

Representative elementary volume estimation for porosity, moisture saturation, and air-water interfacial areas in unsaturated porous media: Data quality implications

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[1] Achieving a representative elementary volume (REV) has become a *de facto* criterion for demonstrating the quality of μ CT measurements in porous media systems. However, the data quality implications of an REV requirement have not been previously examined. In this work, deterministic REV for porosity, moisture saturation (S_w), and air-water interfacial area (A_i) were estimated using a set of 49 μ CT images of eight unsaturated homogeneous porous media with heterogeneity in moisture distributions present in varying degrees. Estimated porosity REV were $<8 \text{ mm}^3$ for all cases, smaller than typical μ CT image sizes ($\sim 100 \text{ mm}^3$). Estimated S_w and A_i REV were $<55 \text{ mm}^3$ for cases with homogeneous moisture distributions but could not be estimated for cases with heterogeneous moisture distributions, due to the absence of a distinct “REV plateau” within the maximum imaged volume. Conventionally, S_w and A_i data from such non-REV cases would be excluded. The implications of excluding data on the basis of REV were examined by comparing A_i - S_w data measured on image windows of increasing size against the expected linear A_i - S_w relationship. At measurement scales exceeding porosity REV, random fluctuations in A_i - S_w data were excluded, even for cases containing heterogeneous moisture distributions. In contrast, requiring measurement scales to exceed S_w and A_i REV appeared overly restrictive and resulted in visible loss of reliable A_i - S_w data. We attribute these findings to overestimation of REV due to inherently problematic estimation of deterministic REV in real systems. Implications of these findings for ensuring μ CT data quality and the efficient use of μ CT data are discussed.

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1. Introduction

[2] Technological advances and increased availability of facilities for noninvasive high resolution three-dimensional imaging, such as x-ray microtomography (μ CT), have resulted in a considerable increase in three-dimensional visual data related to small-scale features of porous media. Quantifying small-scale features is fundamental to improving our understanding of the underlying basis of macroscopic fluid and solute transport behavior. In order to achieve the high spatial resolution (e.g., $\sim 10 \mu\text{m}$) and sufficient x-ray penetration through the sample, the samples used for μ CT imaging are typically quite small (e.g., 3–7 mm inner diameter “microcolumn”) [Wildenschild *et al.*, 2002; Altman *et al.*, 2005]. Moreover, only a central subvolume of the original three-dimensional image is used for quantitative analysis to exclude wall effects that influence

media packing and fluid distributions. Consequently, quantitative measurements are typically made on a three-dimensional region of $<100 \text{ mm}^3$ [Clausnitzer and Hopmans, 1999; Culligan *et al.*, 2004; Al-Raoush and Willson, 2005a; Brusseau *et al.*, 2008; Costanza-Robinson *et al.*, 2008; Narter and Brusseau, 2010; Porter *et al.*, 2010].

[3] As shown in Figure 1 for porosity in an idealized system, at small spatial scales (region I) random fluctuations in porosity, associated with pore scale heterogeneity, are observed. Porosity measurements made at this scale can only be considered as unreliable artifacts of the measurement scale. For homogeneous porous media, a minimum representative elementary volume (REV) is defined as the left-hand boundary of region II; porosity measurements made at this scale are scale-independent and accurately represent a larger system [Bear, 2002]. For heterogeneous porous media, REV can theoretically be achieved at scales intermediate between the erratic fluctuations of region I and the macroscopic heterogeneity of region III, although the presence of region II for real heterogeneous systems may be difficult to delineate with confidence [Zhang *et al.*, 2000; Baveye *et al.*, 2002].

[4] The magnitude of REV is most notably linked to the average grain diameter of the porous medium; however, an

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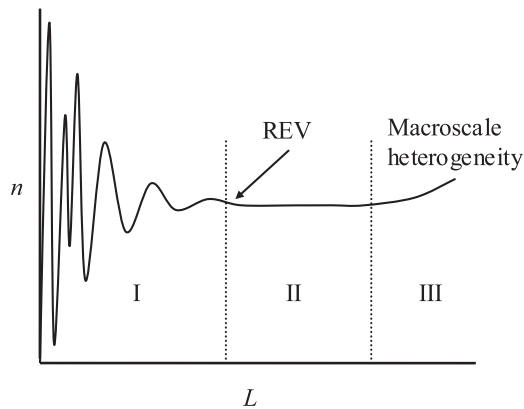


Figure 1. Conceptual schematic representing the idealized relationship between porosity (n) and the scale of the measurement (L).

REV can be defined for each porous medium property or system condition of interest (e.g., porosity, moisture saturation, permeability) [Baveye and Sposito, 1984; Mayer and Miller, 1992; VandenBygaart and Protz, 1999; Zhang *et al.*, 2000; Kanit *et al.*, 2003; Razavi *et al.*, 2007; Nordahl and Ringrose, 2008; Salama and Van Geel, 2008; Li *et al.*, 2009]. We find it useful to distinguish between porous medium *properties*, which are fixed for a given porous media system (e.g., porosity), and system *conditions*, which can vary spatially or temporarily depending on system boundary conditions (e.g., moisture saturation). Despite this REV complexity, REV has been investigated experimentally for only a few natural porous media and typically for a single variable (e.g., porosity) [Baveye *et al.*, 2002; Al-Raoush and Willson, 2005a; Razavi *et al.*, 2007; Brusseau *et al.*, 2008; Brusseau *et al.*, 2009]. The few studies comparing REV across multiple system variables in natural media have been qualitative in nature [Baveye *et al.*, 2002; Wildenschild *et al.*, 2005]. The limited data available suggest that REV is often achieved at typical μ CT scales, but not for all media nor for all system variables.

[5] REV is most commonly measured in μ CT deterministically, as the scale associated with the onset of the region II plateau shown in Figure 1. Variables that fail to exhibit this plateau within the scale of the measurement are deemed not to have achieved REV, and measured values are considered suspect or excluded from analysis [Mayer and Miller, 1992; Reeves and Celia, 1996; Clausnitzer and Hopmans, 1999; VandenBygaart and Protz, 1999; Zhang *et al.*, 2000; Baveye *et al.*, 2002; Kanit *et al.*, 2003; Culligan *et al.*, 2004; Al-Raoush and Willson, 2005a; Altman *et al.*, 2005; Razavi *et al.*, 2007; Brusseau *et al.*, 2008; Nordahl and Ringrose, 2008; Li *et al.*, 2009; Narter and Brusseau, 2010; Porter *et al.*, 2010]. For example, Al-Raoush and Willson [2005b] cautioned against generalizing their results, because the image size used was smaller than literature REV estimates for residual NAPL saturation. Likewise, Altman *et al.* [2005] advised that μ CT works best for fine-grained samples because it increased the likelihood of achieving REV within the small image volume. Achieving REV has become a *de facto* criterion for demonstrating the quality of μ CT measurements.

[6] From a conceptual standpoint, achieving REV ensures that measurements avoid scales that are associated with random pore scale heterogeneity (region I). In practice, however, few studies have examined whether an accurate measure of REV can be reliably obtained for real porous media [Zhang *et al.*, 2000; Baveye *et al.*, 2002]. Zhang *et al.* [2000] found that the deterministic approach to measuring REV could be problematic, particularly when heterogeneity in the solid phase was present, because the region II plateau was indistinct. Given the importance of achieving REV, its complicated functional dependence, and some question of whether it can be determined reliably, a critical examination of our ability to delineate REVs deterministically for a variety of system variables and degrees of heterogeneity is needed.

[7] In this work, an extensive data set consisting of 49 μ CT images for a suite of glass beads and natural porous media was used to examine our ability to estimate deterministic REV for porosity (n), moisture saturation (S_W), and total air-water interfacial area (A_I). The porous media packing was relatively homogeneous in all cases, but heterogeneity was present in varying degrees with respect to moisture distributions, allowing the influence of heterogeneity on S_W - and A_I -REV delineation to be examined. Finally, the accuracy of estimated REVs and the usefulness of requiring REV criteria to be met were assessed by examining the reliability of A_I - S_W data obtained at multiple measurement scales.

2. Experimental

2.1. Porous Media and Column Preparation

[8] The set of 49 three-dimensional images used in the current work represents a subset of those described previously [Costanza-Robinson *et al.*, 2008]. Sand-sized spherical glass beads (MO-SCI Specialty Products) and two commercial silica sands, Accusand and Granusil (Unimin Corporation), were sieved to achieve both poorly sorted mixtures and well-sorted fractions of varying texture. Table 1 provides relevant porous media and system properties. Porous media were homogeneously packed in custom anodized aluminum microcolumns (4.7 mm internal diameter, 40 mm height) fitted with PEEK-encased stainless steel dispersion frits (Isolation Technologies) and sealed with aluminum compression fittings or threaded PTFE caps. Visual inspection of grain-size distribution in the images, as well as measured solids fraction ($\text{Volume}_{\text{solids}}/\text{Volume}_{\text{total}}$) along the depth axis, confirmed that the porous media were, in fact, homogeneous.

[9] Two wetting methods were used: (1) wet packing of porous media already prepared at the desired moisture saturation and (2) dry packing followed by water imbibition to near saturation and subsequent drainage to the desired column-averaged moisture saturation. The wetting methods resulted in moisture distributions ranging from quite uniform to considerably nonuniform with depth. Because moisture saturation and air-water interfacial areas are correlated, the variation in moisture saturation within and between images caused a similar range of spatial heterogeneity in interfacial areas. For both wetting methods, iodide-doped water (13% or 20% iodide by mass, as KI) was used

Table 1. Select Porous Media Properties and Average Moisture Saturation for Images

Texture (Number of Images)	Median Diameter (d_{50} , μm)	Uniformity Coefficient (U , $-$) ^a	Specific Geometric Solid Surface Area ^b (cm^{-1})	Average Moisture Saturation for Images (S_w , %)
<i>Glass Beads</i>				
Medium ($n = 4$)	345	1.2	113	16, 40, 57, 70
Coarse ($n = 5$)	650	1.1	55	16, 17, 31, 42, 72
Mix ($n = 7$)	403	4.6	97	12, 25, 45, 54, 64, 69, 71
<i>Accusand</i>				
Medium ($n = 5$)	375	1.2	101	14, 30, 33, 48, 90
Coarse ($n = 7$)	516	1.2	73	18, 22, 33, 62, 65, 71, 96
<i>Granusil</i>				
Fine ($n = 7$)	200	1.7	162	12, 31, 52, 57, 86, 91, 91
Coarse ($n = 8$)	513	1.7	65	8, 15, 26, 46, 46, 58, 71, 79
Mix ($n = 6$)	211	2.9	163	21, 45, 50, 71, 89, 91

^aUniformity coefficient, $U = d_{60}/d_{10}$.

^bVolume-normalized specific solid surface area (SA) calculated under the assumption of smooth spheres, calculated as $SA = 6(1-n)/d_{50}$, where n is porosity and d_{50} is the median particle diameter.

to enhance image contrast and improve quantitative image analysis.

2.2. Image Collection and Processing

[10] Synchrotron x-ray microtomography (μCT) was performed on the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) Beamline 13-BM-D at the Advanced Photon Source at Argonne National Laboratory using methods that have been validated previously [Costanza-Robinson *et al.*, 2008]. Briefly, images of a 5.5 mm vertical section of the packed column were obtained at 10.6–11.3 μm resolution 100 eV above and below the x-ray absorption edge of iodide. Data reconstruction and pre-processing were performed using algorithms developed at GSECARS [Rivers, 2006]. Quantitative image analysis was limited to a central subvolume of the full three-dimensional image (approximately $3.76 \times 3.76 \times 5.43$ mm) to minimize the influence of wall effects. This central subvolume is referred to hereafter simply as the “image.” All image processing algorithms were performed in three dimensions. A median smoothing algorithm was used to reduce image noise (Blob3D Software) [Ketcham, 2005], and a multistep segmentation process was used to assign image voxels (three-dimensional pixels) to the solid, air, or water phases [Costanza-Robinson *et al.*, 2008]. The product of this multistep image manipulation is a segmented image, in which each of the bulk phases (air, water, solid) is represented by an unique gray scale intensity. Measurements of porous media properties (e.g., porosity) and systems conditions (e.g., moisture saturation) were made from these segmented images. Representative gray scale and segmented image cross sections are shown in Figure 2.

[11] Volumes and surface areas of each phase (solid, air, water) were extracted from segmented images using Amira 4.1.1 (Visage Imaging, San Diego, CA), software that facilitated implementation of an automated REV analysis. The volume of each phase was measured by counting the number of voxels associated with each phase, from which moisture saturation and porosity were calculated. A smoothed triangular mesh was generated to approximate the surface area of the air phase, from which total air-water interfacial areas were calculated. Total air-water interfacial areas represent the interfacial contributions of water adsorption to

grain surfaces, which creates thin water films, as well as capillarity, which creates interfaces between bulk water and air, such as pendular rings. Thin water films cannot be imaged directly by μCT due to image resolution constraints; however, the assumption that the silica surfaces are fully wetted by water allows the surface area of the air phase to be taken as the total air-water interface [Brusseau *et al.*, 2006; Brusseau *et al.*, 2007; Costanza-Robinson *et al.*, 2008]. Total specific air-water interfacial areas (A_i), referred to hereafter simply as “air-water interfacial areas,” are expressed as the area of the total air-water interface normalized by the associated system volume ($\text{cm}^2/\text{cm}^3 = \text{cm}^{-1}$).

2.3. REV Estimation

[12] A conventional deterministic approach to REV estimation was used, in which porosity, moisture saturation, and interfacial area were measured for multiple three-dimensional image windows as the size of window increased. Two window geometries were examined (Figure 3). A traditional point-centered cube geometry was used, in which cube dimensions were increased symmetrically in all directions from a single-voxel starting point. Cube REV was assessed for slightly overlapping upper and lower locations within each image. Additionally, a core centered cuboid window geometry was used, in which a core of fixed height, equal to the height of the image, was expanded symmetrically in the x and y dimensions. The core geometry averages over the depth heterogeneity in moisture distributions and at maximum volume encompasses the full image.

[13] As shown in Figure 3, the window length-scale (L) was defined for both geometries as the edge length of the square cross section; this definition results in the two geometries having different relationships between L and total window volume (V). For the cube geometry, L represents $V^{1/3}$; for the core geometry L represents an effective width of the core and, due to small variations in the height of each image, has a more complicated relationship to volume. The maximum window volumes for the cube and core geometries were approximately 53 and 77 mm^3 , respectively. The definition of L for the core geometry was chosen because it can be readily converted into an effective sample diameter, the dimension that is most critical for microtomography image resolution and noise. Because of

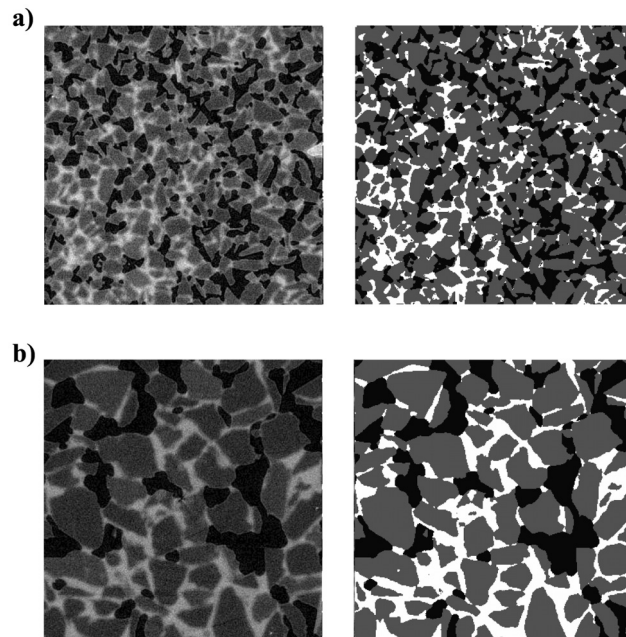


Figure 2. Two-dimensional image slices (x - y plane) showing representative (left) median-smoothed and (right) segmented data for (a) Granusil Fine and (b) Granusil Coarse.

these differences in how L is defined, core and cube REV estimates are expected to differ and cannot be directly compared. REV estimates for the cube are useful for literature comparisons, as this geometry is commonly used; in contrast, core REV estimates provide values of direct experimental applicability.

[14] REV data analogous to the conceptual schematic shown in Figure 1 (i.e., an REV plot) were obtained for each image, for three system variables (n , S_w , and A_I), and for the core window geometry and for both upper and lower locations of the cube geometry, resulting in a total of 147 “cases” for each variable from the original 49 images. Each case was categorized as homogeneous or heterogeneous with respect to each variable, based on a visual assessment of whether the REV plot exhibited a distinct plateau or not. For cases that were homogeneous with respect to a given variable, REV was determined using an REV

criterion modeled after *Li et al.* [2009]. REV was taken as the minimum window length scale (L) at which the absolute value of the relative gradient error (ε_g) in the measured system variable, shown here for porosity (n), remained below 0.2:

$$\varepsilon_g = \frac{|n^{i+1} - n^{i-1}|}{n^{i+1} + n^{i-1}} \frac{1}{\delta}, \quad (1)$$

where i refers to the window increment number and δ is the magnitude of the increment in L . In physical terms, the relative gradient error REV criterion requires changes in the measured variable over a given length-scale increment to be relatively small proportional to the size of the increment. Both the visual classification and choice of the ε_g criterion (e.g., <0.2) rely on a subjective judgment regarding the magnitude of acceptable variation in the measured property and what constitutes a “clear plateau.” A sensitivity analysis on a subset of homogeneous cases indicated that the ε_g criterion implemented here corresponded well to our own visual plateau assessments and to similar literature assessments [e.g., *Reeves and Celia*, 1996; *Clausnitzer and Hopmans*, 1999; *Zhang et al.*, 2000; *Culligan et al.*, 2004; *Razavi et al.*, 2007; *Narter and Brusseau*, 2010; *Porter et al.*, 2010]. An advantage of the semiquantitative ε_g approach used here is that once the ε_g criterion is established, REV can be estimated in an automated and reproducible manner across numerous images, which allows quantitative relationships between REV and other variables to be readily evaluated.

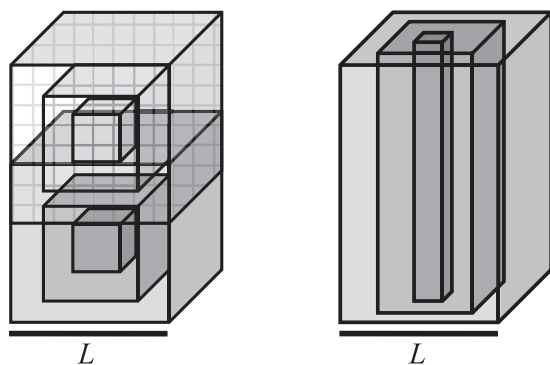


Figure 3. Two image window geometries used for REV analysis: (left) point-centered cube (cube) applied to two overlapping image locations (upper and lower) and (right) core centered cuboid (core). The window length scale (L) is defined as the edge length of the square cross section.

3. Results and Discussion

3.1. Porosity REV

[15] Figures 4a and 5a show porosity values and relative gradient errors (ε_g) as a function of the upper cube window

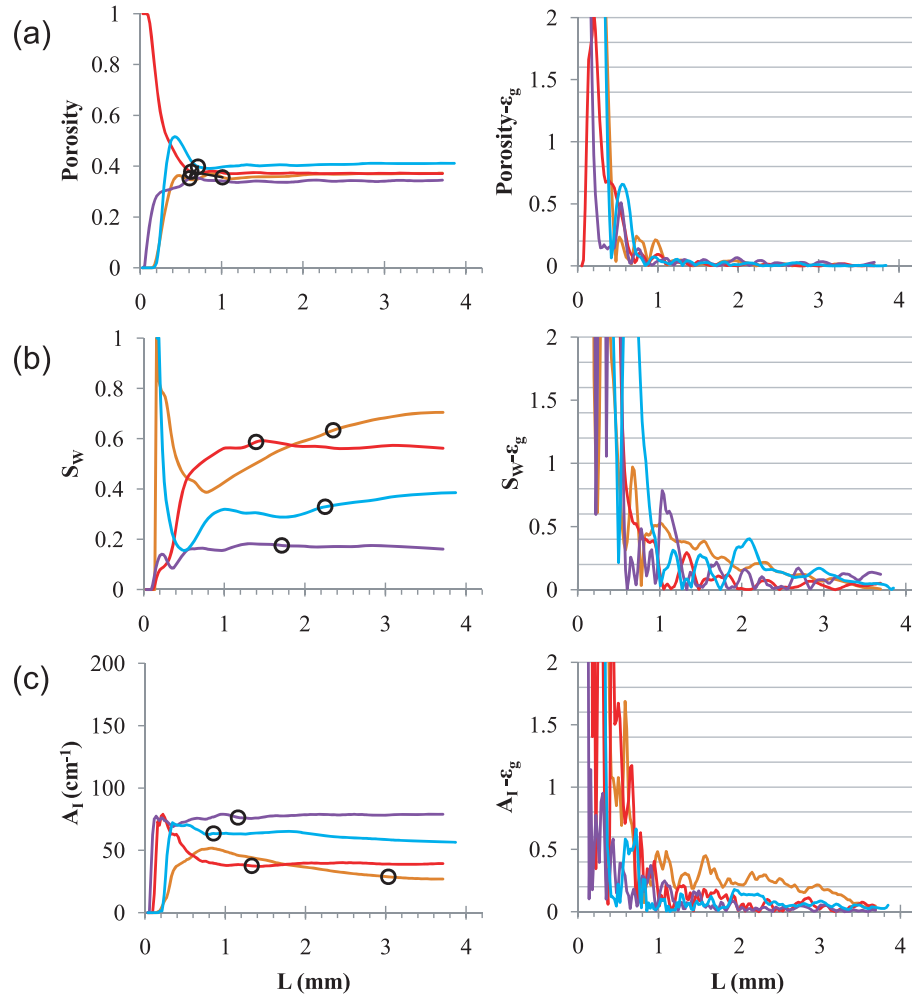


Figure 4. (left) System variable and (right) relative gradient error (ε_g) versus length scale of the upper cube window for Glass Bead Medium: (a) porosity, (b) moisture saturation, and (c) total air-water interfacial area. Colors represent individual cases. Open circles (Figure 4, left) and the lowest gridline (Figure 4, right) indicate $\varepsilon_g < 0.2$.

size for two representative media. At small window size, erratic variation in both porosity and ε_g was observed for incremental growth in window size, which is consistent with sub-REV scales (Figure 1, region I). At larger window sizes, porosity values exhibited the characteristic REV region II plateau, and the variability and magnitude of ε_g decreased well below the 0.2 REV criterion. This behavior was observed for porosity in all 147 cases, as expected for homogeneous porous media. As shown by the open circles in Figures 4a and 4b, the REV estimated using the $\varepsilon_g < 0.2$ REV criterion visually corresponded with our assessment of the beginning of the plateau in porosity values, suggesting that the criterion is reasonable. These findings indicate that porosity REV was routinely achieved for the homogeneous sandy systems and image sizes studied here.

[16] Porosity REV for the cube geometry ranged between 0.37 and 2.0 mm (0.05–8 mm³), depending on the porous medium, which is equivalent to approximately 1–7 grain diameters. This range is consistent with the limited number of literature estimates of between 2 and 20 grain diameters for similar glass bead and sand systems [Clausnitzer and

Hopmans, 1999; Culligan *et al.*, 2004; Al-Raoush and Willson, 2005a; Razavi *et al.*, 2007]. Average porosity core-REV estimates were generally lower than for the cube geometry, consistent with the different length-scale definitions of the two geometries. Core porosity REV ranged from 0.12 to 0.36 mm (~0.07–0.6 mm³), representing a core width of less than a single grain diameter for some media. The fact that REV was achieved within such narrow core windows is attributed to the substantial volume contribution of the large window height. Actual REV volumes (rather than length scales) overlapped for the two window geometries, but were smaller on average for the core estimates. Smaller core-REV volumes may indicate that even subtle variation in porosity with depth is sufficient to influence the cube REV; the core geometry, in contrast, would tend to average out variation in the depth dimension. These findings indicate that image sizes typically used in μ CT (~100 mm³) are routinely much larger than porosity REV and that, within the constraints of achieving representative packing and excluding wall effects, even smaller samples of similar media could be considered.

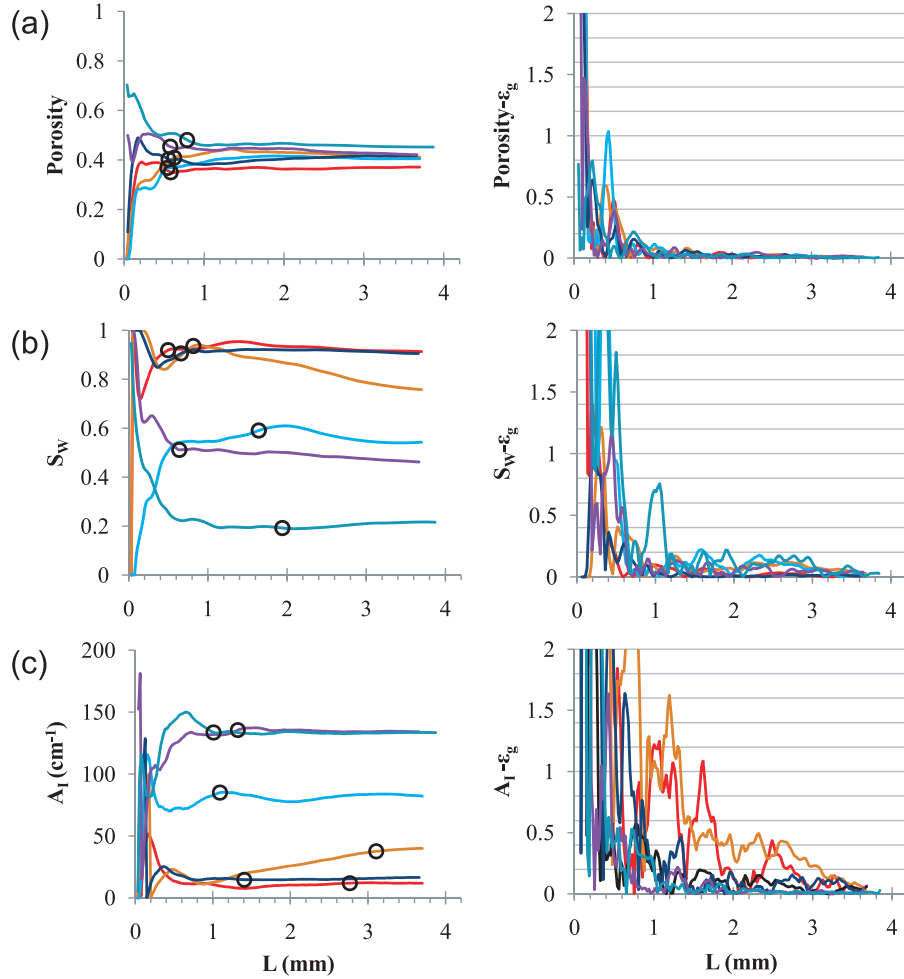


Figure 5. (left) System variable and (right) relative gradient error (ε_g) versus length scale of the upper cube window for Granusil Mix: (a) porosity, (b) moisture saturation, and (c) total air-water interfacial area. Colors represent individual cases. Open circles (Figure 5, left) and the lowest gridline (Figure 5, right) indicate $\varepsilon_g < 0.2$.

3.2. Moisture Saturation and Interfacial Area REV

[17] The scale dependence of measured moisture saturation and interfacial area, and of the associated relative gradient errors, was qualitatively similar to that observed for porosity, as shown for two representative porous media (upper cube locations) in Figures 4b, 4c, 5b, and 5c. In most cases, a distinct plateau in measured conditions delineating REV region II was observed, indicating relative spatial homogeneity in the system conditions studied. The ε_g analysis generally resulted in REV estimates that appeared reasonable (see Figures 4 and 5, open circles), although in a few cases the REV estimate appeared somewhat low (e.g., Figure 4b, blue and orange). Importantly, 34% and 48% of the cube geometry cases for moisture saturation and interfacial areas, respectively, were visually determined to be heterogeneous with respect to these system conditions. This was the case for only 12% and 20% of the core geometry cases for moisture saturation and interfacial area, respectively.

[18] As shown for representative examples in Figure 6, for cases in which moisture saturation was relatively uniform with depth (black lines), a distinct region II plateau was observed for A_I -REV plots. In contrast, when large

moisture saturation-depth gradients were present (colored lines), a distinct plateau was absent and measured values trended in a roughly linear manner as window size increased. Fewer core geometry cases exhibited this heterogeneous behavior, a finding that is attributed to the fixed height dimension of the core geometry, which both captures larger total volume and averages over any heterogeneity in the depth dimension, as discussed above relative to porosity. Applying the core geometry (dashed lines) is shown in Figure 6 to yield smaller REV for the homogeneous- A_I case, and both smoother REV plots and lower slopes at large window sizes for heterogeneous- A_I cases. Moisture saturation and interfacial areas behaved similarly with regard to the influence of moisture distribution heterogeneity on REV plots. These findings confirm that in a number of cases, despite having a homogeneous solid-phase, system conditions were sufficiently heterogeneous that REV for S_w and A_I could not be determined deterministically. Applying the conventional requirement for achieving REV would exclude measurements of S_w and A_I based on these images.

[19] Whereas cube porosity REV was achieved for $L \leq 2$ mm in all cases ($< 8 \text{ mm}^3$), the cube REV for moisture

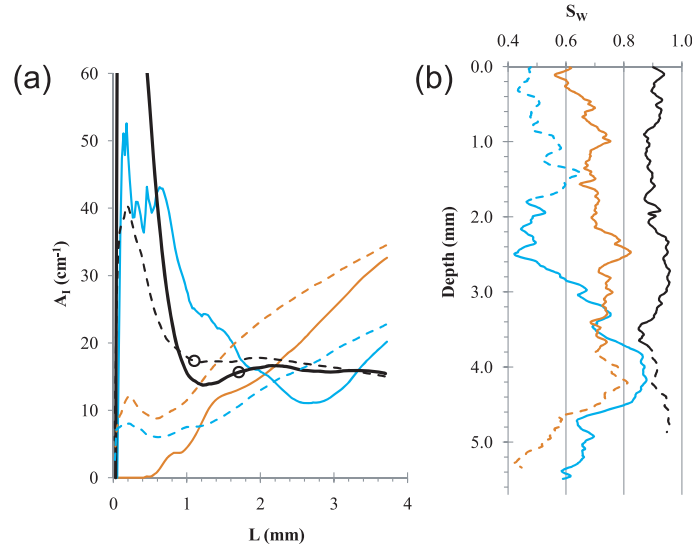


Figure 6. Comparison of (a) interfacial area REV plots and (b) moisture saturation-depth profiles for homogeneous (black) and heterogeneous moisture distribution cases (colors). Solid and dashed lines of a given color in Figure 6a refer to cube and core cases, respectively, for the same image. Likewise, in Figure 6b, the solid lines indicate the image depths captured within the maximum cube window size, while the dashed lines complete the moisture profile for the full image captured by the core geometry. Open circles indicate $\varepsilon_g < 0.2$.

saturation and interfacial area cases ranged up to 3.8 and 3.7 mm (51–55 mm³), respectively, with a median of 2.1 mm for both. Importantly, these S_w - and A_I -REV estimates necessarily only reflect cases that were homogeneous with respect to moisture distributions. For individual porous media, REVs for moisture saturation and interfacial area were on average twice as large as for porosity. These findings are consistent with a body of literature indicating that porosity often achieves REV within a smaller volume than do other variables [Baveye and Sposito, 1984; Zhang *et al.*, 2000; Bear, 2002; Kanit *et al.*, 2003; Stroeven *et al.*, 2004; Al-Raoush and Willson, 2005b; Salama and Van Geel, 2008; Li *et al.*, 2009]. To our knowledge, A_I -REV estimates have not been previously reported, and S_w has been examined only qualitatively; thus, comparisons with the literature are not possible. S_w and A_I -REV estimates for the core window geometry, expressed both as length scales and volumes, were much lower than for the cube-based estimates, consistent with the different definitions of L and core averaging over the moisture heterogeneity in the z dimension. Core REV for these two system conditions was achieved at core widths of approximately 0.4–1.6 mm (~ 0.8 – 13 mm³). Cube and core estimates demonstrate that for cases where both solid-phase packing and moisture distributions were homogeneous, REV was readily achieved for moisture saturation and total interfacial areas within typical μ CT sample and image sizes.

3.3. Relationship Between REV and System Variables

[20] REV estimates derived from both cube (upper and lower locations) and core geometries for cases classified as homogeneous (i.e., contained a plateau in the REV plot) demonstrated the same general trends with regard to dependence on system variables. Because the greater number of cube cases ($\sim 50\%$ more) and smaller volume changes associated with each cube-window size increment yield greater statistical power and sensitivity, we focused the fol-

lowing statistical assessment on cube-REV geometries. Porosity REV exhibited a statistically significant ($p < 0.05$) positive linear correlation with median grain diameter (d_{50}), as would be expected [Mayer and Miller, 1992; Razavi *et al.*, 2007] (Figure 7), although considerable variation in REV was observed for a given grain size. REV length scales are often normalized by d_{50} (i.e., L/d_{50}) to arrive at a number of grain diameters that is predictably required to achieve REV. Importantly, by normalizing out the dominant influence of grain size, expressing REV as L/d_{50} allows secondary influences on REV to be more clearly observed. Figure 8 shows that a greater number of grain diameters was generally required to achieve porosity REV for media with broader grain-size distributions (i.e., larger uniformity coefficient U , see Table 1), although

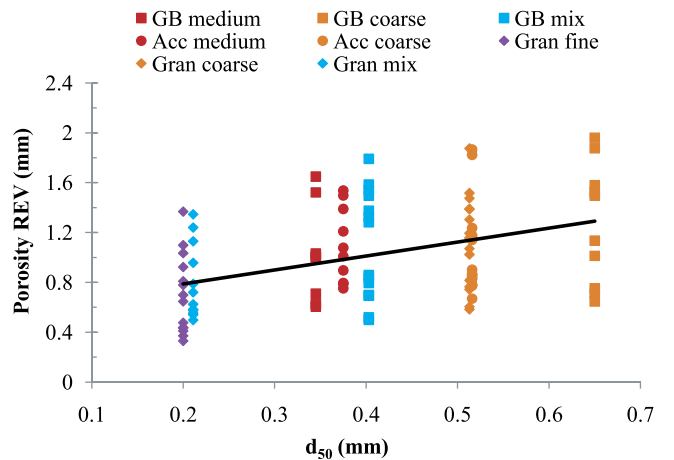


Figure 7. Porosity-REV estimates versus median grain diameter (d_{50}) for both upper and lower cube locations. The linear correlation was significant ($p < 0.05$).

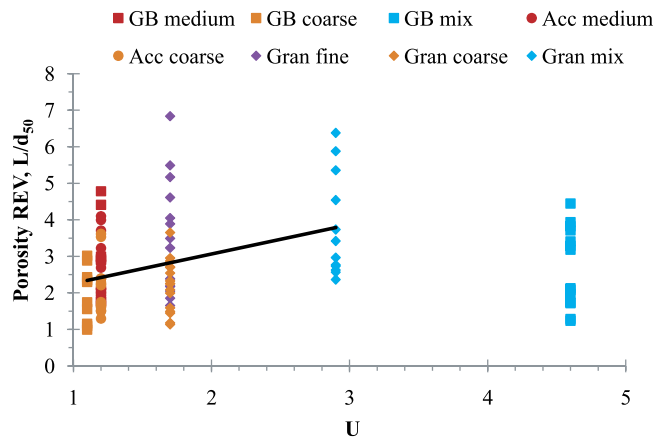


Figure 8. Median grain diameter-normalized REV (L/d_{50}) for porosity versus uniformity coefficient (U), where $U = d_{60}/d_{10}$. The linear correlation, excluding GB Mix data, was significant ($p < 0.05$).

considerable spread in REV- L/d_{50} values is still present. This trend only became statistically significant when data for Glass Bead Mix were excluded ($p < 0.05$). A general positive relationship between the REV L/d_{50} and U is consistent with the notion that greater variation in grain size is associated with greater variation in the separation distances between grains, and consequently, a greater number of grain diameter multiples are required to sample this heterogeneity and achieve REV. The unexpectedly small REV L/d_{50} for glass bead mix relative to its large U is consistent with the findings of Razavi *et al.* [2007], who reported fewer grain diameters were required to achieve REV for glass beads than for natural media with similar grain-size distributions. Although the exact cause of this finding is not clear, it is possible that smooth spherical beads can slip past each other more readily than can rough, irregularly shaped natural grains, allowing beads to achieve a more uniform arrangement during the column packing and tamping process. These findings suggest that a complex set of solid-phase features influence REV, including median grain size, grain-size distribution, and possibly, grain shape and surface roughness.

[21] A significant linear correlation between S_W REV and d_{50} was observed ($p < 0.05$), but not between A_I REV and d_{50} . Neither S_W nor A_I REV was correlated with U . Conceptually, REV for a given property should be proportional to the average separation length between features contributing to the property. For example, the solid grains separate voids and account for the expected correlation between porosity REV and d_{50} . The observed correlation between S_W REV and d_{50} is consistent with this notion, in that for water-wettable porous media, such as those examined in this work, the water features (e.g., water-filled pores and pendular rings) would be expected to be separated, on average, by distances related to the median grain size. That A_I REV was not correlated to d_{50} suggests that the average separation between air-filled pores, which contribute to A_I , is governed more strongly by other factors. In fact, both S_W REV and A_I REV were highly correlated with the window-averaged moisture saturation ($p < 0.001$), as shown in Figure 9. These findings differ with qualitative

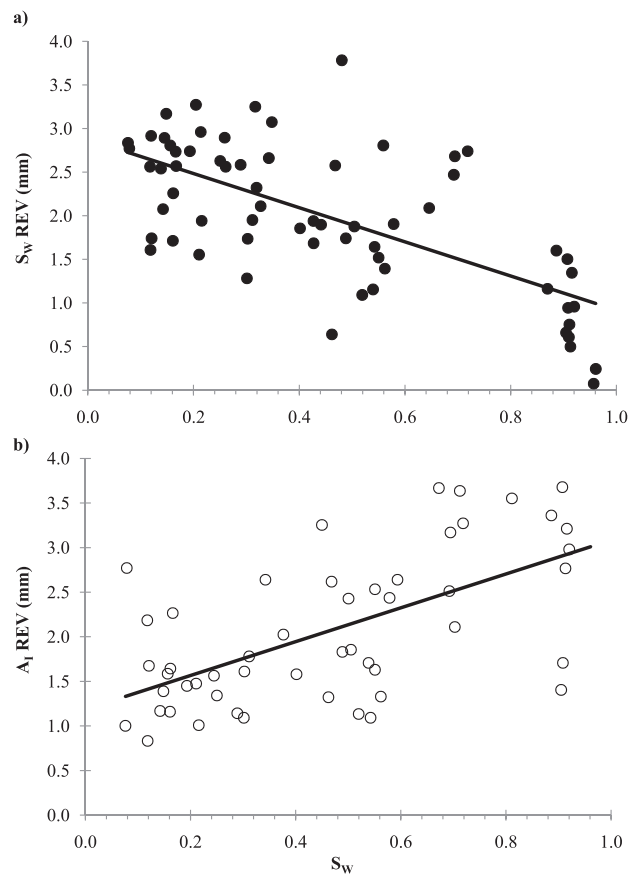


Figure 9. Cube-REV estimates versus window-averaged moisture saturation for (a) moisture saturation and (b) air-water interfacial area. Both linear correlations were highly significant ($p < 0.001$).

REV literature that indicates S_W REV is independent of S_W [Reeves and Celia, 1996; Culligan *et al.*, 2004]. The discrepancy could be caused by differences among studies in how REV was delineated. Our ε_g -sensitivity analysis indicated, however, that although REV magnitudes change with the magnitude of our ε_g criterion, the trends in REV do not. It is also possible that the difference is due to the uniformity of media and moisture distributions studied. The media examined in the literature were glass beads and a simulated homogeneous pore network, while our findings reflect both model and natural media of variable grain-size uniformity, indicating that our finding is robust across media types. It is likely that the inherent difficulty in delineating REV yields sufficient scatter in the data (e.g., Figures 7–9), that larger datasets, such as that presented in this work, are necessary for clear REV trends to be delineated. Although the exact cause of the differences are not clear, we suggest that the inverse correlation observed between S_W REV and S_W would be expected, given that in a wetter system, the average separation length between water-filled pores, and therefore S_W REV, would be smaller. Likewise, the direct relationship observed for A_I REV and S_W is attributable to the fact that in wetter systems, the air-filled pores that contribute to interfacial area would have greater average separation. This analysis suggests that the REV estimates and their functional dependence determined here

are reasonable. Additional image analysis, beyond the scope of the current work, could be used to investigate these relationships in more depth.

[22] In summary, these results indicate that REV for a given variable depends on the nature of the porous medium, as is widely accepted [Baveye and Sposito, 1984; Mayer and Miller, 1992; VandenBygaart and Protz, 1999; Zhang et al., 2000; Baveye et al., 2002; Kanit et al., 2003; Razavi et al., 2007; Nordahl and Ringrose, 2008; Salama and Van Geel, 2008; Li et al., 2009]. However, REV was also shown to depend on the applied boundary conditions for a particular porous medium insofar as they determine heterogeneity in moisture distributions, a complication that was discussed hypothetically by Baveye and Sposito [1984], but has received little attention since. Further investigation of these boundary condition-dependent REVs is needed, for example, by examining a single region of a single porous media sample subject to different boundary conditions, rather than by the more problematic comparison across multiple samples made here. Nonetheless, our findings suggest that REV for system conditions may be highly porous media- and boundary-condition dependent and, therefore, particularly difficult to estimate a priori.

3.4. Data Quality Implications of Applying REV Requirements

[23] Achieving REV theoretically ensures the representativeness and reliability of μ CT data; however, because practical delineation of REV requires subjective assessments of what constitutes a plateau and where the plateau begins, and because deterministic REV cannot be delineated for heterogeneous properties/conditions that lack an REV plateau, it is important to evaluate the practical implications of an REV requirement on resulting data quality. The effect of requiring REV to be achieved was assessed separately for cases that exhibited homogeneous and heterogeneous moisture distributions. The established linear relationship between moisture saturation and total interfacial areas measured using μ CT was used as the point of reference for evaluating the reliability of image-derived A_I - S_W data measured at various scales. For more detail on the A_I - S_W relationship, readers are referred to earlier work [Brusseau et al., 2006; Costanza-Robinson et al., 2008].

[24] Figure 10 shows cube and core data for representative cases that were homogeneous with respect to moisture distributions, including A_I - S_W data for all image window sizes of each case (Figure 10a); data from each case only for windows larger than case-specific porosity REV (Figure 10b); and data from each case only for windows larger than both case-specific S_W and A_I REV (Figure 10c). This last data treatment represents the most common and conservative application of an REV requirement. The uncensored data, shown in Figure 10a, exhibit considerable variability, and the expected linear A_I - S_W relationship is confused by random, nonrepresentative fluctuations in A_I and S_W . Figure 10b shows that excluding A_I - S_W data for windows smaller than porosity REV improves overall data quality by removing nearly all of the large random fluctuations. Comparison of Figures 10a and 10b suggests that the porosity-REV requirement was useful for excluding data measured within the random fluctuations of region I for homogeneous moisture distribution

systems and that both cube and core window geometries, as well as the ε_g REV criterion used in this work, serve this purpose sufficiently well. In contrast, comparison of Figures 10b and 10c reveals a disadvantage of further requiring measurement scales to achieve S_W and A_I REV. Although the data in Figure 10c also appear reliable and conform to the expected linear behavior, the data are sparse and represent, in our estimation, a net loss of reliable information, rather than an improvement in data quality. These observations may suggest that the S_W - and A_I -REV estimates determined in this work are too large. In particular, measurement scales that appear to have exceeded the scale of random pore scale heterogeneity (region I) for moisture saturation and interfacial areas were estimated to be sub-REV for these variables. In contrast, visual inspection of the REV plots suggested that the ε_g -based REV estimates appeared generally reasonable, if possibly too small. We attribute this apparent contradiction to the fact that deterministic REVs are difficult, if not impossible, to delineate precisely in real systems due to imperfect region II plateaus.

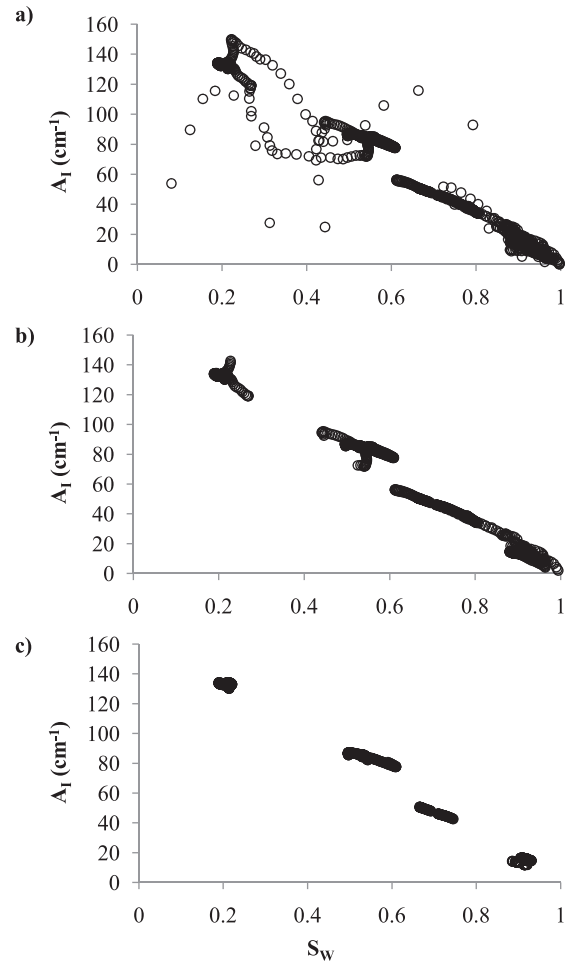


Figure 10. A_I - S_W data for image (cube and core) windows of varying size for Granusil Mix homogeneous moisture distribution cases: (a) complete, uncensored data; (b) data only for windows larger than case-specific porosity-REV; and (c) data only for windows larger than both case-specific S_W and A_I REV.

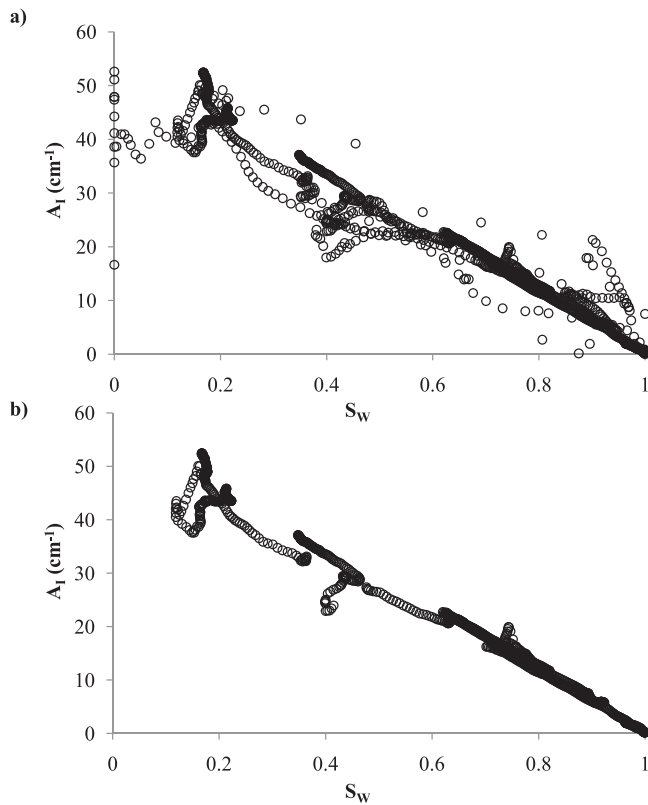


Figure 11. A_I - S_W data for cube image windows of varying size for Accusand Coarse heterogeneous moisture distribution cases: (a) complete, uncensored data and (b) data only for windows larger than case-specific porosity REV.

[25] The effect on data quality of requiring REV to be achieved was further evaluated by examining the reliability of A_I - S_W data for heterogeneous moisture distribution cases (cube and core) measured at different scales. Recall that for these cases, A_I - and S_W -REV estimates were not possible due to the absence of REV plateaus. The uncensored data, shown in Figure 11a, exhibit erratic behavior that is typical of systems at sub-REV scales. In contrast, Figure 11b only includes data for windows larger than case-specific porosity REV, which exhibit the expected linear A_I - S_W relationship. The fact that cases that were patently heterogeneous with respect to moisture distributions, lacking any hint of a region II S_W and/or A_I plateau, yield seemingly reliable A_I - S_W data supports our conclusion that REV for these variables was achieved at smaller scales than were estimated deterministically. Specifically, it appears that the distinct region II plateau ideally conceptualized as existing at intermediate scales for macroscopically heterogeneous systems (e.g., Figure 1) is severely compressed or fully absent in real systems that exhibit some degree of heterogeneity with respect to the property/condition of interest.

4. Conclusions

[26] Our assessments of μ CT A_I - S_W data reliability suggest that reliable delineation of deterministic REV is difficult or perhaps unattainable in practice, even for homo-

geneous media and system conditions, because of difficulty in delineating the region II plateau. Both because of subjectivity in delineating the onset region II plateau, whether visually or using a ε_g criterion, and because of the wide diversity in porous media and system conditions, it is not clear that condition REV would always be overestimated as they were here. For other porous media and other system variables, they might well be underestimated; the current work cannot constrain this possibility. Moreover, while ε_g thresholds might be optimized for various porous media and system conditions to yield “better” REV estimates, this approach would be equally subjective unless constrained by a firmly established, and currently unavailable, “true REV.”

[27] Despite uncertainty in the exact REV magnitude, our A_I - S_W data quality assessment indicates that typical μ CT image volumes yield reliable measurements and are likely to exceed the minimum REV scale for porosity, moisture saturation, and total specific air-water interfacial area for homogeneous porous media. This conclusion suggests that studies in which REV was reportedly not achieved, based on the absence of a clear region II plateau, or in which data were censored to conform to an REV requirement, may need to be re-evaluated [VandenBygaart and Protz, 1999; Zhang et al., 2000; Baveye et al., 2002; Al-Raoush and Willson, 2005a, 2005b]. Use of the conventional cube window geometry might also be reconsidered in this regard because for the cube geometry, REV is assessed using what is typically only a portion of the wall-excluded image, increasing the likelihood of misclassifying an image as sub-REV. In contrast, the core geometry, or more generally, a window geometry that approximates the image geometry, has the dual advantages of capturing a larger portion of the imaged volume and averaging over depth, which is often the most heterogeneous dimension (e.g., textural layering, moisture saturation gradients). Importantly, however, even the core geometry appeared to yield overestimated S_W and A_I REV estimates in this work. Further work is needed to examine the influence of window geometry on REV assessments.

[28] Given the great potential for μ CT imaging to further our understanding of heterogeneous systems, and the desire to preserve reliable μ CT data, alternative means of ensuring data quality are needed. In this work, conformity of the image data from multiple window sizes with each other and with expected behavior served as a useful data quality indicator, similar to approaches used elsewhere [Hilpert and Miller, 2001; Dalla et al., 2002; Joekar-Niasar et al., 2008]. The correspondence between expected and measured behavior indicated that requiring porosity REV to be achieved was sufficient for ensuring the reliability of A_I - S_W data, even for systems in which A_I and S_W exhibited considerable heterogeneity. Consistent with this porosity-REV approach, Pyrak-Nolte et al. [2008] implemented a porosity-REV requirement and obtained reliable measurements of capillary-air-water interfacial area and moisture saturation in two-dimensional micromodels. It is not clear, however, whether the porosity-REV approach to ensuring data quality would successfully extend to systems containing a heterogeneous solid phase. Moreover, while the porosity-REV approach was useful for constraining A_I - S_W data to reliable scales of measurement, further

evaluation of the approach is needed for a wider range of system properties and conditions. In particular, when examining system variables for which definitive benchmark behavior has not yet been established, the deterministic approach, even if overly conservative, may be advisable.

[29] Because achieving porosity REV was largely sufficient for ensuring reliable data, a condition that is readily achieved for conventional μ CT image sizes, we suggest that for systems containing a homogeneous solid phase, it may be possible to routinely extract numerous volume-averaged measurements for various system variables from multiple windows of each image, as done here (Figures 10 and 11). This multiple-window approach is not new [Pyrak-Nolte et al., 2008], but is not routine in μ CT image analysis. Boundary conditions might even be chosen specifically to introduce macroscopic heterogeneity in system conditions (e.g., a large gradient in moisture saturation) with the intent of gathering a greater range of information from a single image. This approach would be particularly useful for delineating nonlinear relationships between system variables, such as the parabolic relationship observed for capillary-interfacial areas and moisture saturation [Culligan et al., 2004; Brusseau et al., 2006; Porter et al., 2010], using many fewer images. Moreover, because porosity REV is relatively small, subject to porous media packing constraints, even smaller sample sizes than are in conventional use may yield reliable information. Use of smaller samples would lead to improved spatial resolution in the images and the ability to discern even smaller features, such as grain surface roughness.

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