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Key Points:

- Water flow in near-saturated sand is investigated by neutron imaging
- Entrapped air is redistributed from fine material to coarse material
- Entrapped air bubbles in preferential pathways reduce hydraulic conductivity

Supporting Information:

- Readme
- Figure S1
- Figure S2
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Water and entrapped air redistribution in heterogeneous sand sample: Quantitative neutron imaging of the process

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Abstract Saturated flow in soil with the occurrence of preferential flow often exhibits temporal changes of saturated hydraulic conductivity even during the time scale of a single infiltration event. These effects, observed in a number of experiments done mainly on heterogeneous soils, are often attributed to the changing distribution of water and air in the sample. We have measured the variation of the flow rates during the steady state stage of the constant head ponded infiltration experiment conducted on a packed sample composed of three different grades of sand. The experiment was monitored by quantitative neutron imaging, which provided information about the spatial distribution of water in the sample. Measurements were taken during (i) the initial stages of infiltration by neutron radiography and (ii) during the steady state flow by neutron tomography. A gradual decrease of the hydraulic conductivity has been observed during the first 4 h of the infiltration event. A series of neutron tomography images taken during the quasi-steady state stage showed the trapping of air bubbles in coarser sand. Furthermore, the water content in the coarse sand decreased even more while the water content in the embedded fine sand blocks gradually increased. The experimental results support the hypothesis that the effect of the gradual hydraulic conductivity decrease is caused by entrapped air redistribution and the build up of bubbles in preferential pathways. The trapped air thus restricts the preferential flow pathways and causes lower hydraulic conductivity.

1. Introduction

Saturated hydraulic conductivity (K_s) measured in steady state flow laboratory experiments often varies in time in the case of prolonged infiltration. When the experiment is repeated on the sample, a different value of K_s may be obtained. Long-term K_s changes are often attributed to changes of the pore space geometry related to the growth of bacteria film [Allison, 1947; Thullner, 2010] or to the development of surface seals [Fohrer et al., 1999]. Even when the soil structure remains unaltered, the hydraulic conductivity can vary in time due to the changing amount of entrapped gas bubbles in pores [e.g., Christiansen, 1944]. With the presence of entrapped air bubbles, the soil cannot still be considered to be fully saturated, and therefore, the term quasi-saturated hydraulic conductivity (K_{QS}) suggested by Faybishenko [1995] is more appropriate for characterizing the sample. There is a wealth of experimental evidence showing the extent of the impact of entrapped air on the flow. Zlotnik et al. [2007] reviewed early experiments and found that K_{QS} of sand samples can be reduced by 5–50% due to the presence of entrapped air when compared to the fully saturated state. Even more pronounced K_{QS} changes due to the presence of entrapped air were observed on intact samples of sandy loam soils by Faybishenko [1995].

In the laboratory, the effects of entrapped air can be easily avoided through an initial wetting of the sample under vacuum [e.g., Smith and Browning, 1946], while in the field, the air is trapped naturally during infiltration and its impact on the flow cannot be overlooked. Heilwell et al. [2004] studied the dissolution of entrapped air and its effect on permeability in field conditions below a recharge pond by a gas-partitioning tracer test and found the amount of entrapped air to be 7–26% of the porosity. The entrapped air clearly causes considerable changes of K_{QS} ; however, the dynamics of entrapped air is not yet fully understood and not considered in simulation models.

Recently, noninvasive imaging techniques have provided detailed insight into materials including the flow in porous media and can also be employed to locate the bubbles of entrapped air. However, not many experiments have been focused on the imaging of blobs of entrapped air in natural soils. *Amin et al.* [1997] discovered the pockets of entrapped air in two-dimensional images obtained by magnetic resonance imaging (MRI) conducted on sandy loam soil (Dystric Cambisol), the same soil in which *Cislerova et al.* [1990, 1988] detected large differences in the steady state infiltration rate between two recurrent ponded infiltrations in the field and in the laboratory. MRI (a single horizontal 2-D slice) of recurrent ponded infiltration on a small sample of the same soil in the study of *Votrubova et al.* [2003] and *Cislerova et al.* [2002] showed that many regions from which water drained out after the first infiltration were not fully refilled during the second infiltration performed under the exact same boundary conditions. The findings were later confirmed by *Snehota et al.* [2010] in a similar experiment done on the same soil with concurrent three-dimensional (3-D) MRI. While the analysis of the MRI provides good estimates of the difference of the entrapped air volume between two reference stages [*Jelinkova et al.*, 2011], the spatial information is often blurred by distortions of the magnetic field [*Hall et al.*, 1997; *van As and van Dusschoten*, 1997] in some natural soils. Furthermore, the MR relaxometry technique needed to obtain a quantitative measurement of water content distribution is often quite time consuming (hours). The geometry is better represented by X-ray computed tomography, which is also substantially faster. In a study of potassium iodide transport in an undisturbed soil column of Hagerstown silt loam, *Luo et al.* [2008] detected air blobs entrapped in large biopores through the use of 3-D X-ray computed tomography (up to 30% air filled macroporosity in some horizontal slices) and suggested that further research is needed to explain how the air is entrapped and changed under different conditions. X-ray CT tomography is rather insensitive in the detection of water, and due to the similar density of water and the bulk density of soil it is relatively difficult to trace water content changes in the images.

Due to its higher imaging contrast between water and other soil constituents neutron imaging has attracted increasing attention in soil physics. Neutron imaging is able to map the water content distribution in soils in 2-D [e.g., *Badorreck et al.*, 2010; *Carminati et al.*, 2007] and 3-D [e.g., *Moradi et al.*, 2011].

The aim of the present study is to visualize and quantify the entrapped air redistribution during a ponded infiltration experiment using neutron imaging. The study objectives are (i) to study the mechanism of wetting front propagation in a packed heterogeneous sample and the consequent air entrapment at the very beginning of the infiltration and (ii) to monitor mass transfers of water and air during additional steady state stages of the infiltration-outflow experiment.

2. Material and Methods

2.1. Sample Description

The sample was carefully packed into a quartz glass column with an inner diameter of 34 mm. The plastic cylinders, used temporarily as a support, helped to create the axial symmetrical architecture in the sample built up from three sandy materials (see Figure 1). The aim was to reproduce the material distribution patterns observed in many soils, e.g., Cambisols [*Cislerova and Votrubova*, 2002; *Cislerova et al.*, 2002], in whose dense regions (stones and fine soil matrix) of lower hydraulic conductivity are surrounded by coarse weathered material of the hydraulic conductivity of 2 or more orders of magnitude higher. Such soils are common in many mountainous headwater catchments where soil profile saturates frequently due to high-intensity rainfall and shallow impermeable bedrock [*Kulasova et al.*, 2014]. In sample prepared for this experiment, a matrix formed by fine corundum sand (FS) (sand for sand tank apparatus, F220 according the FEPA Standard 44-D-1986, Synthetic sand, Eijkelkamp, Netherlands) was surrounded with a structure of coarse quartz sand (CS) (FH31, Quarzwerke Frechen, GmbH, Frechen, Germany) representing preferential flow pathways. The preferential flow pathways formed 38.6% of the whole sample volume and were interrupted in selected verticals by insets of medium coarse quartz sand (MS) (ST56, Sklopisek Strelec a.s., Czech Republic), the inner geometry of the sample is illustrated in Figure 1. Inner structure of the sample can resemble the dual permeability media considered in dual permeability approach [*Gerke et al.*, 2013]. The sample was saturated from the bottom during the packing. The cross-sectional area of the soil sample was 9.08 cm² and its total volume was 79.44 cm³. At the top, a coarse circular nylon mesh with cutout indentions on the perimeter protected the surface of the soil while allowing the free movement of air.

Figure 1. (left) Diagram of the composition of the packed sample. Circles indicate the position of medium coarse sand. (right) X-ray tomogram cutout of the packed sample. X-ray imaging was done on a partly wet sample to enhance the contrast between fine and coarse sand sections (more water was retained in the fine sand due to capillary forces). Lighter gray values represent the regions of fine sand that have a higher total density. Cylindrical blocks of fine sand FS1 through FS4 are annotated for the description of processes later in the text.

Grain size distribution of three sands obtained by sieving and hydrometer methods is shown in Figure 2. Other physical and hydraulic properties of the three sands were determined by measuring small homogeneously packed samples. Retention curves were measured in the sand tank and in the pressure extractor [Klute, 1986] and fitted with the van Genuchten model. K_s was determined by the falling head method [Klute and Dirksen, 1986]. For the physical properties of the three sands, see Table 1 and Figure 2.

2.2. Experimental Setup

The bottom of the sample was provided with an aluminum funnel (see Figure 3). The soil was supported by a coarse nylon mesh (300 μm mesh opening) stretched over a perforated aluminum plate. The funnel was fitted in an aluminum sample holder

attached to a positioning turntable in a NEUTRA beam line (<http://www.psi.ch/sinq/neutra>). Digital peristaltic pumps (Reglo Digital 4 Channels, ISM 597 D, Ismatec®) supplied heavy water to the top of the sample. The data logger (CR3000, Campbell Scientific, Logan, Utah, USA) secured a constant level of ponding by dosing the known amount of water each time the water level switch indicated that the water level had dropped below a predefined level. The outflow was collected in a miniature outflow collector similar to the one used by Stingaciu *et al.* [2010], which consisted of a small funnel connected through 1.5 mm internal diameter tubing to a peristaltic pump and further to a fraction collector. The design assured that any volume dripping into the funnel was transferred into the vial in the fraction collector with a known constant time delay.

2.3. Neutron Imaging

Neutron radiography (NR) was used in the experiments to monitor the time resolved progress of the fast transient infiltration, while the neutron tomography (NT) method was utilized to produce 3-D images of the water distribution within the sample during selected steady state stages of the experiment. The principle of the NR and NT imaging methods are described in detail elsewhere [e.g., Lehmann, 2009].

Figure 2. Particle size distribution of fine (FS), medium coarse (MS), and coarse (CS) sands used for sample packing.

NR images are the result of the transmission measurement using a two-dimensional area detector plane perpendicular to the neutron beam.

For the NT imaging, the sample is rotated in small angular steps covering the total angle range of at least 180° . The tomography reconstruction algorithm [Natterer, 2001] then produces the 3-D volume data of linear attenuation coefficients describing the composition of the sample.

Neutron imaging was carried out at the Neutron Transmission

Table 1. Physical Properties of Three Sand Grades^a

Material	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Residual Water Content θ_r (cm ³ /cm ³)	Saturated Water Content θ_s (cm ³ /cm ³)	α (1/cm)	n	K_s (m/s)
Coarse sand	1.71	2.68	2.80×10^{-2}	0.408	3.7×10^{-2}	5.913	1.29×10^{-4}
Medium coarse sand	1.66	2.68	2.10×10^{-2}	0.476	3.1×10^{-2}	2.295	7.26×10^{-5}
Fine sand	1.88	3.92	1.95×10^{-1}	0.511	1.7×10^{-2}	2.225	1.97×10^{-5}

^aBulk density and the van Genuchten model fitting parameters for the retention curves of the three sands.

Radiography (NEUTRA) beam line of the Swiss Neutron Spallation Source (SINQ) at the Paul Scherrer Institute (PSI) in Villigen, Switzerland [Lehmann *et al.*, 2001]. The parameters of the neutron beam were as follows: a neutron flux of 1.1×10^7 neutrons cm⁻² s⁻¹, with a thermal Maxwellian spectrum with the most probable energy of 25 meV and the collimation ratio of L/D 350. The detector was a 100 μ m thick LiF/ZnS scintillator screen photographed by a cooled CCD camera. The image exposure time was 6 s. The field of view of the detector was 112.2 mm, the image matrix size was 1024 $\times$ 1024 pixels, which resulted in a nominal pixel size of 0.11 mm $\times$ 0.11 mm. The sample was fixed on a rotating table using a custom made aluminum stand. For NT, 201 radiographs were taken for each tomography. A reconstruction algorithm then produced a 3-D map of the local neutron attenuation coefficients. The reconstruction was done using the MUHREC software package [Kaestner, 2011].

2.4. Infiltration-Outflow Ponding Experiment Observed by Neutron Imaging

Before the experiment, the sample was dried in the laboratory oven at 105°C for 24 h. Since the water content at the beginning of the infiltration experiment was close to zero, no H₂O was present in the sample to mix with D₂O during the experiment. Beginning the experiment from a desiccated state allowed for the subsequent evaluation of water content by neutron radiography, as an image of the dry sample containing no water could be taken to obtain an ideal reference image. An independent bench test revealed that none of the three sands exhibited hydrophobicity when oven dried.

To obtain the reference image, a tomogram of the dry sample was acquired (by NT). For all the images, the sample stayed in the same fixed position. The flow experiment consisted of one infiltration run followed by a gravity drainage. A constant upper boundary condition was set up, the pressure head was maintained at 0.6 cm (ponding).

2.5. Quantitative Evaluation of the Water Content From Neutron Imaging

In neutron imaging, the bulk properties of materials can be calculated when the attenuation in the object is described quantitatively. The exponential law of attenuation (Beer-Lambert) can be applied directly

Figure 3. Schematic drawing of the experimental setup used in the NEUTRA beam line.

according to (equation (1)) [Kasperl and Vontobel, 2005]. The transmitted intensity I of the uncollided neutron beam is

$$I = I_0 e^{-\Sigma d} \quad (1)$$

where I_0 is the intensity of the beam before it enters the sample, I is the intensity of the beam after it passes through the sample, the attenuation coefficient Σ (cm^{-1}) comprises the atom density and the microscopic cross sections associated with various interactions of neutrons passing through the object of the thickness d (cm). Kang *et al.* [2013] expressed the image intensity behind the dry I_{DRY} and wet I_{WET} samples corrected for spatial and temporal fluctuations of the neutron beam, spatial variability of the scintillator and the noise of the CCD camera

$$I_{\text{WET}} = f_r \frac{I_{\text{WET_SAMPLE_IMAGE}} - I_{\text{DC}}}{I_{\text{OB}} - I_{\text{DC}}} \quad (2)$$

$$I_{\text{DRY}} = f_r \frac{I_{\text{DRY_SAMPLE_IMAGE}} - I_{\text{DC}}}{I_{\text{OB}} - I_{\text{DC}}} \quad (3)$$

where f_r is the rescale factor to correct the neutron temporal beam fluctuations, $I_{\text{WET_SAMPLE_IMAGE}}$ is the raw image of the wet sample, $I_{\text{DRY_SAMPLE_IMAGE}}$ is the raw image of the dry sample, I_{DC} is the image taken with neither beam nor sample, and I_{OB} is the open beam image containing the information on spatial variation of the beam without the sample [Moradi *et al.*, 2009].

$$\Sigma_{\text{WET}} d_{\text{WET}} = \Sigma_{\text{D}_2\text{O}} d_{\text{D}_2\text{O}} + \Sigma_{\text{DRY}} d_{\text{DRY}} \quad (4)$$

$$\Sigma_{\text{D}_2\text{O}} d_{\text{D}_2\text{O}} = \ln(I_{\text{DRY}}) - \ln(I_{\text{WET}}) \quad (5)$$

$$d_{\text{D}_2\text{O}} = \frac{\ln\left(\frac{I_{\text{DRY}}}{I_{\text{WET}}}\right)}{\Sigma_{\text{D}_2\text{O}}} \quad (6)$$

where $\Sigma_{\text{D}_2\text{O}}$ is the linear attenuation coefficient of heavy water and $d_{\text{D}_2\text{O}}$ is the thickness of the water.

The voxel gray values in neutron tomograms represent the attenuation coefficient mixture of materials contained in particular voxels. The water content θ^{ijk} in each voxel (i, j, k) has a linear relationship with the voxel gray value [Kaestner *et al.*, 2007] and can be derived as follows

$$\theta^{ijk} = \frac{A_{\text{WET}}^{ijk} - A_{\text{DRY}}^{ijk}}{\Sigma_{\text{D}_2\text{O}}} \quad (7)$$

where A_{WET}^{ijk} and A_{DRY}^{ijk} is the average of the gray values in the voxel (i, j, k is the position of the voxel in the tomogram). The subscript *WET* denotes the tomogram of the wet sample and *DRY* denotes the tomogram of the dry sample, θ^{ijk} is the water content of the voxel.

2.6. Bench Experiment to Determine K_s on Full Saturation of the Sample

To measure the “true” K_s of a fully saturated sample, the infiltration with degassed water was performed in the laboratory. The setup used for neutron imaging was modified by the inclusion of an in-line membrane degasser (Liqui-Cel MiniModule G541, Membrana GmbH, Germany) on the inlet tubing. The infiltration-outflow experiment was carried out for 24 h until no change of the infiltration rate was achieved.

3. Results and Discussion

3.1. Hydraulic Data

Figure 4 provides the summary of the outflow volumetric flux data recorded during the infiltration-outflow experiment and the time windows of the acquisition of neutron tomography images T0 through T4. The inflow data are also plotted in Figure 4. It was found that due to gradual plastic deformation of the Tygon tubing in the peristaltic pump, the dose volume changed over time. The inflow data were corrected based on additional five test runs in which long-term changes of the peristaltic pump dose volumes were determined gravimetrically. It was determined that rate of dose volume reduction was $6.5 \times 10^{-3}\%$ of the dose volume per minute. The measurement accuracy, that reflects short-term variations of the dose volume, is

Figure 4. Overview of inflow (solid line) and outflow flux (circles with error bars) rates and times of neutron tomography images acquisition (gray columns).

indicated by error bars in Figure 4. Despite the suboptimal accuracy of peristaltic pump metering, the data show that trends of inflow and outflow volumetric fluxes are the same. Note, that plastic deformation of the Tygon tubing and the corresponding decreasing dose volume did not affect the flow rate through the sample since the boundary condition at the surface was determined by pressure head and the exact ponding level was ensured using a level sensor regardless the dose size.

The outflow flux density quickly reached the quasi-steady rate of 0.4 cm min^{-1} , soon after outflow appeared at the bottom of the sample. The flow rate was then gradually decreased for 170 min approximately following a linear trend until it reached a flow rate of 0.31 cm min^{-1} . The gradual decline of the flow rate continued approximately until 290 min after beginning the infiltration, with a quasi-steady state volumetric flux (q_{QS}) value of $0.296 \text{ cm min}^{-1}$, and then the flow remained steady until the end of the infiltration at the 380 min mark. The occurrence of the gradual decrease of q_{QS} in the first hours of the quasi-steady state stage of infiltration is consistent with the outcomes of our earlier experiments conducted on Cambisols [Cislerova et al., 1990; Jelinkova et al., 2011]. They are also in accord with observations of Faybishenko [1995] performed on large (2–5 m high) undisturbed columns of nonswelling loam.

3.2. Two-Dimensional Neutron Imaging

Neutron images of water can be significantly affected by neutron scattering and beam hardening which may bias the local water content measurements. To minimize these adverse effects, heavy water was used, since deuterium scatters neutrons less than hydrogen.

The high level of agreement between the volume of water derived from neutron projections and the volume of water actually measured for the first four recorded NR images is shown in the supporting information Figure S1. Images acquired later were not used for the comparison because the images already included the layer of ponded water on the sample surface, which gradually became too thick to be measured by neutron imaging.

Figure 5 demonstrates the dynamics of the sample wetting. The acquisition time of each image was 6 s. The time given in Figure 5 indicates the middle of the acquisition of a particular image. The wetting started on the left side of the top of the sample below the inlet tubing where water quickly penetrated through the upper coarse sand layer and seeped into the fine sand block FS1 as shown in the image taken at 6 s after

Figure 5. Sequence of neutron radiography images showing the beginning of infiltration into the composed sample. The images are referenced to the image of the dry sample, each exposed pixel, thus, references the water. The blue horizontal stripe in the middle of the FS4 block is an artifact from the rubber o-ring. Number of seconds indicate time since infiltration began.

the beginning of infiltration. The image acquired at 23 s after the beginning already depicts the wetting front propagation into the fine sand block FS2. Water is almost missing in the thin layer of coarse sand above the second fine sand block FS2. The same behavior was captured by the image at the 40 s mark, which shows that while the coarse sand between blocks FS2 and FS3 still contained very little wetting, water had already flowed into the block FS3. This effect is clearly due to higher unsaturated hydraulic conductivity under lower pressure head. Analysis of unsaturated hydraulic conductivity derived by van Genuchten-Mualem model with parameters from Table 1 shows that the cross point of hydraulic conductivity functions of fine and coarse sand is at pressure head -42.6 cm. When pressure head approaches zero the coarse sand becomes more conductive than fine sand. This corresponds to the observed behavior in the NR image taken in time 40 s, where water flowed primarily from the coarse sand channel in the axis of

FS2 block since the FS3 block is wetted in its upper central part first. The wetting front reached the bottom of the sample in 141 s.

It is reasonable to assume that the thin unsaturated layer developed due to the draining of the coarse sand as water is attracted into the next fine sand block by a strong gradient of capillary forces. It also can be expected that the flow through the layered sand is unstable and forms fingers [e.g., Hill and Parlange, 1972; Glass *et al.*, 1989], which would be even more pronounced in heterogeneous sand.

It is clear that the wetting front bypasses parts of the coarse sand regions leaving clusters of entrapped air above the wetting front. As in the findings of Geistlinger *et al.* [2014] who visualized the entrapped air clusters in a sample of packed glass beads in which water imbibed through the bottom, it is clear that the size of the clusters is several times larger than the grain size of the porous media. The precise mechanism of air trapping cannot be rendered exactly given the relatively sparse time and spatial resolution and mainly due to the fact that the wetting front motion was imaged only through the use of neutron radiography, i.e., as a 2-D projection.

One possible explanation that could be suggested for the air trapping in coarse sand material is that the layering of the coarse sand and the related variation of hydraulic permeability causes unsaturated flow in certain small regions of the coarse sand. Unsaturated conditions can lead to the finger formation. Then, after the bottom of the sample is also saturated, the fingers widen and eventually the air phase remains in the form of isolated entrapped air clusters.

3.3. Three-Dimensional Neutron Imaging

The bubbles of entrapped air along with the overall lower water saturation of the coarse sand regions during steady state flow are visible in the tomography images (Figure 6). In contradiction to the gravity driven preferential flow through fractures and macropores in which the flow in the soil matrix (fine material region) is bypassed through the coarse material regions [Dusek *et al.*, 2012], such an event was not fully reproduced in the current experiment. However, the following analysis of the tomography images shows that even the fine sand regions were not fully saturated during the wetting front advancement.

Figure 6 depicts the development of the spatial and temporal distribution of water content in the sample. The NT data T1 taken at the beginning of the quasi-steady stage of the experiment show that the mean water content of the fine sand regions was $0.3938 \text{ cm}^3 \text{ cm}^{-3}$, which is less than the corresponding saturated water content determined in the bench experiment (see Table 1). In the coarse sand regions, the number of trapped air bubbles was detected. The mean water content of the coarse sand regions of the sample was $0.3332 \text{ cm}^3 \text{ cm}^{-3}$.

In Figure 6a, small fissures can be seen in the fine sand block FS1 during the infiltration experiment between the neutron tomography images T1 and T2. A detailed analysis of the local attenuation coefficients showed that these fissures were air filled. Since no external mechanical forces were exerted on the sample during the experiment it is reasonable to assume that the fissures were created by air bubbles. The coarse sand fraction region closely below the FS1 block slightly expanded in a similar manner. Due to this slight volume change, the top of the fine sand block FS1 moved up by approximately 0.8 mm and consequently an artifact appeared when the tomograms were subtracted (see Figure 6b, T2-T1).

3.4. NT-Derived Water Content Differences

To quantify the water content development in coarse and fine sand, the volume of the sample was divided into three vertical sections characterized by the depths 0–2.4 cm (top region), 2.4–6.5 cm (middle region), and 6.5–8.5 cm (bottom region) indicated in the Figure 6a. Figure 7 shows the development of the water content in the form of a box plot. The middle section provided the most reliable results. The fraction of the coarse sand in the middle section represented 40% of the volume of the sample. The average water content of the sample derived from the tomograms was smaller at the beginning of the quasi-steady state stage of the experiment (tomogram T1) than the water content reached at the time before the inflow was turned off (tomogram T2). In contrast to general perception, the overall water content increase of the sample was accompanied by a gradual outflow rate decrease, as seen in Figure 4. For the quasi-steady state stage phase of the experiment, the effective hydraulic conductivity of the sample was calculated using Darcy law based on the known boundary conditions for water in the sample. The constant pressure head equal to the ponding height was assumed at the top while zero pressure head (seepage face boundary condition triggered to constant pressure head) is considered at the bottom. The effective hydraulic conductivity of the sample is then

Figure 6. Results of NT visualized as a vertical section of the 3-D image. (a) Water content maps derived from NT images T1 (at the beginning of the quasi-steady state), T2 (before infiltration was stopped), T3 (during drainage), T4 (after drainage). (b) Maps of water content differences.

proportional to the outflow rate, which means that the quasi-saturated hydraulic conductivity of the sample decreased with the increased water content, contrary to logical expectations. This is, however, consistent with the results of similar experiments conducted on large soil monoliths of undisturbed heterogeneous soils by Faybishenko [1995] or experiments done on medium sized undisturbed columns of heterogeneous soil by [Snehota *et al.*, 2002]. It should be noted that the rate of additional water retention is about 3 orders of magnitude smaller than the flow rate change during the quasi-steady state stage of the experiment.

The flow rate decrease can be well explained by the transfer of water from coarse to fine sand. The exchange of water was most significant in the middle section of the sample, i.e., at a depth of 2.4–6.5 cm where water content in coarse sand decreased by $0.0276 \text{ cm}^3 \text{ cm}^{-3}$. During the same time period, the water content of fine sand in the middle section of the sample gained 0.0467 cm^3 of water, which represents the volume averaged water content gain of $0.0173 \text{ cm}^3 \text{ cm}^{-3}$.

Total mean water content in the sample rose by $0.0196 \text{ cm}^3 \text{ cm}^{-3}$ between the T1 and T2 tomography runs, while the domain of the fine sand itself gained $0.0392 \text{ cm}^3 \text{ cm}^{-3}$ and the domain of coarse sand lost $0.009 \text{ cm}^3 \text{ cm}^{-3}$. It is reasonable to assume that due to overall slow water uptake the corresponding air content decreased by $0.0196 \text{ cm}^3 \text{ cm}^{-3}$. This represents 1.43 cm^3 of air which was removed from the sample between the imaging of T1 and T2, while coarse sand regions accommodated 0.27 cm^3 of air during the same period, a large portion of which was probably transferred from the fine sand region which lost 1.7 cm^3 .

Figure 7. Box plot showing time development of the water content in the top part of the sample. The boxes indicate the median, 25th and 75th percentiles; the ends of the whiskers show the 5th and 95th percentiles.

The increase in moisture content in fine sand is caused by a gradual equilibration of the matric potential of the water in the column. However, at pressure heads close to zero, and thus, below the air entry value of both coarse and fine sands, the air cannot move freely in the porous system.

The form in which the air is being transferred between domains and is excluded from the sample remains unclear. According to *Faybishenko* [1995] a certain portion of the entrapped air can be considered to be mobile and could travel in the soil in the form of air bubbles for several hours of the quasi-steady state infiltration. In the small sample under study, we may assume that the release of individual bubbles from the sample might cause abrupt changes of hydraulic conductivity. Since only gradual changes of outflow rates were observed, such an explanation does not seem to apply in the current study.

3.5. Entrapped Air Redistribution

Corey and Brooks [1975] suggested that the gaseous phase may be transported through restricting liquid films by diffusion. Therefore, it can be hypothesized that the air transfer takes place in the form of dissolved gas due to air supersaturation caused by the dissolution of air bubbles in the regions filled with fine sand and by ebullition or air bubbles in the coarse sand. As pointed out by, e.g., *Holocher et al.* [2002], water entering the soil is in equilibrium with the atmosphere and dissolved gas excess arises from the dissolution of entrapped air bubbles: either due to the change of water pressure or due to capillary pressure on the curved air—pore water interface of the air bubbles. The mass transfer is greatly enhanced by the water flow [*Holocher et al.*, 2003; *Klump et al.*, 2008]. It is possible that the excess air from tiny bubbles in the fine sand domain of the sample causes the growth of larger bubbles in the coarse sand. This process is further

enhanced by capillary forces which attract water into the fine sand and can eventually compress the air pressure in the fine material.

The latter explanation of the residual air transfer is supported by the fact that the upper section of the sample gained water content in both the fine ($0.0212 \text{ cm}^3 \text{ cm}^{-3}$) and coarse sand ($0.0110 \text{ cm}^3 \text{ cm}^{-3}$) fractions. This may occur because air bubbles dissolution prevailed over the bubbles ebullition.

Note that between imaging of the tomograms T1 and T2 approximately 0.9 L of water passed through the sample. Considering that the air solubility at the temperature of 25°C is 0.019 cm^3 at standard atmospheric pressure (SPT)/ m^3 , this amount of water carried approximately 17 cm^3 SPT of dissolved air. Thus, the amount of dissolved air transported through the sample is significant.

The question is whether the dissolution rate justifies the measured increase of water in the fine sand. Air bubbles were observed in both the fine and coarse sands in tomography images T1 and T2, while the latter showed larger bubbles substantially exceeding the pore size. However, this is not unexpected. *Geistlinger et al.* [2014] discovered in an experiment conducted on packed glass beads imaged by micro focus X-ray tomography that more than 50% of the air volume is trapped in the form of bubbles larger than the grain size, often in rather large multipore clusters. *Suekane et al.* [2010] observed both single pore and multiple pore N_2 bubbles in the sample of Berea sandstone.

The mass transfer of air from entrapped air bubbles was estimated following the approach of *Geistlinger et al.* [2005] and *Holocher et al.* [2003]. The calculation is presented fully in the supporting information Text S2, while here only the results will be discussed. The aim of the calculation, which was done without spatial discretization, was to determine a theoretical initial radius of the bubbles which would lead to such a dissolution rate of the bubbles in the fine sand with the average water content increasing by $+0.039 \text{ m}^3 \text{ m}^{-3}$ between the T1 and T2 tomograms as observed in the experiment. For our case, we calculated the dissolution of the air bubbles composed, for simplicity's sake, of only O_2 (21%) and N_2 (79%) gasses. Air entering the sample was assumed to be equilibrated with the atmosphere. Only one size class of the bubbles was considered. The results show a theoretical situation with an average population of 23.8 bubbles per cm^3 of the sample with an initial radius of 1.055 mm and a dissolution rate of $4.94 \cdot 10^{-6} \text{ m}^3 \text{ STP s}^{-1} \text{ m}^{-3}$ contracting to a radius of 0.921 mm at the average dissolution rate of $4.62 \cdot 10^{-6} \text{ m}^3 \text{ STP s}^{-1} \text{ m}^{-3}$. Clearly, the dissolution of the bubbles increases the air concentration to a new, higher, equilibrium concentration. The initial size of the bubbles in the coarse sand was estimated in order to match the known decrease of the water content in the coarse sand due to bubble growth. It was assumed that the air concentration in the water entering the coarse sand is equal to the equilibrium concentration of water from the fine sand.

The calculation of the entrapped air dissolution suggested that the hypothesis of air mass transfer from a smaller air cluster to larger ones via transport of the dissolved air may be valid, since a sufficient mass transfer in the order that was observed in the experiment can be achieved by a small difference of the bubble sizes. Additionally, the actually observed size of the bubbles is similar to the calculated sizes as seen in Figure 6. The detailed calculation and modeling of the dissolution of the bubbles would require precise knowledge of the bubble sizes distribution which possibly could be achieved by segmenting the air clusters in high-resolution images obtained, e.g., by X-ray micro tomography as in the work of, e.g., *Koestel and Larsbo* [2014], *Geistlinger et al.* [2014], or *Herring et al.* [2013].

3.6. Hydraulic Conductivity Measured in the Bench Experiment

A steady state flow rate of 0.36 cm min^{-1} was reached after the experiment with infiltration of degassed water started and the flow rate gradually grew to 0.53 cm min^{-1} after 2.9 h. The experiment continued overnight and then the flow rate of 0.58 cm min^{-1} was recorded at 20.9 h and did not increase further. Assuming that full saturation of the sample was reached, the hydraulic conductivity under the given experimental conditions (ponding height 0.8 cm) of the sample was $0.575 \text{ cm min}^{-1}$ and the intrinsic permeability was $9.81 \times 10^{-12} \text{ m}^2$.

The hydraulic conductivity was also calculated using the flow rates recorded during the experiments with concurrent neutron imaging. The properties of heavy water were taken into account (dynamic viscosity $1.25 \cdot 10^{-3} \text{ kg m s}^{-1}$; density 1107 kg m^{-3}) in order to obtain hydraulic conductivity relevant to H_2O water. The hydraulic conductivity during the experiment with neutron imaging was $0.414 \text{ cm min}^{-1}$ at the beginning of the steady state flow stage, which represents 72% of saturated hydraulic conductivity K_s , while the lowest

quasi-saturated hydraulic conductivity K_{QS} recorded during the same experiment was $0.304 \text{ cm min}^{-1}$ which was only 53% of K_s .

4. Conclusions

The existence of the entrapped air greatly affects the flow during the ponded infiltration. Consequently, ignoring the entrapped air effects may lead to large errors in the estimation of K_s by means of ponded infiltration experiments done on soil columns. The time needed to achieve the steady state flow after the start of infiltration during a ponded infiltration-outflow experiment in a small sample composed of fine sand embedded in continuous regions of coarse sand is several orders of magnitude higher than the time needed to equilibrate the inflow and outflow rates. The value of the hydraulic conductivity of the sample significantly decreases during this period.

In the composed heterogeneous sample of three sands, we visualized and quantified changes in the spatial distribution of water and air during the quasi-saturated flow of heavy water.

The analysis of the neutron tomography images taken during the sample experiment showed significant redistribution of water between the coarse and fine sand regions during quasi-steady flow, in which the coarse sand was gradually dewatered. Consequently, the K_{QS} decreased approximately by 23% during the same period.

Similar effects were detected by Cislérova *et al.* [2002] for heterogeneous natural soil from bulk MRI measurements. Changes in the spatial distribution of water clearly reflect changes in the entrapped air distribution, as hypothesized by Faybishenko [1995].

In the future, the neutron imaging of flow processes in heterogeneous porous media should involve simultaneous monitoring of the air and water phase pressures. The combined knowledge of the water content and the pressure in flow domains with contrasting textures could explain the hypothetical influence of the nonuniformity of the pressure and velocity fields during wetting front advancement and during slow entrapped air redistribution.

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References

- Allison, L. E. (1947), Effect of microorganisms on permeability of soil under prolonged submergence, *Soil Sci.*, **63**, 439–450.
- Amin, M. H. G., R. J. Chorley, K. S. Richards, L. D. Hall, T. A. Carpenter, M. Cislérova, and T. Vogel (1997), Study of infiltration into a heterogeneous soil using magnetic resonance imaging, *Hydrol. Processes*, **11**(5), 471–483, doi:10.1002/(SICI)1099-1085(199704)11:5<471::AID-HYP454>3.3.CO;2-M.
- Badorreck, A., H. H. Gerke, and P. Vontobel (2010), Noninvasive observations of flow patterns in locally heterogeneous mine soils using neutron radiation, *Vadose Zone J.*, **9**(2), 362–372, doi:10.2136/vzj2009.0100.
- Carminati, A., et al. (2007), Water flow between soil aggregates, *Transp. Porous Media*, **68**(2), 219–236, doi:10.1007/s11242-006-9041-z.
- Christiansen, J. E. (1944), Effect of entrapped air upon the permeability of soils, *Soil Sci.*, **58**, 355–365.
- Cislérova, M., and J. Votrubova (2002), CT derived porosity distribution and flow domains, *J. Hydrol.*, **267**(3–4), 186–200, doi:10.1016/S0022-1694(02)00149-X.
- Cislérova, M., J. Simunek, and T. Vogel (1988), Changes of steady-state infiltration rates in recurrent ponding infiltration experiments, *J. Hydrol.*, **104**(1–4), 1–16, doi:10.1016/0022-1694(88)90154-0.
- Cislérova, M., T. Vogel, and J. Simunek (1990), The infiltration-outflow experiment used to detect flow deviations, in *Field-Scale Water and Solute Flux in Soils*, edited by K. Roth et al., pp. 109–117, Birkhäuser Verlag, Basel, Switzerland.
- Cislérova, M., J. Votrubova, T. M. H. G. Amin, T. Vogel, and L. D. Hall (2002), Searching below thresholds: Tracing the origins of preferential flow within undisturbed soil samples, in *Environmental Mechanics: Water, Mass and Energy Transfer in the Biosphere: The Philip Volume*, edited by P. A. C. Raats, D. Smiles, and A. W. Warrick, AGU, Washington, D. C., doi:10.1029/129GM22.
- Corey, A. T., and R. H. Brooks (1975), Drainage characteristics of soils, *Soil Sci. Soc. Am. Proc.*, **39**(2), 251–255, doi:10.2136/sssaj1975.03615995003900020012x.
- Dusek, J., T. Vogel, M. Dohnal, and H. H. Gerke (2012), Combining dual-continuum approach with diffusion wave model to include a preferential flow component in hillslope scale modeling of shallow subsurface runoff, *Adv. Water Resour.*, **44**, 113–125, doi:10.1016/j.advwatres.2012.05.006.
- Faybishenko, B. A. (1995), Hydraulic behavior of quasi-saturated soils in the presence of entrapped air—Laboratory experiments, *Water Resour. Res.*, **31**(10), 2421–2435, doi:10.1029/95WR01654.
- Fohrer, N., J. Berkenhagen, J. M. Hecker, and A. Rudolph (1999), Changing soil and surface conditions during rainfall—Single rainstorm/subsequent rainstorms, *Catena*, **37**(3–4), 355–375, doi:10.1016/S0341-8162(99)00026-0.
- Geistlinger, H., A. Beckmann, and D. Lazik (2005), Mass transfer between a multicomponent trapped gas phase and a mobile water phase: Experiment and theory, *Water Resour. Res.*, **41**, W11408, doi:10.1029/2004WR003885.
- Geistlinger, H., S. Mohammadian, S. Schluter, and H. J. Vogel (2014), Quantification of capillary trapping of gas clusters using X-ray microtomography, *Water Resour. Res.*, **50**, 4514–4529, doi:10.1002/2013WR014657.
- Gerke, H. H., J. Dusek, and T. Vogel (2013), Solute mass transfer effects in two-dimensional dual-permeability modeling of bromide leaching from a tile-drained field, *Vadose Zone J.*, **12**(2), 1–12, doi:10.2136/vzj2012.0091.

- Glass, R. J., T. S. Steenhuis, and J. Y. Parlange (1989), Mechanism for finger persistence in homogeneous, unsaturated, porous media: Theory and verification, *Soil Sci.*, *148*(1), 60–70, doi:10.1097/00010694-198907000-00007.
- Hall, L. D., M. H. G. Amin, E. Dougherty, M. Sanda, J. Votrubova, K. S. Richards, R. J. Chorley, and M. Cislerova (1997), MR properties of water in saturated soils and resulting loss of MRI signal in water content detection at 2 tesla, *Geoderma*, *80*(3–4), 431–448, doi:10.1016/S0016-7061(97)00065-7.
- Heilweil, V. M., D. K. Solomon, K. S. Perkins, and K. M. Ellett (2004), Gas-partitioning tracer test to quantify trapped gas during recharge, *Ground Water*, *42*(4), 589–600, doi:10.1111/j.1745-6584.2004.tb02627.x.
- Herring, A. L., E. J. Harper, L. Andersson, A. Sheppard, B. K. Bay, and D. Wildenschild (2013), Effect of fluid topology on residual nonwetting phase trapping: Implications for geologic CO₂ sequestration, *Adv. Water Resour.*, *62*, 47–58, doi:10.1016/j.advwatres.2013.09.015.
- Hill, D. E., and J. Y. Parlange (1972), Wetting front instability in layered soils, *Soil Sci. Soc. Am. Proc.*, *36*(5), 697–702, doi:10.2136/sssaj1972.03615995003600050010x.
- Holocher, J., F. Peeters, W. Aeschbach-Hertig, M. Hofer, M. Brennwald, W. Kinzelbach, and R. Kipfer (2002), Experimental investigations on the formation of excess air in quasi-saturated porous media, *Geochim. Cosmochim. Acta*, *66*(23), 4103–4117, doi:10.1016/S0016-7037(02)00992-4.
- Holocher, J., F. Peeters, W. Aeschbach-Hertig, W. Kinzelbach, and R. Kipfer (2003), Kinetic model of gas bubble dissolution in groundwater and its implications for the dissolved gas composition, *Environ. Sci. Technol.*, *37*(7), 1337–1343, doi:10.1021/es025712z.
- Jelinkova, V., M. Snehota, A. Pohlmeier, D. van Dusschoten, and M. Cislerova (2011), Effects of entrapped residual air bubbles on tracer transport in heterogeneous soil: Magnetic resonance imaging study, *Org. Geochem.*, *42*(8), 991–998, doi:10.1016/j.orggeochem.2011.03.020.
- Kaestner, A., R. Hassanein, P. Vontobel, P. Lehmann, J. Schaap, E. Lehmann, and H. Fluhler (2007), Mapping the 3D water dynamics in heterogeneous sands using thermal neutrons, *Chem. Eng. J.*, *130*(2–3), 79–85, doi:10.1016/j.cej.2006.06.013.
- Kaestner, A. P. (2011), MuhRec-A new tomography reconstructor, *Nucl. Instrum. Methods Phys. Res., Sect. A*, *651*(1), 156–160, doi:10.1016/j.nima.2011.01.129.
- Kang, M., H. Z. Bilheux, S. Voisin, C. L. Cheng, E. Perfect, J. Horita, and J. M. Warren (2013), Water calibration measurements for neutron radiography: Application to water content quantification in porous media, *Nucl. Instrum. Methods Phys. Res., Sect. A*, *708*, 24–31, doi:10.1016/j.nima.2012.12.112.
- Kasperl, S., and P. Vontobel (2005), Application of an iterative artefact reduction method to neutron tomography, *Nucl. Instrum. Methods Phys. Res., Sect. A*, *542*(1–3), 392–398, doi:10.1016/j.nima.2005.01.167.
- Klump, S., O. A. Cirpka, H. Surbeck, and R. Kipfer (2008), Experimental and numerical studies on excess-air formation in quasi-saturated porous media, *Water Resour. Res.*, *44*, W05402, doi:10.1029/2007WR006280.
- Klute, A. (1986), Water retention: Laboratory methods, in *Methods of Soil Analysis, Part 1 Physical and Mineralogical Methods*, edited by A. Klute, pp. 635–662, Am. Soc. of Agron., Soil Sci. Soc. of Am., Madison, Wis.
- Klute, A., and C. Dirksen (1986), Hydraulic conductivity and diffusivity: Laboratory methods, in *Methods of Soil Analysis, Part 1 Physical and Mineralogical Methods*, edited by A. Klute, pp. 687–734, Am. Soc. of Agron., Soil Sci. Soc. of Am., Madison, Wis.
- Koestel, J., and M. Larsbo (2014), Imaging and quantification of preferential solute transport in soil macropores, *Water Resour. Res.*, *50*, 4357–4378, doi:10.1002/2014WR015351.
- Kulasova, A., K. J. Beven, S. D. Blazkova, D. Rezacova, and J. Cajthaml (2014), Comparison of saturated areas mapping methods in the Jizera Mountains, Czech Republic, *J. Hydrol. Hydromech.*, *62*(2), 160–168, doi:10.2478/johh-2014-0002.
- Lehmann, E. H. (2009), Neutron imaging methods and applications, in *Neutron Applications in Earth, Energy and Environmental Sciences*, edited by L. Liang et al., pp. 319–348, Springer.
- Lehmann, E. H., P. Vontobel, and L. Wiesel (2001), Properties of the radiography facility NEUTRA at SINQ and its potential for use as European reference facility, *Nondestructive Test. Eval.*, *16*(2–6), 191–202, Springer Science + Business Media, LLC. doi:10.1080/10589750108953075.
- Luo, L. F., H. Lin, and P. Halleck (2008), Quantifying soil structure and preferential flow in intact soil using x-ray computed tomography, *Soil Sci. Soc. Am. J.*, *72*(4), 1058–1069, doi:10.2136/sssaj2007.0179.
- Moradi, A. B., H. M. Conesa, B. Robinson, E. Lehmann, G. Kuehne, A. Kaestner, S. Oswald, and R. Schulin (2009), Neutron radiography as a tool for revealing root development in soil: Capabilities and limitations, *Plant Soil*, *318*(1–2), 243–255, doi:10.1007/s11104-008-9834-7.
- Moradi, A. B., A. Carminati, D. Vetterlein, P. Vontobel, E. Lehmann, U. Weller, J. W. Hopmans, H. J. Vogel, and S. E. Oswald (2011), Three-dimensional visualization and quantification of water content in the rhizosphere, *New Phytol.*, *192*(3), 653–663, doi:10.1111/j.1469-8137.2011.03826.x.
- Natterer, F. (2001), *The Mathematics of Computerized Tomography, Classics in Applied Mathematics*, vol. 32, SIAM, Philadelphia, Pa, doi:10.1137/1.9780898719284.
- Smith, R. M., and D. R. Browning (1946), Influence of evacuation upon laboratory percolation rates and wetting of undisturbed soil samples, *Soil Sci.*, *62*(3), 243–253.
- Snehota, M., M. Cislerova, and A. Robovska (2002), Automated set-up designed to measure hydraulic parameters in heterogeneous soil close to saturation, *J. Hydrol. Hydromech.*, *50*(3), 247–257.
- Snehota, M., M. Cislerova, M. H. G. Amin, and L. D. Hall (2010), Tracing the entrapped air in heterogeneous soil by means of magnetic resonance imaging, *Vadose Zone J.*, *9*(2), 373–384, doi:10.2136/vzj2009.0103.
- Stingaciu, L. R., L. Weihermuller, A. Pohlmeier, S. Stapf, and H. Vereecken (2010), Determination of soil hydraulic properties using magnetic resonance techniques and classical soil physics measurements, in *10th International Bologna Conference on Magnetic Resonance in Porous Media*, Am. Inst. Phys., Leipzig, Germany, doi:10.1063/1.3562237.
- Suekane, T., N. Zhou, T. Hosokawa, and T. Matsumoto (2010), Direct observation of trapped gas bubbles by capillarity in sandy porous media, *Transp. Porous Media*, *82*(1), 111–122, doi:10.1007/s11242-009-9439-5.
- Thullner, M. (2010), Comparison of bioclogging effects in saturated porous media within one- and two-dimensional flow systems, *Ecol. Eng.*, *36*(2), 176–196, doi:10.1016/j.ecoleng.2008.12.037.
- van As, H., and D. van Dusschoten (1997), NMR methods for imaging of transport processes in micro-porous systems, *Geoderma*, *80*(3–4), 389–403, doi:10.1016/S0016-7061(97)00062-1F.
- Votrubova, J., M. Cislerova, M. H. G. Amin, and L. D. Hall (2003), Recurrent ponded infiltration into structured soil: A magnetic resonance imaging study, *Water Resour. Res.*, *39*(12), 1371, doi:10.1029/2003WR002222.
- Zlotnik, V. A., D. E. Eisenhauer, D. J. Schlautman, B. R. Zurbuchen, and D. Van Peursem (2007), Entrapped air effects on dipole flow test in sand tank experiments: Hydraulic conductivity and head distribution, *J. Hydrol.*, *339*(3–4), 193–205, doi:10.1016/j.jhydrol.2007.03.013.