4</sub><sup>+</sup> and the CEC Ba<sup>2+</sup> obtained from the difference image analysis of the natural soil samples. Blue represents the original data and red the adjusted data. Blue and red lines represent linear models with its 95 % confidence interval in gray ( $p < 0.01$ ). Dotted line has slope 1.