

Bimodal pore structure of a paddy soil under different fertilization regimes investigated by soil water retention curve and X-ray Computed Tomography imaging

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## 1 **Abstract**

2 Well-structured soils are generally considered to have bimodal pore  
3 structure, including textural pores between soil particles and structural  
4 pores between soil aggregates. Bimodal pore structure has previously been  
5 inferred indirectly from the soil water retention curve (SWRC) but our  
6 understanding of the precise 3-D pore geometry that regulates this curve is  
7 limited. The objective of this study was to investigate the bimodal pore  
8 structure of a paddy soil under different fertilization regimes using both  
9 SWRC and X-ray micro-Computed Tomography (micro-CT), an imaging  
10 approach with the aim of comparing the two methods. Undisturbed soil  
11 aggregates and soil cores were collected from the surface layer of a  
12 long-term unfertilized control (CK), inorganically fertilized (NPK), and  
13 organically and inorganically fertilized (NPKOM) paddy soils. The aggregates  
14 and cores were scanned using micro-CT and pore structure analyzed. The  
15 SWRCs were measured on the same CT-scanned soil cores. Three widely  
16 used unimodal models, three bimodal models, and one trimodal model were  
17 evaluated for their fit to the SWRC and to derive soil pore size distribution  
18 (PSD). Results showed the SWRC of the paddy soil were best fitted with the  
19 bimodal lognormal (BLN) and double-exponential (DE) models, with the  
20 derived PSD showing distinct bimodality. The micro-CT images revealed the  
21 hierarchy structure of the paddy soil and a distinct bimodal pattern in the  
22 PSDs. The structural porosities from BLN, DE models and from CT imaging  
23 are consistent, and all correlated with the natural logarithm of saturated

24 hydraulic conductivity. Long-term application of NPKOM increased structural  
25 porosity though no changes were recorded in the textural porosity  
26 compared with NPK and CK treatment, while the latter two showed a near  
27 identical pore structure. The results of this study showed the consistence of  
28 the SWRC and imaging method in studying soil pore structure and  
29 supported the use of bimodal SWRC models to investigate the pore  
30 structure of the well-structured paddy soil.

31 **Key Words**

32 Soil water retention curve; Pore size distribution; Micro-CT; Paddy soil;  
33 Bimodal porosity

34 **Abbreviations:** BC model, Brooks and Corey (1964) model; ME, mean  
35 error; PSD, pore size distribution; SWRC, soil water retention curve; VG  
36 model, van Genuchten (1980) model; LN model, lognormal model (Kosugi,  
37 1994);

38

## 39 **Introduction**

40 The pore geometry of a soil influences the soil water dynamics, aeration,  
41 microbial activities, and root elongation and therefore is widely used as an  
42 important indicator of soil quality (Pagliai and Vignozzi, 2002). Pores in  
43 well-structured soils are generally considered to have a hierarchical  
44 organization, with textural pores defined as the pores between soil particles  
45 and structural pores considered as those between soil aggregates (Dexter et  
46 al., 2008; Dexter et al., 2009). Quantification of the pore system, including  
47 different soil pore domains, are increasingly necessary to understand soil  
48 processes and functions with respect to their impact on soil quality.

49 The measurement of soil pore structure, however, is not straightforward  
50 because of the opacity of soil (Hajnos et al., 2006). Several different  
51 methods have been used to investigate pore structure, some methods  
52 based on directly two-dimensional (2D) (Pagliai et al., 2004) or  
53 three-dimensional (3D) imaging (Mooney et al., 2008; Munkholm et al.,  
54 2012; Naveed et al., 2014; Peth et al., 2008), while others are based on  
55 indirect calculation according to the assumed relationship between pore  
56 structure and specific soil properties (e.g. water retention, gas transport)  
57 (Hajnos et al., 2006; Pires et al., 2008).

58 The soil water retention curve (SWRC) has been frequently used to  
59 reveal information concerning the arrangement of soil pore system (Pires et  
60 al., 2008). SWRC illustrated the amount of soil water content ( $\theta$ ) under  
61 equilibrium as a function of soil water suction ( $h$ ). The measurement of

62 SWRC is normally conducted at limited water suctions and a model is used  
63 to fit the unmeasured points. Numerous SWRC models, both numerical and  
64 theoretical, have been developed due to its importance in modeling soil  
65 water dynamics and solute transport. For example, the widely used van  
66 Genuchten (1980) (VG) model uses a closed form equation with several  
67 adjustable parameters to empirically fit the SWRC. Whilst the lognormal (LN)  
68 model by Kosugi (1994) is derived theoretically from a lognormal pore-size  
69 distribution (PSD). Despite the form of the SWRC model, a soil PSD can be  
70 derived from SWRC based on the assumption that soil water drains  
71 progressively from decreasing sized pores along with progressive decreases  
72 in soil matrix potential.

73 The available SWRC models can be broadly classified as unimodal,  
74 bimodal and multimodal models according to the shape of the derived soil  
75 PSD. The VG and LN models, as well as the widely used Brooks and Corey  
76 (1964) (BC) model are unimodal. Durner (1994) firstly reported a bimodal  
77 van Genuchten (BVG) model by superimposing two van Genuchten  
78 equations. Two modals of the PSD, corresponding to the inter-particle pores  
79 and inter-aggregate pores respectively, could be identified for the  
80 aggregated soils with the BVG model (Durner, 1994). Similar to Durner  
81 (1994), Kutílek et al. (2006) developed a bimodal lognormal (BLN) model  
82 through superimposing two LN equations. The BLN model can segregate the  
83 pore system to structural and textural domains assuming each domain  
84 showing a lognormal distribution (Romano et al., 2011). Here the structural

85 and textural pores have similar meanings as the inter-aggregate and  
86 inter-particle pores (Durner, 1994), respectively and we will stick with the  
87 former names in this study. More recently, Dexter et al. (2008) proposed a  
88 five-parameter bimodal model in the form of a double-exponential (DE)  
89 equation with each exponential term representing textural and structural  
90 pore spaces, respectively. By extending the DE equation to a  
91 triple-exponential (TE) equation, the macropores can be characterized by  
92 the third exponential term (Dexter and Richard, 2009). It needs to be  
93 pointed out that the BVG and BLN models can also be extended to  
94 multi-modals models in theory, but the number of parameters could be  
95 close to or larger than the usually measured SWRC points which could cause  
96 inaccuracy in the parameter estimation. The development of bimodal and  
97 multimodal models from unimodal models has greatly improved the  
98 understanding soil pore structure (Dexter and Richard, 2009) as well as  
99 assisting with prediction of soil hydraulic properties (Durner, 1994).

100 The bimodal or multimodal SWRC models were theoretically founded on  
101 the assumption of bimodal or multimodal soil PSD. However to date these  
102 models have not been validated using the true soil PSD data. The reason lies  
103 in the difficulty to obtain a soil's PSD that ranges over several orders of scale.  
104 In recent years the application of X-ray Micro-CT and associated image  
105 analysis methods provide means to quantify three-dimensional (3-D) soil  
106 structure from pore scale to core scale (Wildenschild et al., 2002;  
107 Wildenschild and Sheppard, 2013; Helliwell et al. 2013). Recently, Zhou et

108 al. (2013) employed synchrotron, industrial and medical CT systems to  
109 reveal micro- to macro- scale soil structure. The PSD data obtained from  
110 different scales can be combined using a scale fusion methods proposed by  
111 Schluter (2011). A broader PSD can therefore be obtained from micron to  
112 centimeter scales. Although this scale ranges only broadly corresponds to  
113 the wet range of the SWRC (from saturation to -100 kPa) and is not well  
114 suited to the finer pores that usually exist between particles (textural pores)  
115 but more appropriate for structural pores, which are more liable to change  
116 under environmental or anthropogenic impacts (Dexter and Richard, 2009).

117 Paddy soils are normally rich in clay and have complex pore systems at  
118 both aggregate and core scales (Lennartz et al., 2009; Zhou et al., 2016),  
119 hence we hypothesize that the PSD's are bimodal or multimodal. In this  
120 study, we measured SWRC of the paddy soil under different fertilization  
121 regimes and scanned two scales of undisturbed soil samples (aggregate and  
122 core scales). The specific objectives were to: (1) compare the performance  
123 of unimodal, bimodal, and trimodal SWRC models on paddy soil, (2)  
124 compare the pore structure obtained from the SWRC models and from CT  
125 scanning, and (3) investigate the effect of different fertilization regimes on  
126 bimodal pore structure.

### 127 ***SWRC models and equivalent PSD***

128 Three unimodal models (BC, LN, and VG model), three bimodal models  
129 (DVG, BLN, and DE models), and a trimodal (TE) model were examined in  
130 this study. The equations and estimated parameters are listed in Table 1.

131 The  $\theta_S$  and  $\theta_r$  represent the saturated water content and residue water  
132 content, respectively. The BC model incorporated the air entry value ( $h_b$ ) in  
133 the model and  $\lambda$  is the shape factor. The LN model was developed assuming  
134 a lognormal PSD with  $h_m$  and  $\sigma$  representing the mode and variance of the  
135 PSD, respectively. The erfc is the complementary error function. The VG  
136 model has five parameters, i.e.  $\theta_S$ ,  $\theta_r$ ,  $a$ ,  $n$ ,  $m$ . Previous studies showed  $n$   
137 and  $m$  are not independent and the Mualem (1976) constraint ( $m=1-1/n$ ) is  
138 usually used. In this study we follow the constraint and therefore four  
139 parameters were estimated.

140 The BLN model is developed by superimposing two LN models, with  
141 each term representing the matrix and structural domain, respectively. The  
142  $w_1$  is a weighting factor corresponds to the matrix pores, and  $1-w_1$   
143 corresponds to the structural pores;  $h_{mi}$  and  $\sigma_i$  represent the modes and  
144 variance of the PSD of the matrix domain ( $i = 1$ ) and structural domain ( $i =$   
145  $2$ ), respectively. Similar to BLN model, the DVG model is developed by  
146 superimposing two VG models, with each term representing the matrix and  
147 structural domain, respectively. The  $a_i$  and  $n_i$  are shape factors of the textural  
148 domain ( $i = 1$ ) and structural domain ( $i = 2$ ), respectively. The DE and TE  
149 model include two and three exponential terms, respectively.  $C$  is the  
150 residual water content.  $A_1$ ,  $A_2$ , and  $A_3$  are the water content at saturation of  
151 the textural, structural, and macro-pore space, respectively. And  $h_1$ ,  $h_2$ , and  
152  $h_3$  are suctions to empty soil water in the textural, structural, and  
153 macro-pores, respectively. The difference between DE and TE model is the



154 macro-pore term, which corresponds to big cracks or bio-pores that are too  
155 large to hold water at field conditions (Dexter and Richard, 2009).

156 The equivalent PSD function  $f(r)$  can be obtained from SWRC models  
157 using the differential equation:

$$158 \quad f(r) = d\theta/dr \quad (1)$$

159 where  $r$  is the pore radius, which is assumed to be related to  $h$  for a  
160 given saturation by the capillary pressure function:

$$161 \quad h = \frac{2\gamma \cos \beta}{\rho_w g r} \quad (2)$$

162 where  $\gamma$  is the surface tension between the water and air ( $=7.29 \times 10^{-2}$   
163  $\text{Nm}^{-1}$ ),  $\beta$  is the contact angle, which was taken as zero in this study,  $\rho$  is  
164 the density of water ( $=1 \text{ Mg m}^{-3}$ ), and  $g$  is the acceleration of gravity ( $=$   
165  $9.8 \text{ m s}^{-2}$ ).

## 166 **Materials and Methods**

### 167 ***Sampling and measurement***

168 Soil samples were collected from a long-term field experiment of Jiangxi  
169 Institute of Red Soil, Jinxian County, Jiangxi Province, China ( $116^{\circ}10' \text{ E}$ ,  
170  $28^{\circ}21' \text{ N}$ ). The field experiment was started in 1982 to test the effects of  
171 different fertilization strategies on soil quality. Three fertilization treatments  
172 were examined: (a) a control without fertilization, CK; (b) an inorganic  
173 fertilization with  $90 \text{ kg N ha}^{-1}$ ,  $20 \text{ kg P ha}^{-1}$ , and  $62 \text{ kg K ha}^{-1}$  for each  
174 growth season, NPK; and (c) a combination of organic manure ( $22.5 \text{ t ha}^{-1}$ )  
175 and same amount of inorganic fertilizers as NPK, NPKOM. The experiment

176 followed a completely random block design with three replicated blocks.  
177 There were a total of nine plots, with each plots having an area of 46.67 m<sup>2</sup>.

178 A bulk soil sample and two undisturbed soil cores (diameter 5.0 cm,  
179 height 5.1 cm) were collected from the surface layer (0 – 10 cm) in each plot.  
180 The bulk samples were air-dried and three aggregates (~ 3 mm in diameter)  
181 were randomly selected for CT scanning. The cores were subjected to CT  
182 scanning at field moisture content before measurement of saturated  
183 hydraulic conductivity ( $K_s$ ) and SWRC. The  $K_s$  was measured using the  
184 constant water head method. The SWRC was determined with a sandbox at  
185 the wet range (0, 5, 10, 30, 60, and 100 hPa), and using a pressure plate  
186 method at large suction (150, 330, 1000, 3000, 5000, 10000, and 15000  
187 hPa). The cores were then dried in an oven at 105 °C for 24 h to determine  
188 bulk density. Total porosity (TP) was calculated assuming soil density of 2.65  
189 g cm<sup>-3</sup>. One sample was spoiled during the measurement and therefore  
190 there were 17 SWRCs in total.

### 191 ***SWRC fitting, and PSD calculation***

192 All the SWRC models were fitted by the nonlinear least-square  
193 curve-fitting method with Matlab (R2014a; The Mathworks, Inc.). The initial  
194 values, lower and upper boundaries of the fitting parameters were provided  
195 for each fitting. The PSD was derived from SWRC models using equation (1)  
196 and (2).

### 197 ***CT scanning***

198 Soil cores were scanned using an industrial Phoenix Nanotom X-ray  
199 micro-CT (GE, Sensing and Inspection Technologies, GmbH, Wunstorf,  
200 Germany). Detailed scanning information can be found in Zhou et al. (2016).  
201 Briefly, the samples were scanned at a voltage and current of 100 kV and  
202 100  $\mu\text{A}$ , respectively. The filtered back-projection algorithm, which was  
203 implemented in the Datos|x 2.0 software, was used to reconstruct the  
204 image slices. The generated 2000 slices had a size of  $2000 \times 2000$  voxels,  
205 with each voxel representing a volume of  $30 \times 30 \times 30 \mu\text{m}^3$ . The slices were  
206 stored in 8-bit format and each voxel had a grayscale value between 0 and  
207 255 representing the attenuation coefficient of the corresponding material.

208 The scanning of aggregates from the bulk samples was conducted with a  
209 synchrotron-based micro-CT at beam line BL13W1 of the Shanghai  
210 Synchrotron Radiation facility (SSRF). Details of scanning and image  
211 reconstruction can be found in Zhou et al. (2012). The image stack for each  
212 aggregate included 1200 slices with a size of  $2000 \times 2000$  voxels. The slices  
213 were stored in 8-bit format and had a resolution of  $3.7 \times 3.7 \times 3.7 \mu\text{m}^3$ .

## 214 ***Image analysis***

215 Image preprocessing, segmentation, and quantification have previously  
216 been detailed in Zhou et al. (2016) and are only briefly described here. For  
217 the core-scale samples, a region of interest (ROI),  $1000 \times 1000 \times 1000$   
218 voxel<sup>3</sup>, was selected from the central part to avoid artifacts at the boundary.  
219 For the aggregate-scale samples, a ROI of  $500 \times 500 \times 500$  voxel<sup>3</sup> was

220 selected from the central part. The final size of the cubic ROI of soil cores  
221 and aggregates were 30 and 1.85 mm, respectively (Fig. 1). A 3D median  
222 filter was used to reduce noises before segmentation. Images were  
223 segmented by a bi-level method (Vogel and Kretzschmar, 1996).

224 Porosity was determined as the percentage of pore volume to the total  
225 volume of the ROI. The PSD was obtained by morphological "opening"  
226 operations, which firstly "erode" the pores with a spherical structural mask  
227 and then "dilate" the eroded pores with the same structural mask. This  
228 process removes pores smaller than the size of the structural mask. By  
229 progressively increasing the size of the structuring element and determining  
230 porosity after each "opening" operation the PSD was determined. The PSD  
231 of soil cores and aggregates ranged from 30 - 2878  $\mu\text{m}$  and 3.7 - 115  $\mu\text{m}$ ,  
232 respectively. The PSD of the two scales could be combined to have a broader  
233 range. As the PSD of the two scales overlapped at the range 30 - 115  $\mu\text{m}$ ,  
234 only the higher value was used in the combined PSD. A more detailed  
235 introduction of this procedure can be found in Schlüter et al. (2011). There  
236 are two issues to be addressed in the procedure. The first one is that the  
237 averaged PSD of the aggregates from each plot was used to combine the  
238 PSD of soil cores from the same plot. The second one is that the  
239 heterogeneity of soil structure was not fully considered and the PSD of  
240 aggregates was hypothesized to be able to represent aggregate-scale PSD  
241 of the corresponding soil cores.

242 Image processing was performed with the open-source software

243 ImageJ ver. 1.47 (Rasband, 1997-2011) except for the segmentation which  
244 was conducted with the software Quantim  
245 (<http://www.ufz.de/index.php?en=16562>, verified at 2016-02-20). Image  
246 quantification was performed using a script running in Matlab (R2014a; The  
247 Mathworks, Inc.).

### 248 ***Statistical analysis***

249 The coefficient of determination ( $R^2$ ), root mean square error (RMSE),  
250 and the Akaike Information Criterion (AIC) were used to compare the  
251 overall performance of SWRC models calculated within Matlab (R2014a; The  
252 Mathworks, Inc.). The  $R^2$  was calculated as

$$253 \quad R^2 = 1 - \frac{SSE}{SST} \quad (3)$$

254 where  $SSE$  is the residual sum of squares,  $SST$  is the total sum of  
255 squares.

256 The RMSE was calculated as

$$257 \quad RMSE = \sqrt{\frac{1}{N} \sum (\theta_{mean} - \theta_{fitted})^2} \quad (4)$$

258 where  $N$  is the number of data points,  $\theta_{mean}$  is the mean value of  
259 measured water content, and  $\theta_{fitted}$  is the fitted water content.

260 The AIC was calculated as:

$$261 \quad AIC = 2K + N \ln\left(\frac{SSE}{N}\right) \quad (5)$$

262 where  $K$  is the number of parameters to be estimated in the model. As  $N$   
263 is small the corrected AIC,  $AIC_c$  was used.

$$AIC_c = AIC + \frac{2K(K+1)}{N-K+1} \quad (6)$$

The mean error, ME, was used here to compare model performance at different data points. ME was calculated for each measured data point separately:

$$ME = \frac{1}{n} \sum |\theta_{measured} - \theta_{fitted}| \quad (7)$$

where n is the number of fitted curves,  $\theta_{measured}$  is the measured water content at certain suction.

The below statistical analysis was performed with the SAS software program (SAS institute, 2011). We used ANOVA to compare the differences in soil porosities among different treatments. Mean values were tested using the Fisher's least significant difference (LSD) at the P = 0.05 level. Pearson correlation coefficients were conducted to evaluate the linear relationship between soil porosities and the natural logarithm of  $K_s$ .

## Results

### **SWRC fitting**

All the tested SWRC models showed good overall performance with the lowest mean  $R^2$  of 0.95 for the BC model (Table 2). An example of the fitting of SWRC of the studied paddy soil with different models is shown in Fig. 1. The bimodal and trimodal models showed superior performance than any of the tested unimodal models (Fig. 1). Best fitting was found with the BLN, TE, and DE models, with  $R^2$  close to 1 and lowest RMSE and AICc values (Table 2). Figure 2 shows the mean ME at different suctions. The ME increased

286 considerably from low to high suctions for the unimodal models, while ME  
287 was constantly low over the whole range for the multimodal models except  
288 BVG model.

### 289 ***Pore structure from SWRC models***

290 The derivative of SWRC can be easily transformed to PSD by converting  
291 suction to equivalent diameter using Equation (10) and an example of the  
292 derivative was shown in Fig. 3. It is not surprising that all the unimodal  
293 models failed to capture the second modal of the PSD. Considerable  
294 differences were found for the shape of PSD among the unimodal models,  
295 with the peak of the modal shifted rightward from BC to VG and LN model.  
296 Distinct bimodality was found for the derivatives of all the samples with BLN  
297 and DE models. The DVG model was able to capture the bimodality for 11 of  
298 the 17 samples but failed for the other 6 samples. The TE model showed  
299 tri-modality with the two peaks in the left region very close. The estimated  
300 suctions where the PSD peaked overlapped at the textural domain for BLN,  
301 DE, and TE models (Fig. 3). For the structural domain, the suctions at the  
302 peaks of BVG, BLN and DE model overlapped located between the peaks of  
303 structural and macro-pore domain of the TE model (Fig. 3).

304 A segregation of pore space into textural and structural domains was  
305 possible with the bimodal and multimodal models. The DVG model was not  
306 further considered partially because it failed to capture the bimodality of 6  
307 out the 17 samples and partially because its performance in fitting SWRC  
308 was not as good as BLN and DE models. The TE model can segregate

309 macropore space besides textural and structural pore spaces. However, in  
310 this study the macropores were ascribed to structural pores. In this case the  
311 difference between DE model and TE model were negligible and only the DE  
312 model was further considered. The structural and textural porosity  
313 calculated from BLN and DE models are shown in Fig. 4. The structural  
314 porosity derived from DE model ( $P_{str_{DE}}$ ) was lower than those from the BLN  
315 model ( $P_{str_{BLN}}$ ), while the textural porosity showed an opposite trend. Both  
316 the structural and textural porosities derived from BLN and DE models were  
317 significantly positively correlated ( $P < 0.001$ ), respectively.

318 Application of NPKOM significantly increased structural porosity relative  
319 to CK and NPK treatments ( $P < 0.5$ ), while the latter two treatments showed  
320 no significant difference ( $P > 0.05$ ) (Table 3). No significant difference in  
321 textural porosity was found among the different fertilization treatments ( $P >$   
322  $0.05$ ) (Table 3).

### 323 ***Pore structure from CT imaging***

324 The structure of the paddy soil differed at both the aggregate and core  
325 scale (Fig. 5). A hierarchical structure was observed for the core scale  
326 samples, which were composed of aggregates that were separated by pores  
327 in the form of cracks, planes or channels. The aggregates had a dense  
328 structure with most inter-aggregate pores disconnected. The cumulative  
329 porosities of aggregates (with pore diameter 3.7 - 114.7  $\mu\text{m}$ ) and cores  
330 (with pore diameter 30 - 2878  $\mu\text{m}$ ) were combined to include a wider range  
331 (3.7 - 2878  $\mu\text{m}$ ) and the PSD derived (Fig. 6). The PSD showed distinct



332 bimodality, with two peaks observed for all the samples as seen in Fig. 6.  
333 The two peaks located in the intra-aggregate and inter-aggregates domains  
334 respectively, which were separated by the minimum of the PSD between the  
335 two peaks. The intra- and inter- aggregate porosities, corresponded to the  
336 structural and textural porosities, respectively, were determined based on  
337 the separation of two domains. Application of NPKOM significantly increased  
338 the CT imaging-based structural porosity ( $P_{str_{CT}}$ ) and textural porosity  
339 ( $P_{tex_{CT}}$ ) relative to the CK and NPK treatments ( $P < 0.05$ ), while the latter  
340 two treatments showed no significant difference ( $P > 0.05$ ) (Table 3).

341 ***Bimodal porosities derived from SWRC models and from CT imaging,***  
342 ***and their relationship with  $K_s$***

343 The  $P_{str_{CT}}$  was lower than the structural porosities from the SWRC  
344 models ( $P_{str_{BLN}}$  and  $P_{str_{DE}}$ ), but they were positively correlated ( $P < 0.01$ )  
345 (Fig. 7). CT imaging can only reveal pores larger than the pixel size, which  
346 is  $3.7 \mu m$  in this study, and therefore cannot provide complete information  
347 of textural porosity as per the definition. The  $P_{tex_{CT}}$  was therefore much  
348 lower than textural porosities estimated from SWRC ( $P_{tex_{DNL}}$  and  $P_{tex_{DE}}$ )  
349 and no significant correlation was found between them ( $P > 0.1$ ).

350 The relationship between the natural logarithm of  $K_s$  ( $\ln(K_s)$ ) and  
351 structural porosities ( $P_{str}$ ) and total porosity (TP) is shown in Fig. 8. The TP,  
352  $P_{str_{DE}}$ ,  $P_{str_{BLN}}$ , and  $P_{str_{CT}}$  were all lineally correlated with  $\ln(K_s)$  with p  
353 values  $< 0.05$ . The  $P_{str_{DE}}$  and  $P_{str_{BLN}}$  did not improve the correlation as  
354 compared with TP. A stronger Pearson correlation coefficient was found

355 between  $P_{str_{CT}}$  and  $\ln(K_s)$  ( $R^2 = 0.57$ ,  $p < 0.001$ ), indicating  $P_{str_{CT}}$  is more  
356 related to the saturated hydraulic conductivity.

## 357 **Discussion**

### 358 **Bimodality of pore space in paddy soil**

359 The well-structured soils are believed to have hierarchical structures,  
360 and their pore space can be segregated to textural pores between soil  
361 particles and structural pores between aggregates (Dexter et al., 2008).  
362 Quantification of the structural and textural porosity has been conducted  
363 with SWRC models (Bruand & Cousin, 1995; Pires *et al.*, 2008). However,  
364 we could see from Fig. 3 that the modality of the PSD depends heavily on the  
365 selected SWRC models. In this study, we first compared seven widely used  
366 SWRC models, including three unimodal models (BC, LN, and VG model),  
367 three bimodal models (DVG, BLN, and DE models), and a trimodal (TE)  
368 model. The fitting of the SWRC using all the seven models was generally  
369 good and with  $R^2 > 0.95$ . However, the goodness of fit, as shown in Fig. 2  
370 and Table 2, indicated that bimodal models (BLN and DE model) best fitted  
371 the SWRC data and indicated the existence of a bimodal PSD (Fig. 3). The  
372 fitting results convinced us the use of bimodal models to investigate the  
373 hierarchical pore structure in the paddy soil. The PSD derived from both the  
374 BLN and DE models showed evident bimodal structure and that the  
375 structural and textural porosities inferred from both models were linearly  
376 correlated (Fig. 4).

377 The CT imaging revealed hierarchical structure of the paddy soil as  
378 shown in Fig. 5. By combining the PSD of soil aggregates and cores, a  
379 bimodal pore structure was also observed (Fig. 6). From SWRC modeling,  
380 morphological observation of CT images and quantitative image analysis,  
381 we can conclude paddy soil has a bimodal pore structure, which was in  
382 consistent with previous study on structured soils (Durner, 1994; Kutilek *et*  
383 *al.*, 2006; Resurreccion *et al.*, 2010).

### 384 **Comparison of the SWRC modeling and CT imaging methods**

385 The BLN and DE models have distinct physical meanings related to the  
386 bimodal pore space and they generated consistent pore structure  
387 information. The  $P_{strCT}$  was comparable to the structural porosities from  
388 SWRC models and showed linear correlation with them. Moreover,  $P_{strCT}$ ,  
389  $P_{strBLN}$  and  $P_{strDE}$  are all positively correlated with  $\ln(K_s)$  with the  $P_{strCT}$   
390 showed the highest correlation. The  $P_{texCT}$ , however, only included pores  
391 large than  $3.7 \mu m$  due to resolution limitation and was therefore lower than  
392 textural porosities calculated from SWRC (Table 3). These results suggest  
393 the use of either SWRC or CT imaging to quantify the structural porosity is  
394 feasible, but only SWRC modeling is capable of investigating textural  
395 porosity. Compared to SWRC modeling, CT imaging is fast and can provide  
396 detailed information on the macropores that are more related with soil  
397 water transport processes (Luo *et al.*, 2008; Rezanezhad *et al.*, 2009).  
398 However, direct quantification of multi-scale soil pore structure is still not  
399 feasible for many soil scientists. One difficulty lies in the limited accessibility

400 and high price of the non-destructive CT devices despite the fast  
401 development of CT techniques in recently years. Another difficulty is that  
402 soil pores range over several orders of scale, which makes it impossible to  
403 quantify soil pores with any single technique (Wildenschild *et al.*, 2002).  
404 SWRC has been proven to be able to provide valuable information about the  
405 pore structure as long as it is accurately modelled using suitable models.

#### 406 **Fertilization effects on bimodal pore structure**

407 The structural porosity is more liable to change under external  
408 influences (e.g. compaction) while the textural porosity is more stable  
409 (Bruand & Cousin, 1995; Kutilek *et al.*, 2006). Similar results were also  
410 found in this study when soil is fertilized differently for a long term.  
411 Application of NPKOM significantly increased structural porosity relative to  
412 CK and NPK treatments but did not change textural porosities ( $P > 0.05$ )  
413 (Table 3). The  $P_{\text{texCT}}$  was highest in NPKOM probably because only large  
414 pores in the textural pore range were included. Application of NPK in the  
415 paddy soil showed no effects in changing the soil pore structure compared  
416 with the CK treatment, which highlight the importance to further study of  
417 the mechanisms of inorganic fertilization on soil quality.

#### 418 **Conclusions**

419 In this study we first compared seven widely used models on the fitting  
420 of SWRC data and the two bimodal (BLN and DE) models showed best  
421 performance. The CT imaging also revealed the hierarchy structure of the  
422 paddy soil. Both SWRC modeling and CT imaging methods validated the

423 bimodal pore structure of the paddy soil. The bimodal (BLN and DE) SWRC  
424 models generated similar textural and structural porosities, with the latter  
425 positive correlated with structural porosities from CT imaging. Long-term  
426 application of NPKOM improved structural porosity but did not change  
427 textural porosity compared with the NPK and CK treatment, while the latter  
428 two showed near identical pore structure. The results of this study  
429 supported the use of bimodal SWRC models to investigate the pore  
430 structure of the well-structured paddy soil.

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506 Figure Captions

507 Figure 1 Example fitting of SWRC with unimodal (left) and bimodal and  
508 multi-modal (right) models.

509 Figure 2 Mean fitting errors of the SWRC fitted to different models.

510 Figure 3 PSD patterns derived from SWRC with unimodal (left) and bimodal  
511 and multi-modal (right) models.

512 Figure 4 Correlation of the structural and textural porosities respectively  
513 between BLN and DE models.

514 Figure 5 Two-dimensional CT slices of soil aggregates and soil cores from CK,  
515 NPK, and NPKOM treatments.

516 Figure 6 Fusion of the cumulative pore size distribution of aggregate and  
517 core scale (above) and the derivative pore size distribution (bottom).

518 Figure 7 Correlation of the structural porosities from SWRC models and from  
519 CT imaging.

520 Figure 8 Correlation between porosities and the natural logarithm of  $K_s$   
521 ( $\ln(K_s)$ ).



Table 1 Three unimodal models, three bimodal models, and a triple-modal model.

Categories	Model	Abbr.	Equation	Parameters
Unimodal	Brooks and Corey (1964)	BC	$\theta(h) = \theta_r + (\theta_s - \theta_r) \left(\frac{h_b}{h}\right)^{-\lambda} \quad \text{for } h < h_b,$ $\theta(h) = \theta_s \quad \text{for } h_b \leq h \leq 0$	$\theta_s, \theta_r, h_b, \lambda$
	Lognormal pore-size distribution (Kosugi, 1994)	LN	$\theta(h) = \theta_r + (\theta_s - \theta_r) 1/2 \operatorname{erfc}[\ln(h/h_m)/(\sqrt{2}\sigma)]$	$\theta_s, \theta_r, h_m, \sigma$
	van Genuchten (1980)	VG	$\theta(h) = \theta_r + (\theta_s - \theta_r) [1 + (\alpha h)^{-n}]^m$	$\theta_s, \theta_r, \alpha, n, m$
Bimodal	Double van Genuchten model (Durnel, 1994)	DVG	$\theta(h) = \theta_r + (\theta_s - \theta_r) \left\{ w_1 [1 + (\alpha_1 h)^{-n_1}]^{1-1/n_1} + (1 - w_1) [1 + (\alpha_2 h)^{-n_2}]^{1-1/n_2} \right\}$	$\theta_s, \theta_r, w_1, \alpha_1, n_1, \alpha_2, n_2$
	Double lognormal model (Romano et al., 2011)	DLN	$\theta(h) = \theta_r + (\theta_s - \theta_r) \left\{ w_1 1/2 \operatorname{erfc}[\ln(h/h_{m1})/(\sqrt{2}\sigma_1)] + (1 - w_1) 1/2 \operatorname{erfc}[\ln(h/h_{m2})/(\sqrt{2}\sigma_2)] \right\}$	$\theta_s, \theta_r, w_1, h_{m1}, \sigma_1, h_{m2}, \sigma_2$
	Double-Exponential equation (Deter et al., 2008)	DE	$\theta(h) = C + A_1 \exp(-h/h_1) + A_2 \exp(-h/h_2)$	$C, A_1, h_1, A_2, h_2$
Trimodal	Triple-Exponential equation (Dexter and Richard, 2009)	TE	$\theta(h) = C + A_1 \exp(-h/h_1) + A_2 \exp(-h/h_2) + A_3 \exp(-h/h_3)$	$C, A_1, h_1, A_2, h_2, A_3, h_3$

Table 2 Predictive performances of the tested models on the measured soil water retention data

Model	BC	LN	VG	DVG	DLN	DE	TE
$R^2$	0.95(0.89, 0.97)	0.96(0.93, 0.98)	0.96(0.90, 0.98)	0.98(0.95, 1.00)	1.00(0.99, 1.00)	0.99(0.99, 1.00)	1.00(0.99, 1.00)
RMSE	0.021(0.009, 0.029)	0.0177(0.0081, 0.0255)	0.0195(0.0089, 0.0270)	0.0118(0.0020, 0.0279)	0.0045(0.0014, 0.0072)	0.0076(0.0020, 0.0146)	0.0050(0.0017, 0.0081)
AIC <sub>c</sub>	-90.5(-110.4, -81.3)	-94.9(-114.2, -84.4)	-92.4(-111.8, -82.9)	-95.72(-132.6, -64.1)	-113.2(-141.1, -99.3)	-110.8(-146.1, -94.3)	-113.5(-136.7, -96.3)

Table 3 Total porosity (TP), structural porosity (Pstr), and textural porosity (Ptex) determined with bimodal lognormal (BLN) model, double-exponential (DE) model, and from CT imaging (CT)

Porosity (cm <sup>3</sup> cm <sup>-3</sup> )	BLN			DE			CT		
	CK	NPK	NPKOM	CK	NPK	NPKOM	CK	NPK	NPKOM
TP	0.55b	0.57b	0.62a	0.55b	0.57b	0.63a	0.07b	0.11ab	0.17a
Pstr	0.15b	0.16 b	0.24a	0.13b	0.14b	0.21a	0.04b	0.08ab	0.12a
Ptex	0.40a	0.41a	0.38a	0.43a	0.41a	0.42a	0.03b	0.03b	0.05a