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**A lumped bubble capacitance model controlled by matrix structure to describe  
layered biogenic gas bubble storage in shallow subtropical peat**

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23 **Abstract**

24 Methane (CH<sub>4</sub>) accumulates in the gaseous phase in peat soils, being released to the  
25 atmosphere at rates higher than those for diffusion and plant-mediated pathways. An  
26 understanding of the mechanisms regulating gas bubble storage in peat remains  
27 incomplete. We developed a layered capacitance model to compare the bubble storage  
28 ability of peat over different depths. A peat monolith (0.395 m × 0.243 m × 0.247  
29 m) was collected from the US Everglades and kept submerged for 102 days from a  
30 condition of minimum bubble storage to bubble saturation. Time-lapse  
31 electromagnetic wave velocity and power spectrum data were used to estimate  
32 changes in both gas content and relative average dimensions of stored bubbles with  
33 depth. Bubble capacitance, defined as the increase in volumetric gas content (m<sup>3</sup> m<sup>-3</sup>)  
34 divided by the corresponding pressure (Pa), ranges from 3.3 × 10<sup>-4</sup> to 6.8 × 10<sup>-4</sup> m<sup>3</sup>  
35 m<sup>-3</sup> Pa<sup>-1</sup>, with a maximum at 5.5 cm depth of. Bubbles in this hotspot were larger  
36 relative to those in deeper layers, whilst the decomposition degree of the upper layers  
37 was generally smaller than that of the lower layers. X-ray computed tomography on  
38 peat sections identified a specific depth with a low void ratio, and likely regulating  
39 bubble storage. Our results suggest that bubble capacitance is related to (1) the  
40 difference in size between bubbles and peat pores, and (2) the void ratio. Our work  
41 suggests that changes in bubble size associated with variations in water level driven  
42 by climate change will modify bubble storage in peat soils.

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46 **Keywords:** Peat, methane storage, gas bubbles, lumped capacitance model, X-ray

47 computed tomography, pore structure

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67 **1. Introduction**

68 Following almost one decade of stable values in the 1990s, the atmospheric  
69 concentration of methane (CH<sub>4</sub>), the second most important greenhouse gas, has  
70 increased since 2007, mandating a higher Global Warming Potential (GWP) in the  
71 most recent IPCC (Intergovernmental Panel on Climate Change) report (IPCC, 2013)  
72 relative to the previous assessment (IPCC, 2007). The IPCC notes that peatlands may  
73 contribute to the variability and uncertainty of global CH<sub>4</sub> emissions (Ciais et al.,  
74 2014). In peat soils, CH<sub>4</sub> is produced by methanogens under anaerobic conditions, and  
75 released to the atmosphere via three pathways: diffusion, transport through vascular  
76 plants and bubbling of CH<sub>4</sub>-enriched gas, i.e. ebullition. The contribution of peat soils  
77 to the global CH<sub>4</sub> flux is underestimated when CH<sub>4</sub>-enriched gas bubbles are  
78 neglected, especially as the upward transport and ebullition of CH<sub>4</sub>-enriched gas  
79 bubbles is suggested to be the dominant pathway for CH<sub>4</sub> emission in peatlands  
80 (Coulthard et al., 2009; Glaser et al., 2004). A detailed description of the storage of  
81 gas bubbles needed to supply ebullition is lacking (Ebrahimi & Or, 2017; Granberg et  
82 al., 2001), in part due to the scale discrepancy between the apparent CH<sub>4</sub> fluxes  
83 measured over a whole peat column and the physical properties of a small peat section  
84 that control CH<sub>4</sub>-enriched gas bubble storage. A layered model structure to describe  
85 field-scale ebullition emissions from a mudflat of an estuarine temperate marsh was  
86 recently proposed (Chen et al., 2017). In this paper, we use a general lumped  
87 capacitance model (Frank et al., 2006) as a conceptual framework to quantify the  
88 differences in bubble storage ability between layers of a peat monolith.

89

90 Two basic assumptions are considered in early computational models of bubble  
91 storage, corresponding to two stages: In stage 1, the initial CH<sub>4</sub> transfer from the  
92 dissolved to gaseous phase is assumed to start when the sum of the partial pressures of  
93 all gases in a gas bubble is larger than the total ambient pressure including  
94 atmospheric pressure, hydrostatic pressure and the pressure to move soil particles  
95 (Rothfuss & Conrad, 1994; Walter et al., 1996). Assuming biogenic CH<sub>4</sub> is the major  
96 volatile component in peats and other wetland soils, a critical partial pressure of CH<sub>4</sub>  
97 can be estimated for initial bubble formation, e.g. 260 matm at 10 degrees Celsius,  
98 equivalent to a dissolved CH<sub>4</sub> concentration of 500 μM (8.0 mg L<sup>-1</sup>), or a constant  
99 mixing ratio of 25% CH<sub>4</sub> in the bubble (Shannon et al., 1996; Walter et al., 1996).  
100 These homogenous thresholds were based on consideration of the equilibrium  
101 concentrations, i.e. the solubility of CH<sub>4</sub> in water, e.g. Hutchison (1957). In stage 2,  
102 given that peat and other wetland soils are very porous, most gas bubbles (~70%  
103 amount) are assumed to be released immediately to the atmosphere after formation  
104 (Walter et al., 1996; Walter & Heimann, 2000), and remaining gas bubbles are  
105 assumed to be trapped until the water table drops below the depth where they are  
106 located, or until the percentage of the pore space dominated by gas bubbles exceeds a  
107 certain critical threshold (~30%) (Walter et al., 1996).

108

109 However, continuous observations of the gas content of peat samples during  
110 controlled incubations (Baird et al., 2004; Beckwith & Baird, 2001) suggest that

111 bubbles can grow at CH<sub>4</sub> concentrations below the equilibrium concentrations  
112 referenced above (e.g. 8 mg L<sup>-1</sup>). Observations in organic-rich sediments, e.g. Martens  
113 & Albert (1994) also indicate that degree of supersaturation of CH<sub>4</sub> in near-surface  
114 pores is not high enough for direct initial formation of a bubble in a water body, i.e.  
115 homogeneous nucleation. A reasonable explanation for bubble accumulation under  
116 relatively low pore-water CH<sub>4</sub> concentrations is heterogeneous nucleation that starts  
117 with a gas nucleus trapped on a solid particle surface (Boudreau, 2012). Jones et al.  
118 (1999) suggest that a key requirement for heterogeneous nucleation of gas bubbles is  
119 the presence of gas cavities at solid surfaces. The nucleation energy barrier for  
120 forming a bubble in a cavity is much lower than in pore water because less interfacial  
121 free energy is needed for the bubble to grow (Boudreau, 2012). The tiny crevices  
122 where the free gas-liquid surface needed for continuous bubble formation is  
123 maintained, are commonly termed nucleation sites.

124

125 Furthermore, CH<sub>4</sub>-enriched gas bubbles play an important role in CH<sub>4</sub> storage,  
126 possibly containing more CH<sub>4</sub> than the pool of the dissolved phase (Fechner-Levy &  
127 Hemond, 1996). A bubble grows outward into the porewater from the solid surface  
128 until it is large enough to rise from the nucleation site, breaking away and leaving the  
129 nucleus site essentially in its original configuration (Boudreau, 2012) (Figure 1a-c).  
130 After detachment from cavities, gas bubbles may enter the atmosphere via two  
131 processes. Firstly, bubbles may directly rise unimpeded through pore throats from  
132 depth to the surface, resulting in regular steady ebullition (Coulthard et al., 2009)

133 (Figure 1b - 1c). Alternatively, a released bubble may be re-trapped again by a narrow  
134 pore throat, generating a new nucleation site, resulting in additional bubble nucleation  
135 sites and subsequent accumulation (Li & Yortsos, 1995b; Yortsos & Parlari, 1989)  
136 (Figure 1b - 1c). Coulthard et al. (2009) proposed reduced complexity models to  
137 simulate bubble dynamics in peat; their results show that the accumulation of bubbles  
138 look somewhat like inverted sandpiles. Results from a laboratory observation on  
139 ebullition in peat soils support this hypothesis (Ramirez et al., 2015). In fact, trapped  
140 gas bubbles in the matrix may act as a buffering reservoir, regulating changes in  
141 surrounding dissolved CH<sub>4</sub> concentrations (Granberg et al., 2001). The trapped gas  
142 bubbles can be released by environmental forcing or over-accumulation, termed  
143 episodic ebullition (Glaser et al., 2004).

144

145 Bubble dimension is a key parameter controlling bubble storage (DelSontro et al.,  
146 2015; Kettridge & Binley, 2008; Ramirez et al., 2016; Terry & Slater, 2017). The  
147 estimated effective radii of gas bubbles in natural peat vary widely, from less than  $1 \times$   
148  $10^{-5}$  m (Kettridge & Binley, 2008) to  $5 \times 10^{-2}$  m (Terry & Slater, 2017). A minimum  
149 bubble dimension threshold for significant CH<sub>4</sub>-enriched gas bubble storage may exist,  
150 as the gaseous CH<sub>4</sub> in small bubbles dissolves back to the ambient water more rapidly  
151 (DelSontro et al., 2015).

152

153 In this paper, we develop an electrical-circuit-like model from the general lumped  
154 capacitance model to explain the layered storage and charge up of CH<sub>4</sub>-enriched gas

155 bubbles (Stage 2 referenced above), after initial heterogeneous nucleation in a peat  
156 column (Stage 1 referenced above). This conceptual model is applied to discuss the  
157 effects of vertical variations in peat structure on bubble storage in a peat monolith.  
158 Time-lapse electromagnetic wave speed and power spectra data acquired with a  
159 ground penetrating radar (GPR) instrument are used to estimate changes in both  
160 volumetric gas content of each layer and the relative average dimensions of stored gas  
161 bubbles between depths. X-ray Computed Tomography (CT) on resin-impregnated  
162 peat samples from the same monolith is used to determine void ratio variations with  
163 depth. Our findings suggest that bubble capacitance of a specific peat layer is directly  
164 related to the ratio of pore throat size to gas bubble size, as well as the void ratio.

165

## 166 **2. Lumped capacitance model of gas bubble storage (charge up) and release** 167 **(discharge)**

168 A layered model of a peat column for bubble storage and release (Figure 1a-1c) was  
169 recently proposed (Chen et al., 2017). We build on this work by defining a  
170 one-dimensional model consisting of lumped components similar to an electric circuit  
171 or a hydraulic circuit (Kirby, 2010). Entrapment (storage) of gas bubbles in pore  
172 throats is represented by the dielectric polarization of a capacitor (Figure 1d). Using  
173 this analogy, hydraulic/gravitational energy driving the bubble flux is equivalent to  
174 the total potential difference provided by a power source,  $\Delta\psi_T$ . Increasing the  
175 volume of entrapped gas bubbles normalized to the total volume of the layer at a  
176 depth  $D$ , i.e. the volumetric increase in gas content of the layer  $\Delta\theta_g$ , corresponds to

177 increasing the total stored electric charge  $Q$ . Gas bubbles accumulate in pore throats:  
178 the average capillary potential over all the bubble entrapping pore throats at depth  $D$   
179 increases analogous to the increase in potential difference between the two terminals  
180 of the dielectric medium of the capacitor,  $\Delta\psi_C$  (Figure 1d). When a resistor is  
181 connected to the capacitor in series, the charging rate is regulated by both the resistor  
182 and capacitor. The amount of time it takes the resistor-capacitor (RC) circuit to reach  
183 a steady state condition, e.g. when the potential difference across the capacitor  $\Delta\psi_C$   
184 reaches 63% of the full-charge value  $\Delta\psi_T$  (Figure S2, Hamilton, 2007), is referred  
185 to as the RC time constant  $\tau_c$  of the circuit. It takes a time  $= 7\tau_c$  to reach 0.1% of  
186 its full-charge value  $\Delta\psi_T$ . This time constant  $\tau_c$  depends on both the capacitance  $C$   
187 of the capacitor and the resistance  $R$  of the coupled resistor,

$$188 \quad \tau_c = R \times C \quad (1).$$

189 Similarly, bubble resistance  $R$  in our conceptual model serves to regulate the bubble  
190 accumulation rate associated with layer dimensions (i.e. thickness for the  
191 one-dimensional model), pore structure and fluid properties. Table 1 summarizes the  
192 analogy between components of an electrical circuit model, water capacitance model  
193 and our bubble capacitance model.

194

195 We divide the peat column into  $n$  layers ordered from the ground surface (Layer  
196 number  $i = 1$ ) to a certain depth  $D_i$  ( $i = n$ ), with the surface water layer defined as  
197 Layer 0. The water level is maintained at a distance  $d_0$  above the column surface,  
198 followed by the  $n$  peat layers of equal thickness,  $d_i=d$  (Figure 1). The matrix

199 component of each layer is represented by a capacitor ( $C_i$ ) and a resistor ( $R_i$ ) in series  
200 and the component that each layer contributes to the total water height is represented  
201 by a battery cell (potential energy source). The matrices of the individual layers are  
202 organized in parallel to express the capacitance of the whole peat column as the sum  
203 of the capacitances of all layers (the total gaseous volume is re-normalized to the total  
204 volume of all peat layers), whereas the water heights add in series to provide linear  
205 partial potential differences corresponding to capacitor-resistor couples. The positive  
206 terminal of the  $i$ th resistor-capacitor couple is connected to the positive terminal of the  
207 corresponding  $i$ th battery cell, and all the negative terminals of the resistor-capacitor  
208 couples are connected to the negative terminal of the surface battery cell, which is  
209 grounded to a reference zero potential. With this arrangement, the potential difference  
210 between the two terminals of each resistor-capacitor couple ( $\Delta\psi_{Ti}$ ), represents the  
211 cumulative fluid from the bottom of the  $i$ th layer to the surface of the overlying water  
212 layer, and is expressed in terms of hydraulic pressure (unit: Pa),

$$213 \quad \Delta\psi_{Ti} = \rho_f g D_i, \quad (2)$$

214 where  $\rho_f$  is the mass density of the fluid phase, i.e. water density neglecting gas  
215 bubbles ( $997.05 \text{ kg m}^{-3}$  at  $25^\circ \text{ C}$ ),  $g$  is the gravitational acceleration ( $9.81 \text{ m s}^{-2}$ ), and  
216  $D_i$  is the depth from the bottom of the  $i$ th layer to the water surface,

$$217 \quad D_i = \sum_{k=0}^i d_k \quad (3),$$

218 where  $d_k$  represents the thickness of a single layer.

219

220 Our lumped capacitance model assumes that initial gas bubbles already exist and

221 therefore focuses on Stage 2); the initial formation of CH<sub>4</sub>-enriched gas bubbles, i.e.  
222 Stage 1, can be explained by the general concept of heterogeneous bubble nucleation  
223 from gas cavities for various solutions (Jones et al., 1999). Following initial  
224 nucleation, gas bubbles grow larger via solution transfer along concentration gradients,  
225 crossing the interface between pore water and the gas bubbles (Li & Yortsos, 1995a).  
226 The formation of a new gas bubble at an initial heterogeneous nucleation site,  
227 subsequent growth and the later detachment from blocking pore throats is regulated  
228 by capillary pressure. The buoyancy effect resulting from gravitation has been  
229 considered the major energy source driving bubble transport across pore throats in  
230 opposition to the capillary effect (Chen & Slater, 2015; Glaser et al., 2004; Tokida et  
231 al., 2005).

232

233 In a bubble-filled cavity where the gaseous phase is in equilibrium with the dissolved  
234 phase in solution (no growth/no dissolution), the pressure difference between the two  
235 sides of the meniscus of the bubble can be described by the Laplace equation for low  
236 wetting angles (Clennell et al., 2000; Jones et al., 1999; Li & Yortsos, 1995a).  
237 Laboratory and numerical simulations suggest that bubble clusters can branch out  
238 from multiple specific nucleation sites to fill the pore network (Li & Yortsos, 1995b;  
239 Yousfi et al., 1990) (Figure 1). Therefore, concepts similar to the standard water  
240 retention curve can be used to relate volumetric gas content to capillary potential  
241 energy for a single peat layer (Figure 2). We divide the relationship between  
242 gas/water content and potential energy into three zones based on pressure ranges

243 (Figure 2): Zone I describes regular water retention associated with trapped air  
244 bubbles and will not be discussed further; Zone II describes biogenic CH<sub>4</sub>-enriched  
245 bubble retention of a single layer; Zone III describes highly variable retention mainly  
246 resulting from a capacitor breakdown effect.

247

248 We first consider the bubble dynamics associated with Zone II. When the battery cells  
249 are connected to the capacitors, indicating submergence by water (Table 1), a  
250 transient direct current (DC), representing transient bubble transport, flows through  
251 the circuit to charge the capacitors, such that the potential differences across all  
252 capacitors starts increasing from zero. Once the potential difference between the  
253 terminals of the *i*th capacitor is equal to the corresponding potential difference of the  
254 power supply,  $\Delta\psi_{Ti}$  (i.e. hydraulic pressure), the capacitor is fully charged and the  
255 transient current (i.e. bubble transport via a corresponding branch of the pore network)  
256 stops. Then the capacitor acts as an open circuit, i.e.  $R_C = \infty$ . Analogous to the  
257 definition of capillary capacity describing water storage (Richards, 1931) in Zone I,  
258 i.e. regular water retention (Figure 2), the term ‘bubble capacitance’  $C_i$  (unit: m<sup>3</sup> m<sup>-3</sup>  
259 Pa<sup>-1</sup>) associated with the potential difference  $\Delta\psi_{Ti}$  in Zone II describing biogenic  
260 CH<sub>4</sub>-enriched bubble accumulation is defined as,

261 
$$C_i = \frac{\Delta\theta_{g(i)}}{\Delta\psi_{Ti}}, \quad (4)$$

262 where  $\Delta\theta_{g(i)}$  (unit: m<sup>3</sup> m<sup>-3</sup>) is the maximum change in volumetric gas content from  
263 the initial state  $\theta_{g(\text{ini})}$  to the final gas-saturated state  $\theta_{g(\text{sat})}$  (Figure 2). Bubble  
264 capacitance represents the total volume of gas bubbles held at pore throats in a layer

265 under a specific hydraulic pressure, accounting for variations in bubble size and other  
266 factors. The total volume of the gas bubbles stored in the capacitors can decrease by  
267 gas bubble transport associated with episodic ebullition. Episodic ebullition events  
268 can be driven by decreases in the static hydraulic pressure on the bubbles (Chen &  
269 Slater, 2015; Glaser et al., 2004; Tokida et al., 2005), i.e. lowering the applied  
270 potential difference  $\Delta\psi_{Ti}$ .

271

272 We next consider the bubble dynamics occurring in Zone III. Above a particular  
273 electric field strength, the dielectric in a capacitor becomes a conductor. The voltage  
274 at which this occurs is called the breakdown voltage. However, the breakdown  
275 voltage of a material is not a precise value as there is a probability of the material  
276 failing at a given voltage. For gas bubbles in peat, once a critical potential difference  
277  $\Delta\psi_T$  similar to the breakdown voltage is applied, the  $i$ th peat layer no longer behaves  
278 as a capacitor but becomes a conductor. Bubble mobility after leaving nucleation sites  
279 is high as gas bubbles are relatively small, traveling freely through the interconnected  
280 pore space during stage 2 (Beckwith & Baird, 2001; Chen & Slater, 2015; Rosenberry  
281 et al., 2006). This effect may result in highly variable gas retention as observed in  
282 hydrate-controlled methane seepage from continental margin sediments (Berndt et al.,  
283 2014). Therefore, the shape of the corresponding curve is uncertain and not plotted on  
284 Figure 2.

285

### 286 **3. Observation Methodologies**

#### 287 **3.1. Site and sample collection**

288 Laboratory observations were performed on a submerged peat monolith extracted  
289 from Water Conservation Area 3 (WCA-3) in the US Florida Everglades (Figure 3a).  
290 The site corresponds to one of the locations included in the study by Wright & Comas  
291 (2016), has a thickness of 0.72 m, and is characterized predominantly by Loxahatchee  
292 peat, thus dominated by water lily (*Nymphaea odorata*) plant species with a typical  
293 organic content of 92% (Craft and Richardson, 2008). The site is located in a slough,  
294 and is perennially inundated with an average water depth of 0.5 m.

295

296 A peat monolith was extracted by pushing a plastic mould box, with bottom and top  
297 removed, into the ground and then digging out the base with a saw (Comas & Slater,  
298 2007; Parsekian et al., 2012). The monolith was cut in the laboratory (0.395 m in  
299 length  $L$ , 0.243 m in width  $W$ , and 0.247 m in height  $H$ , Figure 3b), transferred into a  
300 fitted sample box and equipped with non-invasive sensors and instruments similar to  
301 that described in Chen & Slater (2015).

302

#### 303 **3.2. Noninvasive observations of bubble accumulation and release**

304 Laboratory observations, divided into three stages, were made over 102 days (5 Jun  
305 2014 - 14 Sep 2014). Stage I involved bubble accumulation under constant conditions  
306 of water level, atmospheric pressure and temperature to charge the ‘bubble capacitors’  
307 of the peat monolith (from Day 1 to Day 53). Stage II involved environmental-forcing

308 to generate episodic ebullition events that discharge bubble capacitors (from Day 54  
309 to Day 67). During this stage, a flow-through chamber device measured CH<sub>4</sub>  
310 concentration of the air in the headspace above the peat surface to determine the CH<sub>4</sub>  
311 concentration of the bubbles released by changing water levels. Stage III involved  
312 bubble accumulation under constant conditions of water level again to recharge those  
313 lost in Stage II, until reaching a saturated state captured in the GPR data, depending  
314 on the capacitance  $C_i$  of each layer (from Day 68 to Day 102).

### 315 **3.2.1. Electromagnetic sensing of bubble concentration and average relative** 316 **dimension**

#### 317 **3.2.1.1. Configuration of GPR instrument and visual validation**

318 A GPR instrument equipped with a high frequency antenna (central frequency = 1200  
319 MHz, MALÅ Geoscience, Sweden) was used to record the reflected electromagnetic  
320 waves from the interface between side of the container and the side of the peat  
321 monolith (Figure 3b). These signals were used to estimate variations in the total  
322 volume (Chen & Slater, 2015; Comas et al., 2007) and also to infer corresponding  
323 relative variations in average sizes of the bubbles between depths (Terry & Slater,  
324 2017).

325

326 Two sets of measurements (details below) were made with a trade-off between  
327 temporal and spatial resolution. High spatial resolution measurements were made at  
328 28 depths ranging from 5 cm to 19 cm with a vertical interval  $d = 0.5$  cm ( $i = 1, 2,$   
329  $3, \dots, 28$ ). Twenty four traces were recorded at each depth between 8 cm to 32 cm

330 from the left side of the monolith with a horizontal interval  $l = 1$  cm ( $j = 1, 2, 3, \dots,$   
331 24). The scanned area ( $0.140$  m  $\times$   $0.240$  m) was smaller than that of the actual  
332 monolith side ( $0.243$  m  $\times$   $0.395$  m) to account for the footprint of the GPR antenna.  
333 Four such scans were collected in Stage I (Day 2, Day 18, Day 40 and Day 53) with  
334 an additional three scans collected in Stage III (Day 68, Day 89 and Day 102),  
335 allowing six time-difference images to be created. Collected signals at all the  
336 sampling points  $(i, j)$  were used to estimate the changes in volumetric gas contents and  
337 then the layered bubble capacitances (Section 3.2.1.2). Four locations P1 ( $i=5, j=2$ ),  
338 P2 ( $i=5, j=14$ ), P3 ( $i=26, j=2$ ) and P4 ( $i=26, j=14$ ) were analyzed to compare relative  
339 bubble dimension between depths (Terry & Slater, 2017) from the 7 time slices using  
340 Matlab [*Mathworks, Inc.* 2012] (Section 3.2.1.3).

341

342 Low spatial resolution measurements at four depths of 5 cm (i.e. layer  $i = 1$ ), 8.5 cm ( $i$   
343 = 8), 12 cm ( $i = 15$ ) and 18.5 cm ( $i = 28$ ) with a horizontal interval of 2 cm were made  
344 during Stage I only. Two measurements per day (one between 9:00-10:00 and another  
345 between 17:00-18:00) were collected from Day 1 to Day 46 to confirm continuous  
346 bubble accumulation with a fine temporal sampling interval. Direct observations of  
347 bubble accumulation were also made by visual counting of gas bubbles appearing on  
348 the transparent edge of the box during Stage I only. Bubble counts as a function of  
349 depth were qualitatively estimated by tracing macroscopic bubbles appearing on the  
350 side of the tank, with tracings digitized for subsequent analysis (Chen & Slater, 2015;  
351 Liu et al., 2016; Ramirez et al., 2015).

352

### 353 3.2.1.2. Bubble capacitance estimation from changes in gas content

354 To estimate the bubble capacitance  $C_i$  (equation 4) of the  $i$ th layer, the total volumetric  
355 content of accumulated gas bubbles  $\Delta\theta_{g(i)}$  was calculated from the difference  
356 between the initial volumetric gas content  $\theta_{g(i,j,ini)}$  and the final bubble-saturating gas  
357 content  $\theta_{g(i,j,end)}$ ,

$$358 \quad \Delta\theta_{g(i)} = \sum_{j=1}^{24} (\theta_{g(i,j,end)} - \theta_{g(i,j,ini)}), \quad (5)$$

359 where the index  $i$  indicates different depths of the monolith beginning from the top  
360 line of GPR scanning, index  $j$  indicates different sub columns referenced to the left  
361 edge of the GPR scanning and  $t$  indicates date of the observation. We assume  
362 minimum gas storage, i.e. the peat column is close to 100% water saturation at the  
363 start of the experiment. The bubble capacitances  $C_i (i, j)$  [ $i = 1, 2, 3, \dots, 28; j = 1, 2,$   
364  $3, \dots, 24]$  cover a part of the strips of the entire volume ( $i', j'$ ) [ $i' = 11, 12, 13, \dots, 38;$   
365  $j' = 9, 10, 11, \dots, 32]$  due to the footprint of the GPR antenna. Gas content  $\theta_{g(i,j,t)}$  is  
366 regarded as the difference between total porosity  $\phi_{(i,j,t)}$  and water content  $\theta_{w(i,j,t)}$ ,

$$367 \quad \theta_{g(i,j,t)} = \phi_{(i,j,t)} - \theta_{w(i,j,t)} \quad (6).$$

368

369 Bulk dielectric permittivity  $\varepsilon_b$  of the peat monolith depends on the dielectric  
370 permittivity and volume concentration of the three phases (solid, gas and liquid). The  
371 bulk relative permittivity  $\varepsilon_b$  was estimated by correcting the two-way travel time  
372  $\Delta t_{em}$  of the electromagnetic signal through the sample monolith. Assuming low  
373 dielectric loss,

374 
$$\varepsilon_b = \left( \frac{\nu \Delta t_{em}}{2W} \right)^2, \quad (7)$$

375 where  $\nu$  is the speed of the electromagnetic wave in free space and  $W$  is the distance  
 376 between the GPR antenna and reflection interface, i.e. 24.3 cm (Figure 3b). Previous  
 377 work directly links the gas content  $\theta_g$  to the bulk dielectric permittivity  $\varepsilon_b$ , e.g. with  
 378 the Complex Refraction Index Model (CRIM) (Comas et al., 2005, 2011). However,  
 379 this requires a reliable estimate of  $\phi_{(i,j,t)}$ , which proved impractical in this study.  
 380 Water content  $\theta_w$  can instead be estimated from the bulk relative permittivity with  
 381 an empirical third order polynomial, e.g. the Topp model for mineral soils (Topp et al.,  
 382 1980), avoiding the need for a porosity estimate. A specific polynomial function with  
 383 calibrated coefficients for *Sphagnum* peat at high saturation conditions (Kellner &  
 384 Lundin, 2001) was directly applied to the sawgrass peat monolith with tolerable  
 385 structure bias,

386 
$$\theta_w = 3.9 \times 10^{-2} + 3.17 \times 10^{-2} \varepsilon_b - 4.5 \times 10^{-4} \varepsilon_b^2 + 2.6 \times 10^{-6} \varepsilon_b^3 \quad (8).$$

387 Substituting equation (7) into (8), the water contents in different saturation states  
 388  $\theta_{w(i,j,t)}$  can be estimated.

389

390 It was not possible to acquire porosity measurements on every individual cell  $[i, j]$   
 391 within the monolith using a gravimetric method. The differential form of equation (6)  
 392 states that the increase in volumetric gas content of each cell approximates the  
 393 decrease in volumetric water content,

394 
$$\theta_{g(i,j,end)} - \theta_{g(i,j,ini)} = \theta_{w(i,j,ini)} - \theta_{w(i,j,end)} + \Delta\phi_{(i,j)}, \quad (9)$$

395 where  $\Delta\phi_{(i,j)}$  is an additional correction term for pore expansion during bubble

396 accumulation (Chen & Slater, 2015). Here, this correction is assumed to be negligible  
 397 as the gas contents were lower than the saturation values associated with significant  
 398 pore expansion. Therefore, bubble capacitance ( $C_i$ ) can be calculated from water  
 399 content estimates ( $\theta_{w(i,j,t)}$ ) determined from dielectric permittivity measurements with  
 400 matrix expansion ignored. Substituting equation (9) into (5), the total increase in  
 401 volumetric gas content is,

$$402 \quad \Delta\theta_{g(i)} = \sum_{j=1}^{24} (\theta_{w(i,j,\text{ini})} - \theta_{w(i,j,\text{end})}), \quad (10)$$

403 where the absolute water contents  $\theta_{w(i,j,\text{ini})}$  and  $\theta_{w(i,j,\text{end})}$  at the start of Stage I and  
 404 the end of Stage III, respectively, were determined from GPR measurements.  
 405 Substituting equations (2), (3) and (10) into (4), the layer-averaged bubble capacitance  
 406  $C_i$  of the  $i$ th layer is,

$$407 \quad C_i = \frac{\sum_{j=1}^{24} (\theta_{w(i,j,\text{ini})} - \theta_{w(i,j,\text{end})})}{\rho_f g \sum_{k=0}^i d_k}, \quad (11)$$

408 where the initial water level relative to the peat monolith surface,  $d_0$ , is 5.7 cm.

409

410 The same approach was used to estimate changes in bulk relative permittivity  $\epsilon_b$   
 411 during the period of higher temporal resolution (twice per day within Stage I). GPR  
 412 measurements were acquired at low spatial resolution (four depths with a horizontal  
 413 interval of 2 cm). These measurements confirmed the temporal continuity of gas  
 414 accumulation due to steady biogenic  $\text{CH}_4$  production over a long time period.

415

### 416 **3.2.1.3. Changes in average bubble dimensions**

417 To obtain some insight into the changes in average bubble dimension during bubble

418 accumulation, the power spectrum of the received GPR signal was calculated  
419 following the approach outlined by Cassidy (2008) and Terry & Slater (2017). Comas  
420 et al. (2005) suggest that clusters of gas bubbles in peat may result in obvious  
421 scattering attenuation in GPR signals. The scattering response is related to signal  
422 frequency, or alternatively the corresponding wavelength of the electromagnetic  
423 signal relative to average bubble size (Terry & Slater, 2017). Small gas bubbles result  
424 in highly frequency-dependent Rayleigh scattering, i.e. less signal attenuation at low  
425 frequencies relative to higher frequencies. As gas bubbles grow larger, the scattering  
426 response becomes more uniform Mie scattering, whereby different frequencies exhibit  
427 similar decay characteristics (Terry & Slater, 2017).

428

429 The total attenuation in the EM signal passing through a multiphase material includes  
430 both scattering and absorption components. Forward simulations for reference signals,  
431 prior knowledge and appropriate assumptions are necessary to solve the inverse  
432 scattering problem, e.g. estimating change in the average dimension of gas bubbles  
433 (Terry & Slater, 2017), or the distribution pattern of light nonaqueous-phase liquids  
434 (LNAPLs) (Cassidy, 2008). Simulation results using the finite-difference time-domain  
435 (FDTD) method show that, in the Rayleigh scattering range, peak frequency shifts  
436 toward lower frequencies with increases in the volumetric content of the scattering  
437 objects when they meet specific geometrical and spatial distribution conditions  
438 (Cassidy, 2008). Terry & Slater (2017) argued that relative changes in the frequency  
439 power spectra are mostly sensitive to the changes in size of bubbles accumulating in

440 peat, i.e. bubble size dominates the frequency spectra for peat soils. As gas content  
441 increases with increasing bubble size, small frequency shifts in the low-frequency  
442 Rayleigh scattering region indicate the dominance of Mie scattering due to the  
443 accumulation of relatively large bubbles, as assumed to occur here.

444

### 445 **3.2.2. Flow-through chamber method for CH<sub>4</sub>-enriched bubble release**

446 Controlled pore pressure changes were achieved by slow inflow of water to increase  
447 the pressure head above the initial saturated condition, and slow outflow to decrease  
448 the pressure head until the initial saturated condition was again achieved (Figure 3b).  
449 Raising and lowering the water table of the bottom chamber was performed at a  
450 controlled slow rate once daily (Figure 3b).

451

452 The CH<sub>4</sub> flux in the upper chamber above the sample monolith was monitored using a  
453 methane analyzer (MA) sealed in a matched calibration shroud (LI-7700, LI-COR  
454 Inc.). At the 1 Hz sampling rate of the methane analyzer ( $f_{MA}=1$  Hz), a pump  
455 transported  $2.8\pm 0.1\times 10^{-4}$  m<sup>3</sup> of CH<sub>4</sub> containing carrier gas between each time slice (1  
456 s). The absolute pore-pressures were measured with three vented pressure transducers  
457 (26PC Series, Honeywell Sensing and Control) installed 4.5 cm, 11.5 cm and 18.5 cm  
458 below the water table (Figure 3b).

459

### 460 **3.3. Peat humification and X-ray CT scanning**

461 At the end of the experiment, the peat sample was destructively extracted

462 layer-by-layer to determine the vertical variations in structure from humification  
463 estimates and X-ray CT scanning measurements. Degree of humification was  
464 estimated for five layers between 0 cm and 24.7 cm depth. Samples from each layer  
465 were squeezed by hand to determine the texture and color of peat, and the color of  
466 drained water. The von Post standard (von Post, 1922) was used to quantify relative  
467 decomposition.

468

469 *Blais* [2005] and *Kettridge and Binley* [2008] demonstrated that it is possible to  
470 extract information on pore size and pore continuity from X-ray images. In this  
471 research, X-ray computed tomography (CT) scanning was used to measure the  
472 corresponding vertical distribution of void ratio hypothesized to control bubble  
473 storage. A peat column (height = 24.7 cm, diameter = 4.4 cm) was extracted from the  
474 peat monolith with a PVC cylinder with minimum compression, and cut into 18 slices  
475 each of height 1.4 cm. To retain the peat structure, each slice was cast by dehydration  
476 with acetone and impregnated with low viscosity resin (Alumilite, Kalamazoo, MI;  
477 Figure 3c) (Quinton et al., 2008). All peat samples were scanned around the center of  
478 rotation with an X-tek Benchtop CT160Xi CT scanner (X-Tek Systems Ltd, UK) and  
479 a dual field image intensifier coupled to a digital charged couple device (CCD))  
480 (*Kettridge & Binley*, 2008, 2011) at 5 micron resolution. The  $360 \times 360$  pixels  
481 forming the middle region of the central 50 radiographs of each peat section were  
482 stacked and used for statistical analysis.

483

484 The histograms of voxel intensities recorded on the peat samples are assumed to  
485 represent the combination of two normal distributions (Rezanezhad et al., 2009),  
486 corresponding to the peat matrix particles and resin, i.e., pores, respectively. The  
487 voxel intensities of all slices of each section were fit with the  
488 Expectation-Maximization algorithm for mixtures of univariate normals using  
489 RStudio (Version 1.0.136, RStudio, Inc. Boston, MA). To account for variations in  
490 CT signal decay between different sections, the voxel number ratios  $r_1$  and  $r_2$   
491 representing the number of voxels in the resin intensity range and the number of  
492 voxels within the peat particle intensity range to the total number of all voxels  
493 respectively, were calculated ( $r_1 + r_2 = 1$ ). The  $r_1$  values indicate relative variations in  
494 void ratio between depths, which can be compared with the vertical distribution of  
495 bubble capacitances  $C_i$ .

496

#### 497 **4. Results**

498 Time-lapse dielectric permittivity measurements provided a 2D image of the  
499 accumulation of gas bubbles within the monolith, allowing the computation of bubble  
500 capacitances representing the maximum bubble storage ability at different depths. The  
501 power spectra of the GPR data provide information on changes in relative bubble  
502 dimensions between layers. The flow-through chamber system confirmed that these  
503 gas bubbles were  $\text{CH}_4$ -enriched, whereas destructive analysis including von Post  
504 numbers and X-ray CT measurements identified distinct variations in physical  
505 properties of peat with depth in the peat block related to the variations in bubble

506 storage. Specific results relating to each measurement are provided below.

#### 507 **4.1. Changes in gas content and bubble capacitance**

508 Based on the bulk relative permittivity results at high spatial resolution (Figure 4a -  
509 4g), the water contents at all 28 measurement depths generally decreased across  
510 Stages I and III (Figure 4h - 4k, and 4l - 4n). The time-difference images suggest that  
511 gas contents at all 28 measurement depths increased across Stages I and III as a result  
512 of bubble accumulation (Figure 4o - 4q, and Figure 4r - 4t), and decreased by bubble  
513 release, i.e. ebullition driven by environmental forcing, during Stage II (Figure 4q -  
514 4r). These increases in gas content were greatest at 5-10 cm depth (Figure 5a),  
515 gradually reaching the maximum gas contents at the end of Stage III (Figure 5b).  
516 However, at some locations in this hotspot layer, e.g. point P1 ( $i=5, j=2$ ), the  
517 maximum change in gas content  $\Delta\theta_{g(5,2)}$  was only 0.57% (Figure 4o - 4t), suggesting  
518 that this region remained water-saturated with little gas bubble accumulation over  
519 time. The final bubble capacitances  $C_i$  (equation (11)) of all layers ranged from  $3.3 \times$   
520  $10^{-4} \text{ m}^3 \text{ m}^{-3} \text{ Pa}^{-1}$  to  $6.8 \times 10^{-4} \text{ m}^3 \text{ m}^{-3} \text{ Pa}^{-1}$ , with the maximum value located at 5.5 cm  
521 depth (Figure 5c).

522

523 Based on the bulk relative permittivity results at high temporal resolution (Figure 6.a),  
524 gas bubbles continuously accumulated at four depths; occasional increases in the bulk  
525 relative permittivity highlight decreases in gas content resulting from minor ebullition  
526 events. Hand-drawing of gas bubbles observed on the chamber side provided a direct  
527 estimation of bubble accumulation (Figure 6b). The areal percentage of macroscopic

528 bubbles in every layer  $i$  increased over the initial state. Consistent with the dielectric  
529 permittivity results, the largest areal percentage of macroscopic bubbles during the  
530 entire measurement period was observed in the 5-10 cm depth layer.

531

#### 532 **4.2. Changes in relative average bubble dimension**

533 Four locations P1 ( $i=5, j=2$ ), P2 ( $i=5, j=14$ ), P3 ( $i=26, j=2$ ) and P4 ( $i=26, j=14$ ) were  
534 selected (Figure 4t) for GPR power spectrum analysis to estimate relative changes in  
535 bubble dimension between layers during bubble accumulation (P2 and P3 in Figure 7,  
536 P1 and P4 in Figure S1 in Supplementary Information). Gas contents at point P2  
537 showed the largest increases among these four points (Figure 4o - 4t); the  
538 high-frequency peaks in the spectra (Figure 7a) are consistent with the dominance of  
539 Mie scattering attenuation (Terry & Slater, 2017), suggesting accumulation of large  
540 gas bubbles. Points P1 and P4 are characterized by little continuous change in the  
541 spectra (Figure S1a and S1b in Supplementary Information), associated with small  
542 changes in gas contents during Stages I and III (Figure 4o - 4t). The small frequency  
543 shift at P1 between Day 18 and Day 40 (Figure S1a) is consistent with steady  
544 ebullition events, along with a few large bubbles being released into the atmosphere  
545 such that the corresponding pore space was invaded by small gas bubbles from deeper  
546 layers. Point P3 showed continuous decreases in the amplitudes of the spectra over  
547 time (Figure 7b). According to the simulated attenuation patterns (Terry & Slater,  
548 2017), the relatively greater attenuation at the high frequencies over time indicates the  
549 dominance of Rayleigh scattering attenuation, which can be ascribed to the increases

550 in the number and/or size of gas bubbles. Attenuation due to absorption should be  
551 reduced in the presence of gas bubbles because of the high resistivity of the bubbles  
552 (Terry & Slater, 2017).

553

#### 554 **4.3. Ebullition during forced changes in hydrostatic pressure**

555 Changes in the CH<sub>4</sub> concentrations recorded during the periods of forced hydrostatic  
556 pressure changes are summarized in Table 2. Decreases in average pressure heads  
557 ranged from 2.0 cm to 10.4 cm, with an average value of 4.08 cm. Corresponding  
558 increases in the CH<sub>4</sub> concentration in the upper chamber  $\Delta c$  ranged from 88.4 mmol  
559 m<sup>-3</sup> to 505.0 mmol m<sup>-3</sup>, with an average value of 252.76 mmol m<sup>-3</sup>, proving that the  
560 released gas bubbles are CH<sub>4</sub>-enriched relative to the atmospheric concentration.

561

#### 562 **4.4. Peat humification and X-ray CT scanning**

563 The von Post scores for humification degree at five depth intervals (Table 3) indicate  
564 that the upper peat (depth 0 - 10 cm) was less decomposed than the lower peat (depth  
565 10 - 25 cm). The shallow peat of the upper layer (depth 5 - 10 cm) showed variations  
566 in humification degree between H2 to H3, containing a peat fabric, e.g. consisting of  
567 undecomposed coarse roots of vascular plants, that retained its overall shape after  
568 oven drying (Figure 8a). The lower peat below a depth of 10 cm exhibited a gradual  
569 increase in decomposition degree per the von Post score H3 to H5 toward the bottom  
570 (Figure 8a). The void ratios  $r_1$ , i.e. the number of voxels in the resin intensity range  
571 relative to the total number of all voxels of the CT scanning images (Figure 8a)

572 exhibit two minima (0.06 and 0.18 at depths of 4.9 cm and 18.9 cm, respectively),  
573 indicating low void ratios relative to other depths in the monolith. The smallest  $r_1$   
574 value at 4.9 cm depth is located just above a peak value of bubble capacitance  $C$  at 5.5  
575 cm depth (Figure 5c), suggesting a barrier structure limiting vertical movement of  
576 bubbles. This suggests that the peat fabric between 5 – 10 cm depth partly regulates  
577 gas accumulation (Chen & Slater, 2015; Comas et al., 2011; Glaser et al., 2004;  
578 Rosenberry et al., 2003). The  $r_1$  values below 16.1 cm depth are overall smaller than  
579 the values for the upper layers between 9.1 cm and 14.7 cm depth, indicating a  
580 decrease in void ratio.

581

## 582 **5. Discussion**

583 The general capacitance model provides a convenient way to physically link peat  
584 physical properties to bubble storage and release, leading to new understanding of the  
585 controls on bubble storage. We conducted laboratory observations on a subtropical  
586 peat monolith for estimating bubble capacitances at different depths and discussing  
587 the roles of peat structure. Gas dynamics were inferred from time-lapse changes in  
588 volumetric gas content and relative average bubble size estimated from  
589 electromagnetic wave velocity and power spectra acquired with the GPR instrument,  
590 coupled to  $\text{CH}_4$  concentrations of released gas bubbles from the peat sample acquired  
591 using a flow-through chamber system. Destructive analysis based on humification  
592 estimates combined with X-ray CT scanning identified distinct variations in the  
593 physical properties of peat between different depths that seem to dictate changes in

594 gas content and average bubble dimensions. The vertical distribution of computed  
595 bubble capacitances  $C$  that represent the maximum bubble storage capability of the  
596 peat revealed a hotspot layer of bubble storage at 5.5 cm depth, below a barrier zone  
597 limiting vertical movement of bubbles.

### 598 **5.1. Initial source of heterogeneous nucleation sites for bubble formation**

599 Our physical model mainly focuses on bubble accumulation (Stage 2) after initial  
600 bubble nucleation (Stage 1). Three possibilities are suggested for the initiation of  
601 heterogeneous nucleation sites: Firstly, we assume that micro bubbles form readily  
602 and act as seeds for later growth (Baird et al., 2004; Coulthard et al., 2009). These  
603 pre-existing seeds can be ascribed to pockets of air bubbles trapped in shallow peat  
604 during water-table rise (Baird et al., 2004; Beckwith & Baird, 2001; Coulthard et al.,  
605 2009), that grow bigger via inward diffusion of biogenic  $\text{CH}_4$ . Secondly, a nucleus  
606 may form in a small pore pocket under conditions of super-saturation, although the  
607 measured dissolved  $\text{CH}_4$  concentration will only represent an ‘average’ value for a  
608 much larger volume with mostly low  $\text{CH}_4$  concentration. Furthermore, the  $\text{CH}_4$   
609 concentration in gas bubbles can vary substantially, e.g. between 9% and 77% over  
610 time (Mustasaar & Comas, 2017), suggesting significant heterogeneity in dissolved  
611  $\text{CH}_4$  concentration in pore water and frequent mass exchange between the gaseous  
612 phase and dissolved phase. Spatiotemporal variations in both dissolved and gaseous  
613  $\text{CH}_4$  concentration observed by (Mustasaar & Comas, 2017) were ascribed to changes  
614 in  $\text{CH}_4$  production within the peat sample, probably in relation to changes in plant  
615 composition and/or quality of organic matter content making up the hotspot area.

616 Thirdly, Boudreau (2012) suggested that, as much sedimentary material is formed  
617 sub-aerially in terrestrial environments, trapping of gas during its formation is likely  
618 common. Such gas bubbles retained in the sediments below the peat may enter the  
619 overlying peat and become trapped again, acting as heterogeneous nucleation sites.

620

## 621 **5.2. Effects of peat void ratio on bubble capacitance**

622 Volumetric gas content estimates from dielectric permittivity measurements indicate a  
623 hotspot of gas bubble accumulation in the upper layer (e.g. 5.5 cm depth with the peak  
624 value of bubble capacitance  $C$ ), as bubbles are not necessarily released immediately  
625 upon formation (Beckwith & Baird, 2001; Rosenberry et al., 2003). Kettridge &  
626 Binley (2008) used X-ray Computed Tomography (CT) to describe the distribution of  
627 individual gas bubbles within *Sphagnum* peat and corresponding peat structures in the  
628 laboratory, and found that most gas bubbles (ranging from  $0.1 \text{ mm}^3$  to  $99.9 \text{ mm}^3$ )  
629 clustered near the surface of a peat sample extracted from ground surface to a depth of  
630 13 cm, being consistent with our GPR-based observations on Loxahatchee peat (Point  
631 2 in Figure 4t).

632

633 Variations in peat stratigraphy have previously been suggested to regulate bubble  
634 storage in specific layers within different soil columns, and control the re-distribution  
635 of gas bubbles (Chen & Slater, 2015; Kettridge & Binley, 2008; Wright & Comas,  
636 2016). The smallest void ratio  $r_1$  at 4.9 cm depth suggests the presence of a barrier  
637 structure in the surface layer, being ascribed to the decay of poorly decomposed roots

638 and stems of vascular plants (Figure 8). This barrier structure is located above the  
639 peak value of bubble capacitance  $C$  found at 5.5 cm depth (Figure 5c). Variations in  
640 the von Post humification metric (Figure 8a) suggest a predominantly two-layer  
641 model: the upper layer (e.g. depth 0 - 10 cm) is less decomposed (Quinton et al.,  
642 2008). Poorly decomposed materials can form a barrier structure supporting bubble  
643 storage immediately below. The lower layer of small  $r_1$  values is associated with more  
644 decomposed peat, causing a decrease in the size of particles and interparticle pores  
645 with depth, and an increase in the amount of solid material per unit volume (Quinton  
646 et al., 2000).

647

### 648 **5.3. Effects of average bubble dimension on bubble capacitance**

649 Based on the changes in the spectra of the EM waves transmitted through peat (Terry  
650 & Slater, 2017), the relative average bubble radii (Figure 7 and Figure S1 in  
651 Supplementary material) at different depths can be estimated and compared with the  
652 vertical distribution of bubble capacitances  $C$ . Although the absorption attenuation of  
653 simulated EM signals due to electrical conductivity is larger than that due to scattering  
654 across all frequencies investigated, the shape of the power spectra reflects both  
655 absorption and scattering contributions, and is particularly sensitive to changes in the  
656 size of bubbles accumulating in peat, i.e. bubble size dominates the frequency spectra  
657 for peat soils (Terry & Slater, 2017).

658

659 This comparison suggests that more large bubbles accumulate in the upper layer (e.g.

660 Point P2 in Figure 7a) relative to the bottom layer (Point P3 in Figure 7b).  
661 Hydroacoustic observations of gas bubbles released from organic-rich lake sediments  
662 into the upper water column indicate that ebullition events are mostly composed of  
663 large bubbles, e.g. diameter  $> 14$  mm in Kiel harbor, Germany (Greinert & Nützel,  
664 2004) or diameter  $> 10$  mm in Lake Wohlen, Switzerland (DelSontro et al., 2015). We  
665 assume that large gas bubbles are stored in the upper layer, resulting in the high value  
666 of bubble capacitance  $C$  at the depth of 5.5 cm (Figure 5), with release of these  
667 bubbles into the water body above (Layer 0 in Figure 1).

668

669 A larger volume of a single bubble in the upper layer is consistent with gas bubble  
670 expansion due to lower pore pressures in the underlying layers; Differences in the  
671 pore-size distribution of the peat sample will lead to differences in the ability of the  
672 peat to trap and subsequently release bubbles (Baird et al., 2004). Three-dimensional  
673 (3-D) analysis of peat pore structure from previous X-ray CT scanning on peat soils  
674 also suggests that the pore network is dominated by a single large pore-size  
675 (Rezanezhad et al., 2009). Therefore, only correspondingly larger gas bubbles can be  
676 held by these pore throats in the upper layer, as bubbles otherwise directly pass by.  
677 Finally, larger bubbles may rise faster than smaller bubbles (Corapcioglu et al., 2004),  
678 and thus are more likely to bypass consumption by methanotrophs (Ramirez et al.,  
679 2016).

680

681       **5.4. Limitations and extension**

682       The 1D layered model structure represents a significant simplification. Indeed, spatial  
683       heterogeneity in bubble storage exists in the horizontal plane as confirmed by the  
684       GPR data (e.g. Points 1 and 2 in Figure 4t). Direct visual observation via the clear  
685       chamber wall qualitatively supports the vertical variation in gas contents over  
686       different depths, but the absolute accuracy is limited because of the wall effect on  
687       bubble storage (Chen & Slater, 2015; Liu et al., 2016). The bubble capacitance  
688       defined in this paper is focused on the volumetric content of stored gas bubbles.  
689       However, CH<sub>4</sub> concentration in gas bubbles was recently found to vary substantially  
690       (Mustasaar & Comas, 2017).

691

692       The form of water deserves consideration when applying equation (8) to estimate the  
693       volumetric water content for the change in gas content from the bulk relative  
694       permittivity of each peat layer. The gas content estimates from equation (8) may be  
695       affected by bound water on peat particle surfaces, depending in part on the  
696       decomposition degree of the layer (Kellner & Lundin, 2001; Yu et al., 1999). In  
697       practice, estimates of bound water needed to improve calibration functions are  
698       difficult to obtain, and may not significantly improve the estimation of volumetric  
699       water content in pores (Kellner & Lundin, 2001). Structural water that constitutes part  
700       of the organic matter lattice has little effect on bulk dielectric properties, compared  
701       with that of pore-filling water (Marfunin, 2012).

702

703 Furthermore, the rigidity of the peat skeleton regulates deformation of the pore space.  
704 Gas bubbles can enlarge the pore space when the exerted pressure is high enough  
705 (Chen & Slater, 2015). Changes in porosity were considered in this paper but were not  
706 estimated for each small cell making up the 2D plane due to lack of measurements  
707 with sufficient accuracy. In addition, the preparation of the peat samples for CT  
708 scanning, involving slicing the peat to remove moisture with acetone followed by  
709 impregnating the peat with resin (Quinton et al., 2008), may have caused some  
710 shrinkage of the pore network. Alternatively, the peat may secrete wax, making it  
711 difficult to image the pore structure (Quinton et al., 2009) and accurately estimate  
712 void ratios. Finally, gas bubbles in peat can not only accumulate behind existing  
713 bubbles lodged in pore necks [*Baird and Waldron, 2003; Strack et al., 2005; Kellner*  
714 *et al., 2006*], as considered in this paper, but also underneath woody layers, or below  
715 well-decomposed layers of peat (Glaser et al., 2004; Rosenberry et al., 2003). Under  
716 the latter condition, fracture mechanisms similar to those occurring in fine-grained  
717 sediments are possible (Jain & Juanes, 2009).

718

719 Our conceptual model is general and applicable to most two-phase fluid problems in a  
720 porous matrix, e.g. other soil types and gas components, extending the system state  
721 analysis with a lumped element model. The concept of ‘bubble capacitance’ links the  
722 gas content to environmental pressures with special water retention curves (Figure 2),  
723 suggesting additional controls on bubble storage and release beyond the ideal gas law.  
724 Using this concept can improve interpretation of observations of gas bubble formation,

725 accumulation and interaction with matrix structure. Changes in gas content might be  
726 estimated from the model if discharging and charging of a bubble capacitor are  
727 assumed reversible. However, the hysteresis phenomenon commonly observed in soil  
728 moisture retention would have to be considered. The time constant  $\tau_c$  of the model  
729 only represents the maximum time required to release a specific volume of gas  
730 bubbles associated with decreases in water level, i.e. the occurrence of individual  
731 episodic ebullitions event cannot be accurately predicted with the model.

732

## 733 **6. Conclusions**

734 Bubble capacitance developed from a general capacitance model provides new  
735 understanding of the effects of capillary pressure and peat structure on bubble storage  
736 using concepts from electromagnetism and hydrostatics. To explore this model,  
737 bubble accumulation in a peat block from a subtropical wetland was observed over  
738 102 days. The results highlight a hotspot layer of bubble accumulation at depths  
739 between 5 and 10 cm below the monolith surface. Based on the corresponding power  
740 spectra of returned electromagnetic energy, bubbles in this shallow hotspot layer were  
741 larger relative to those in deeper layers, whilst the degree of decomposition of the  
742 upper layers was generally smaller than that of the lower layers based on von Post  
743 humification tests. X-ray CT from different depths revealed a barrier structure of low  
744 void ratio ( $r_1$ ) just above this hotspot. Our findings suggest that bubble capacitance of  
745 a peat layer is related to (1) the difference in size between gas bubbles and peat pores,  
746 and (2) the void ratio, both being a function of peat structure. This work has

747 implications for better understanding how changes in water table elevation associated  
748 with climate change and sea level rise (particularly for freshwater wetlands near  
749 coastal areas like the US Everglades) may potentially alter bubble sizes, and thus  
750 bubble storage in peat soils.

751

## 752 **Acknowledgements**

753 This material is partly based upon work supported by the National Science  
754 Foundation under grant EAR 1623895 and National Oceanic and Atmospheric  
755 Administration (NOAA) under grant GC11-337. We thank William Wright (Florida  
756 Atlantic University), and Greg Mount (currently at Indiana University of  
757 Pennsylvania) for assistance in collecting the peat sample. We thank Vassil  
758 Karloukovski (Lancaster University) for providing X-ray CT images and Neil Terry  
759 (United States Geological Survey) for valuable discussions regarding scattering  
760 phenomena. The first author acknowledges the support of the China Scholarship  
761 Council (CSC). Any additional data can be obtained from HydroShare  
762 (<http://www.hydroshare.org/resource/762bbda0582744158d845afe0f6f27e0>).

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994 **Table 3.** Structural parameters of each layer.

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1010 the  $i$ th scanning line and water table;  $d$  and  $l$  are the vertical scanning interval and

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1023 Time-lapse layer-averaged relative permittivity based on GPR measurement. The  
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1027 P3 exhibits frequency shifts over the whole period whilst P2 shows a more constant  
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1030 **Figure 8.** Vertical variation in peat structure: a) values of void ratio  $r_1$ , bubble  
1031 capacitance  $C_i$ , von Post humification and corresponding photos at different depths. b)  
1032 A sample slice of X-ray CT Scanning of peat section and the corresponding histogram

1033 of voxel intensity; c) Histograms of voxel intensity of 18 sections of the peat sample  
1034 showing the volume contrast between resin-filled pore space (r1) and peat particles  
1035 (r2).

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1055 **Tables**

1056 **Table 1.** Analogous parameters in the general capacitance model

		Applications		
		Electric charge storage	Soil water storage	Biogenic gas bubble storage in shallow peat
Stored property	Electrical charge		Water in soil pores	Biogenic CH <sub>4</sub> -enriched gas bubbles
Stored amount	Stored electric charge $Q$		Volumetric content of pore water	Volumetric content of gas bubbles $\theta_g$
Power source	$\Delta\psi_T$	Voltage (Electric potential difference)	Hydraulic potential difference	Buoyancy
Potential difference at equilibrium	$\Delta\psi_C$	Induced potential difference between the two terminals of the dielectric medium	Capillary potential against out flow of pore water	Capillary potential holding gas bubbles against buoyancy effect
Capacitance $C$	Electrical capacitance		(Water) Capillary capacitance	Bubble capacitance

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1061 **Table 2.** Decreases in hydrostatic pressure (average = 4.1 cm, standard error = 3.6 cm)

1062 and corresponding increases in CH<sub>4</sub> concentrations (average = 252.8 mmol m<sup>-3</sup>,

1063 standard error = 180.1 mmol m<sup>-3</sup>) during Stage II.

Events	Average decreases in hydrostatic pressure (cm)	Increases in CH <sub>4</sub> concentration (mmol m <sup>-3</sup> )
1	2.0	213.6
2	3.3	363.3
3	2.6	93.5
4	10.4	505.0
5	2.1	88.4
Average	4.1	252.8
Standard error	3.6	180.1

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1077 **Table 3.** Structural parameters of each layer

Layer i	Depth (cm)	von Post Humification
1	0 – 5	H2 – H3
2	5 – 10	H2
3	10 – 15	H3
4	15 – 20	H4
5	20 – 25	H5

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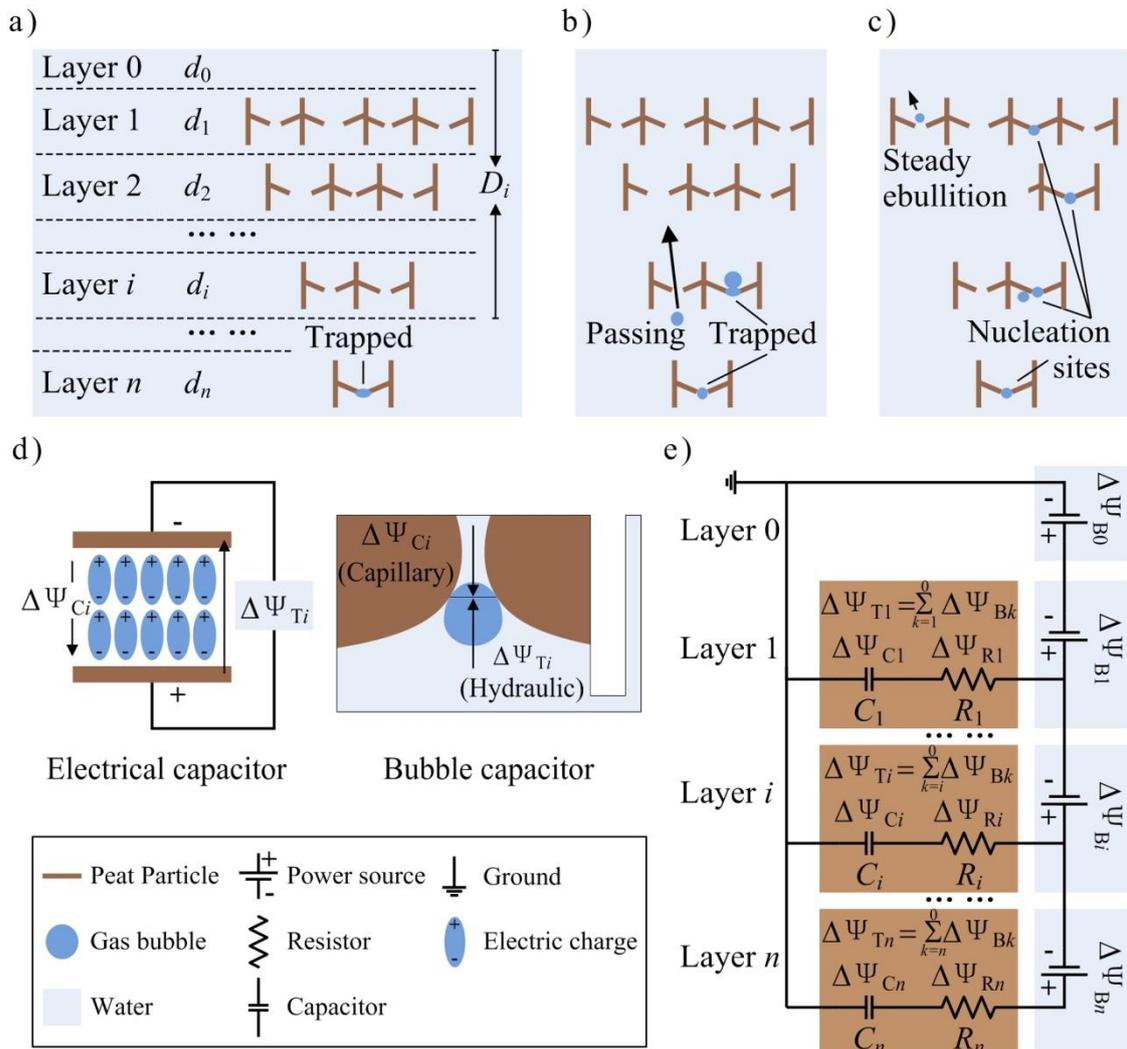
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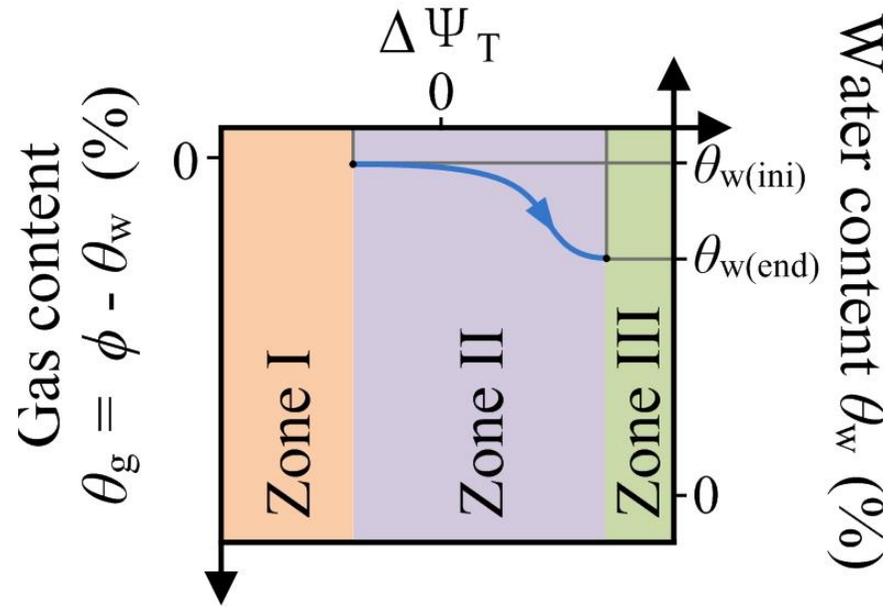
1085 **Figures**



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 1095 of energy source of the  $i$ th layer, respectively.

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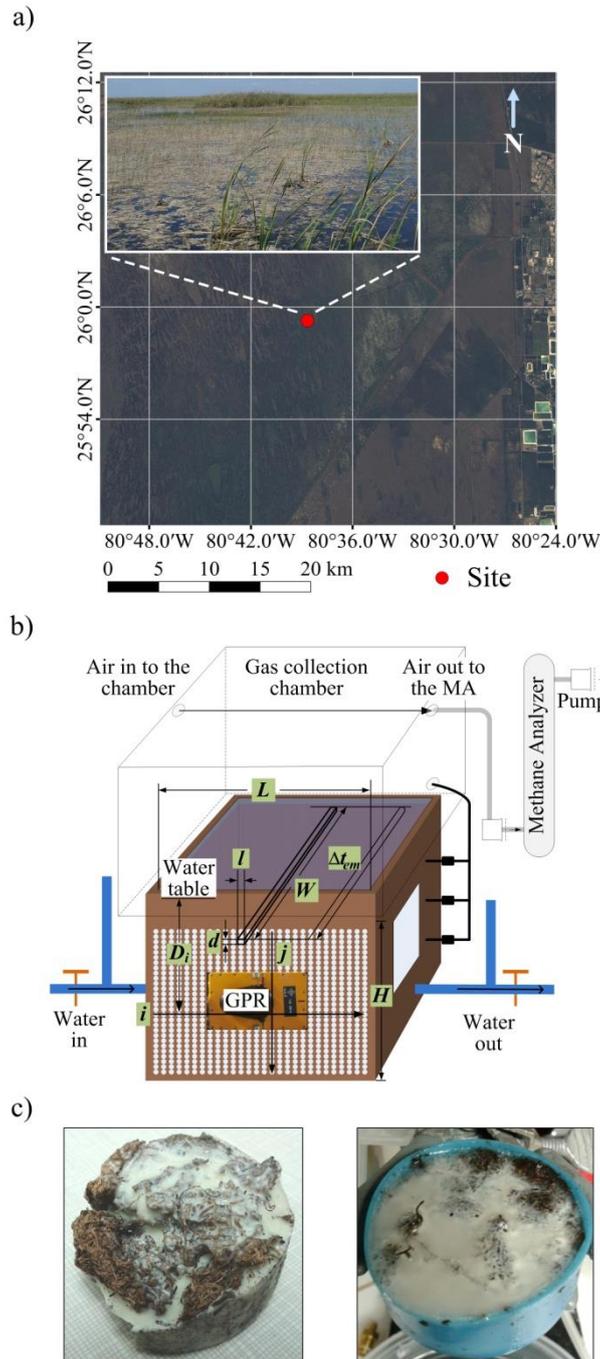
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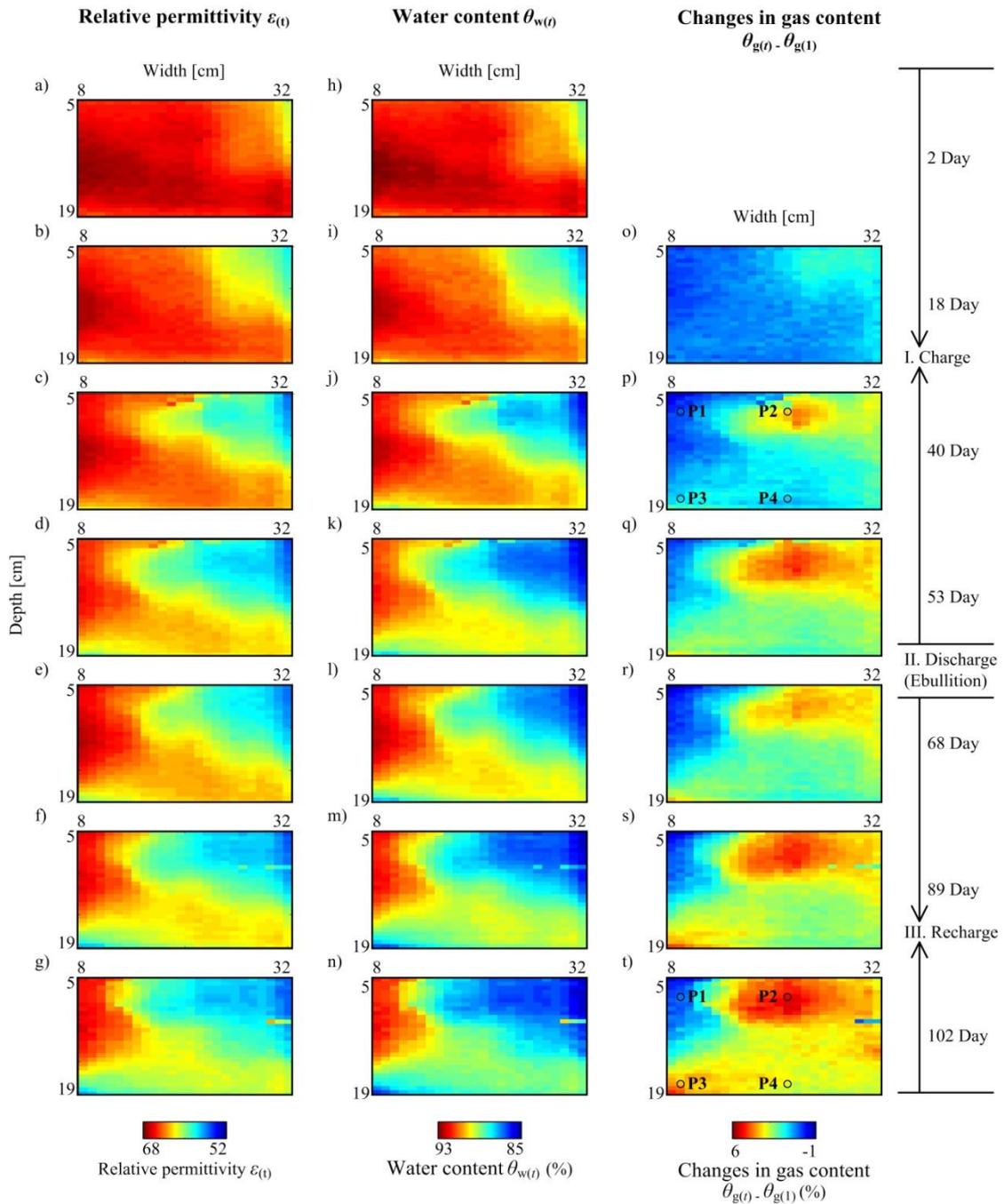
1104  $H$  are the length, width and height of the sample, respectively;  $D_i$  is distance between

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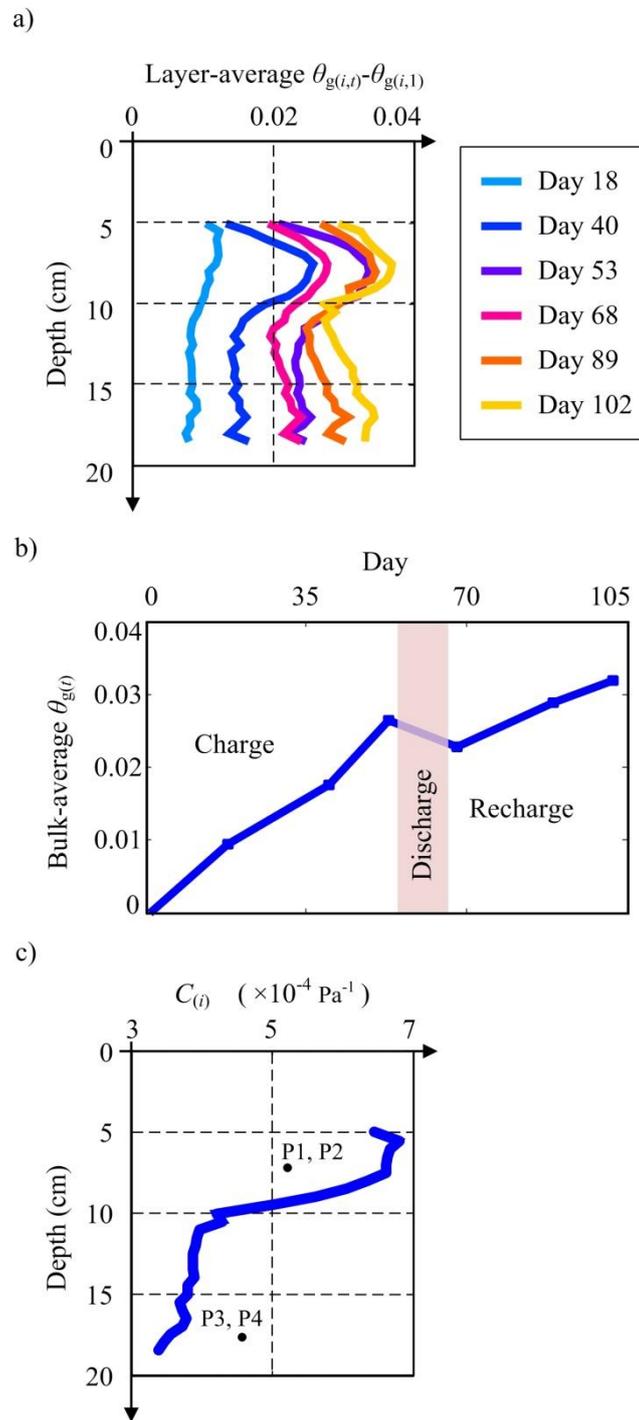
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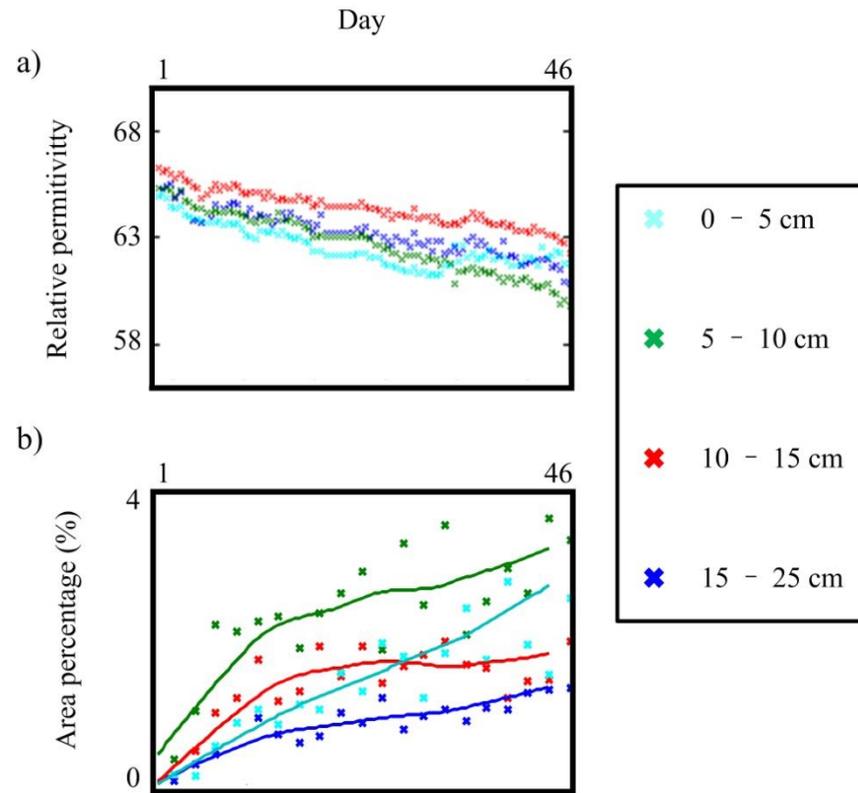
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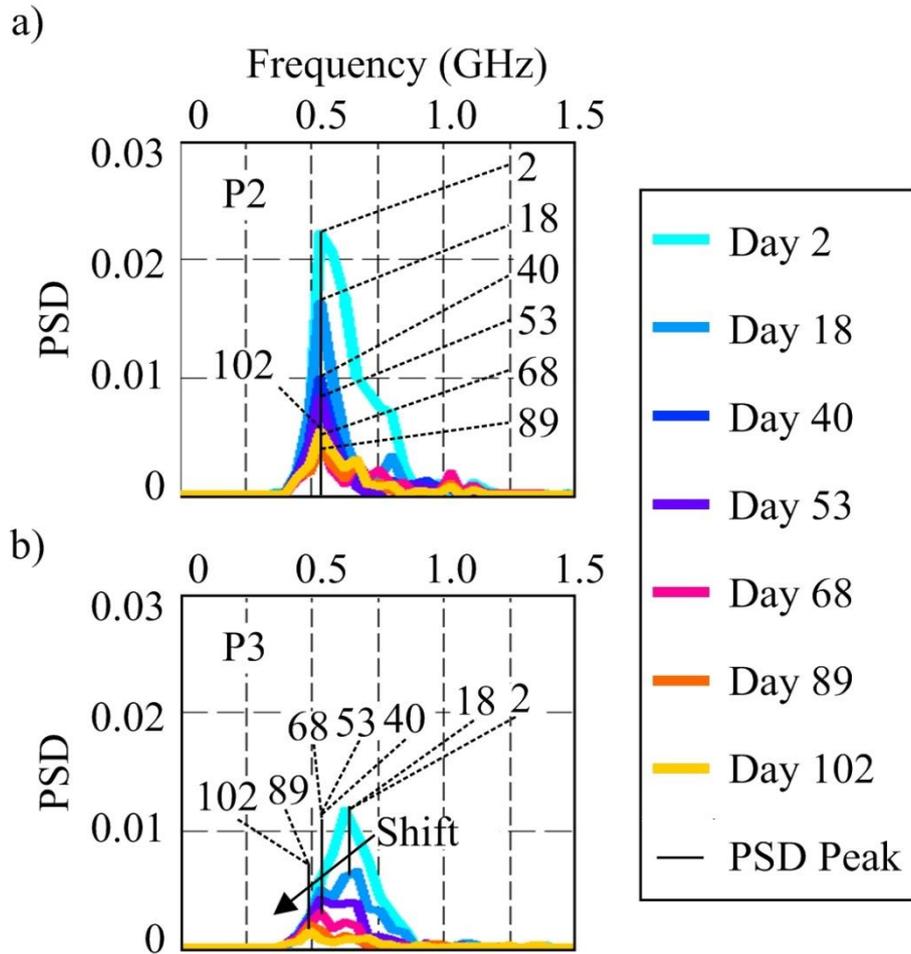
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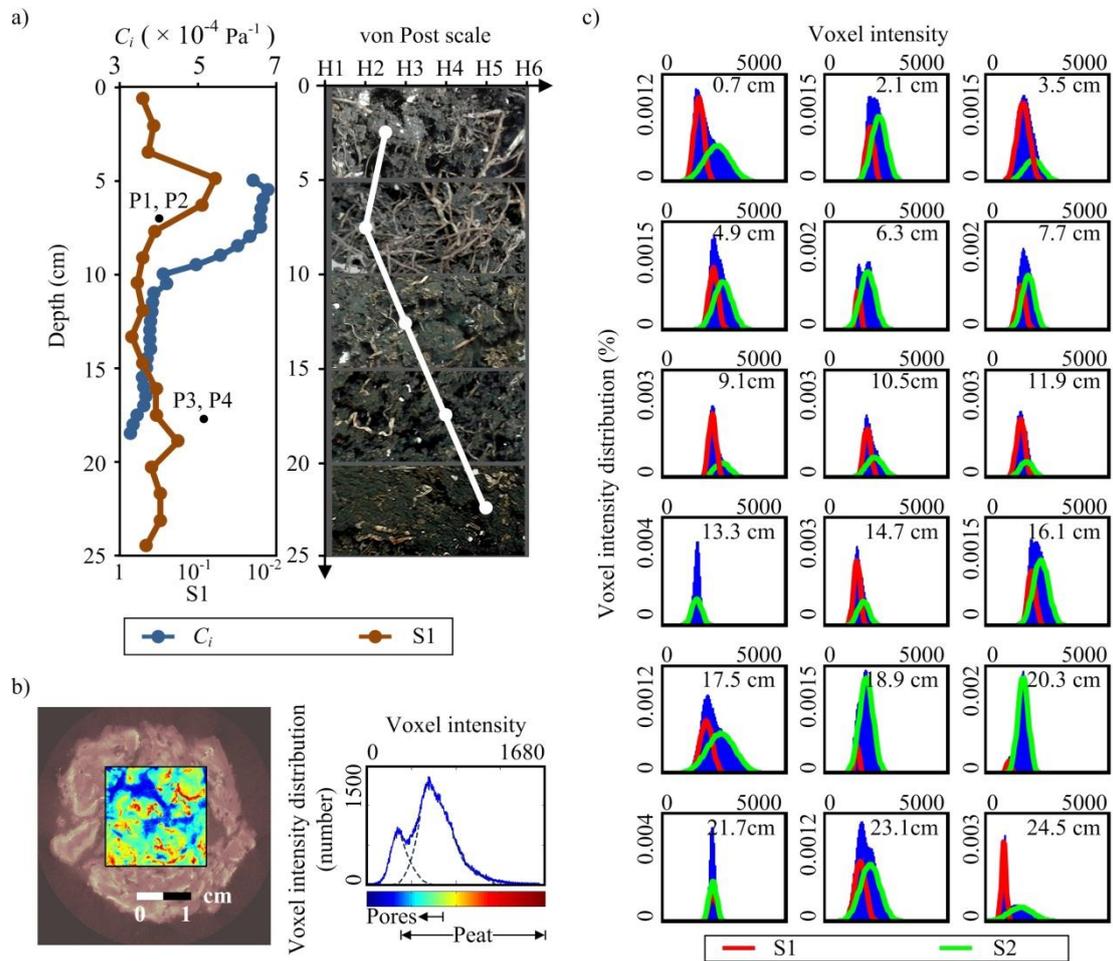
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1140 **Figure 8.** Vertical variation in peat structure: a) values of void ratio  $r_1$ , bubble

1141 capacitance  $C_i$ , von Post humification and corresponding photos at different depths. b)

1142 A sample slice of X-ray CT Scanning of peat section and the corresponding histogram

1143 of voxel intensity; c) Histograms of voxel intensity of 18 sections of the peat sample

1144 showing the volume contrast between resin-filled pore space ( $r_1$ ) and peat particles

1145 ( $r_2$ ).

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1147

Figure 1.

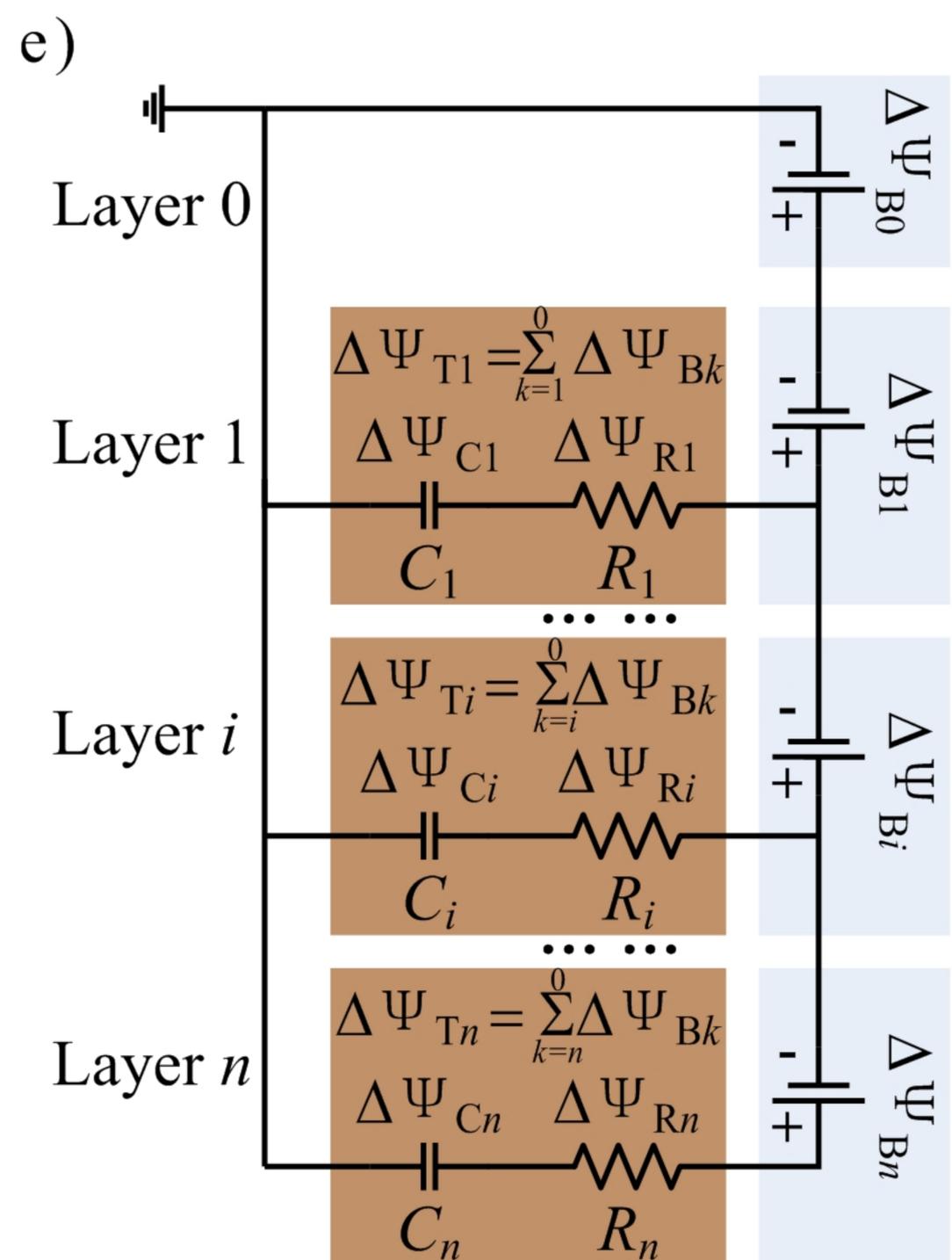
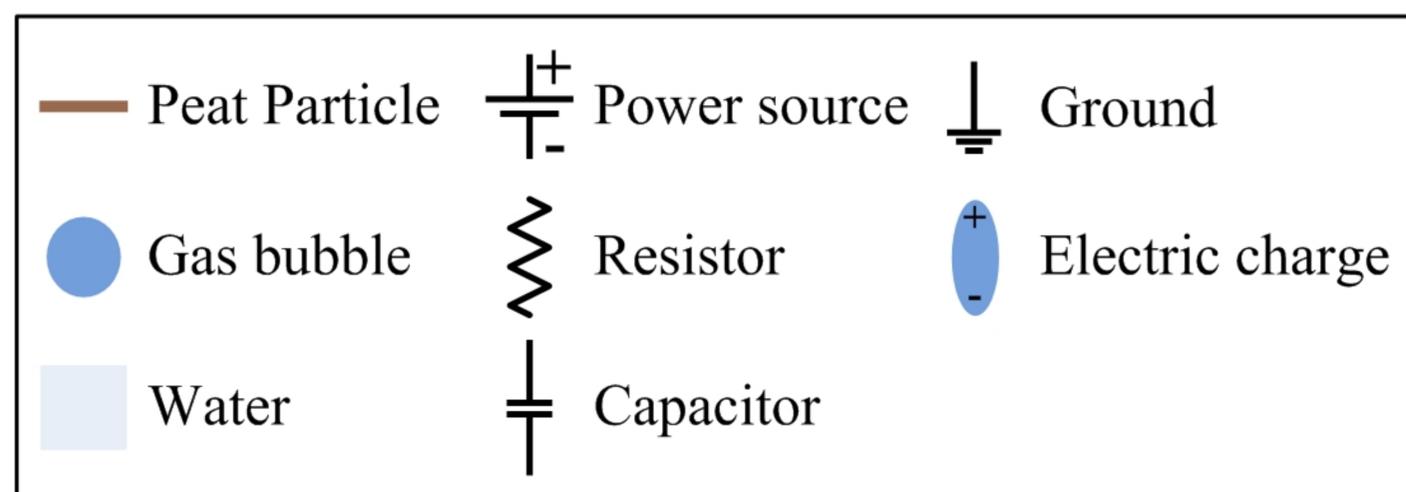
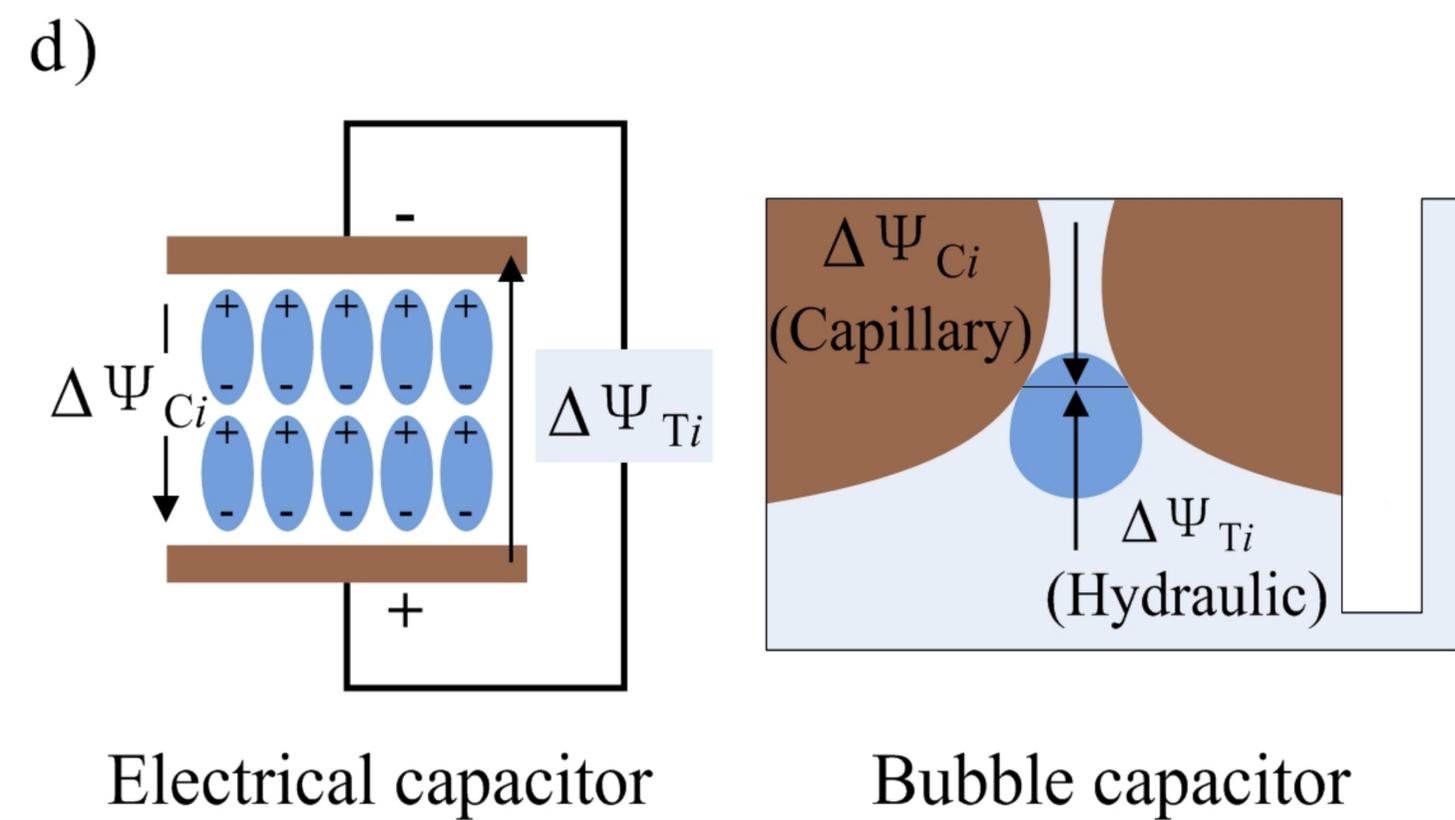
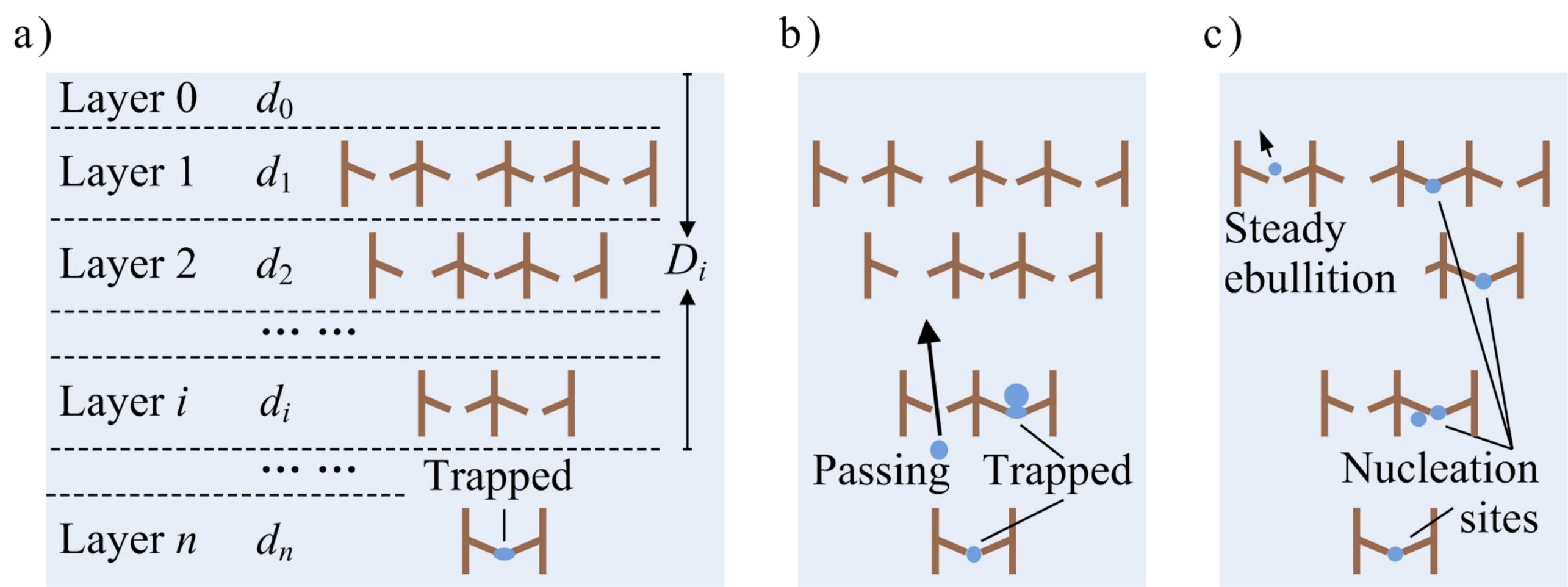
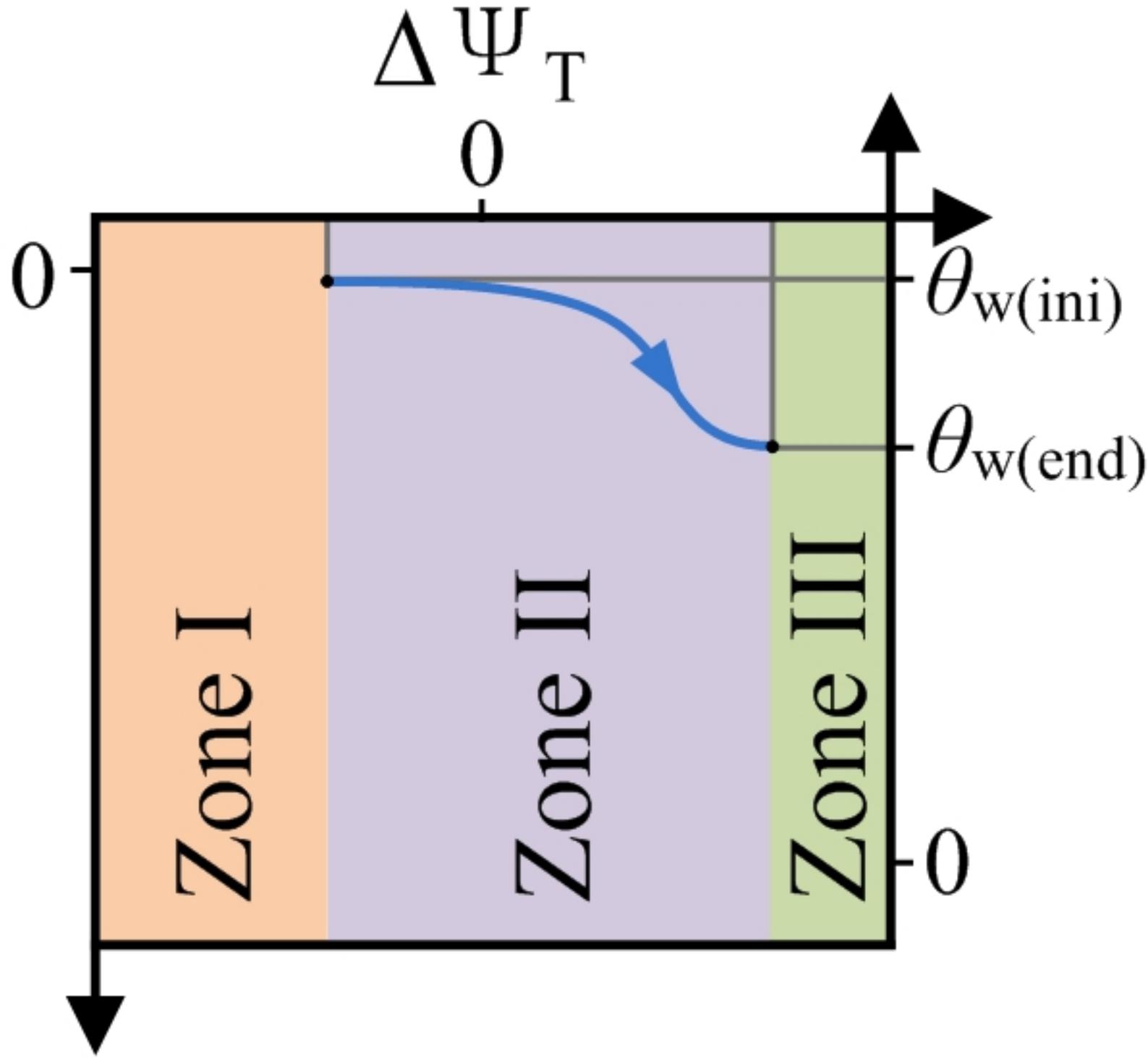


Figure 2.

Gas content

$$\theta_g = \phi - \theta_w \quad (\%)$$



Water content  $\theta_w$  (%)

Figure 3.



**Figure 4.**

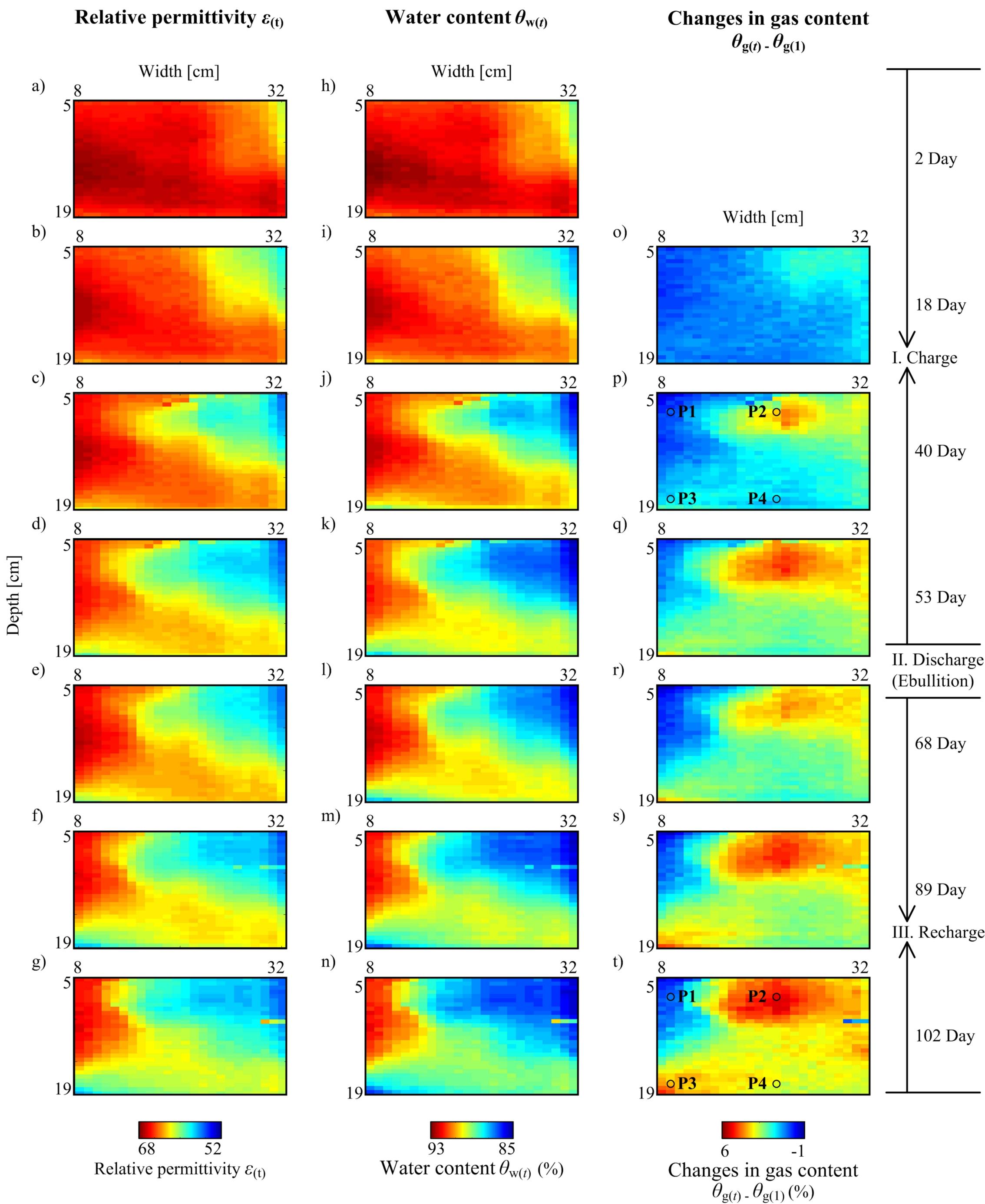
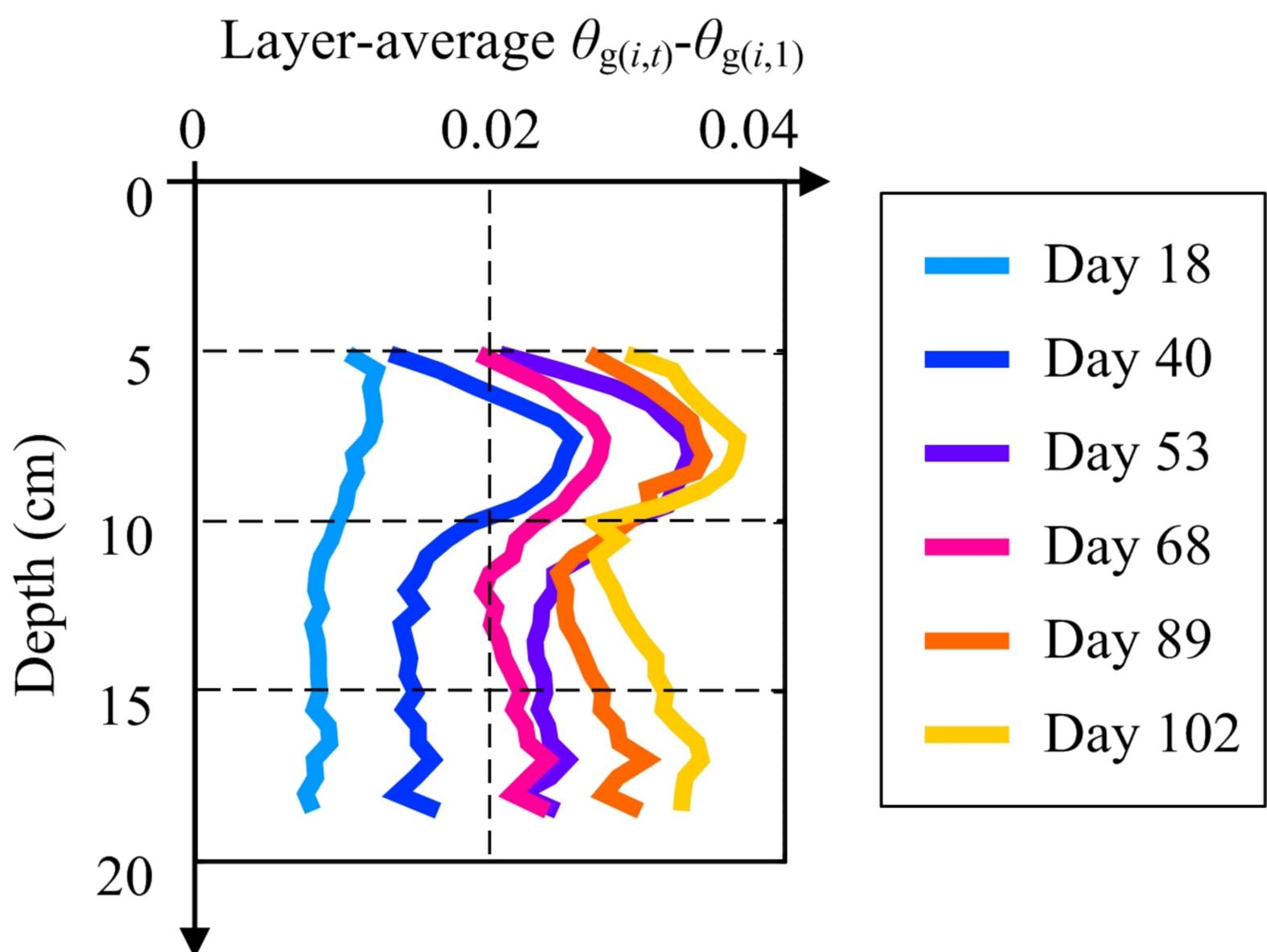
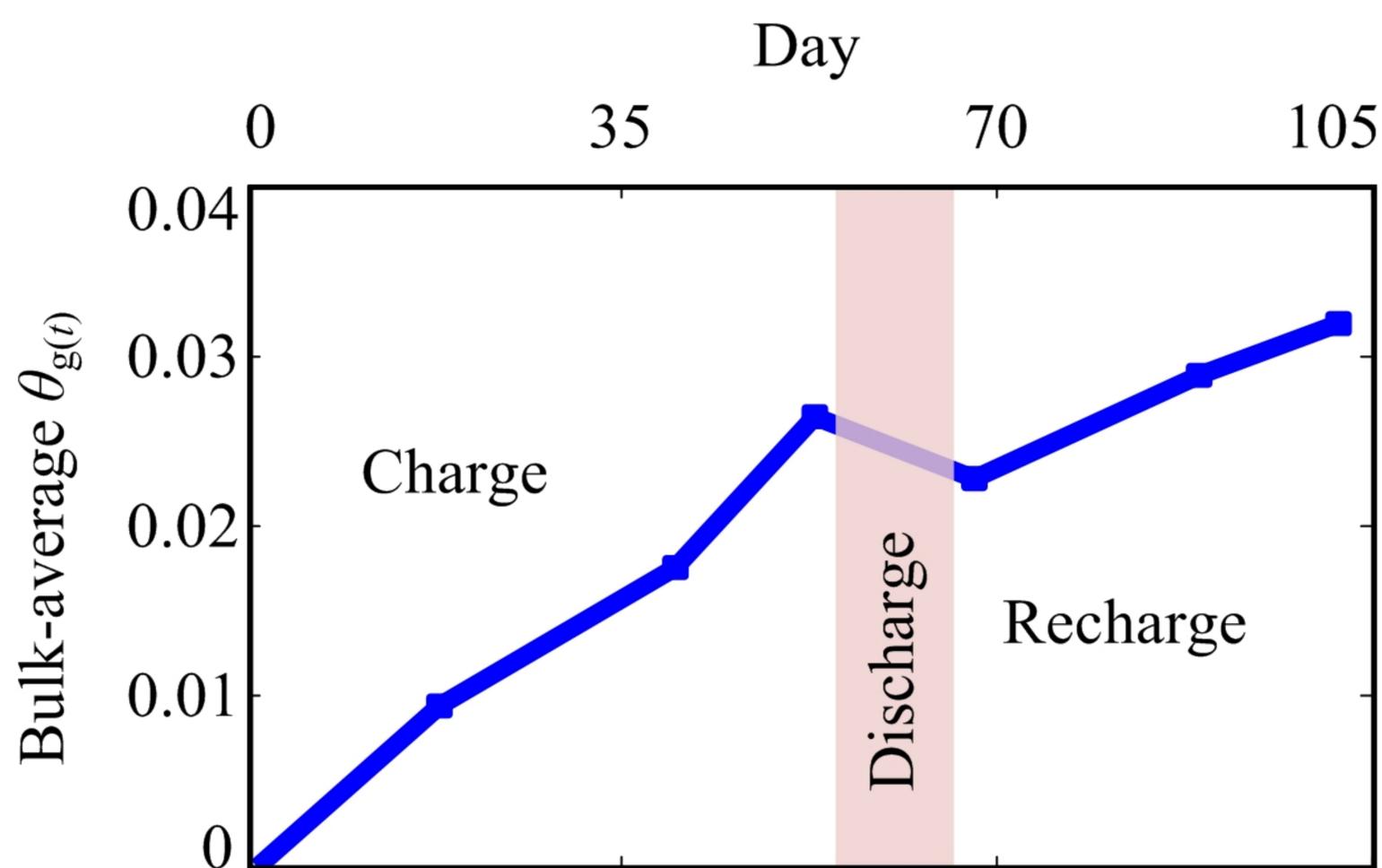


Figure 5.

a)



b)



c)

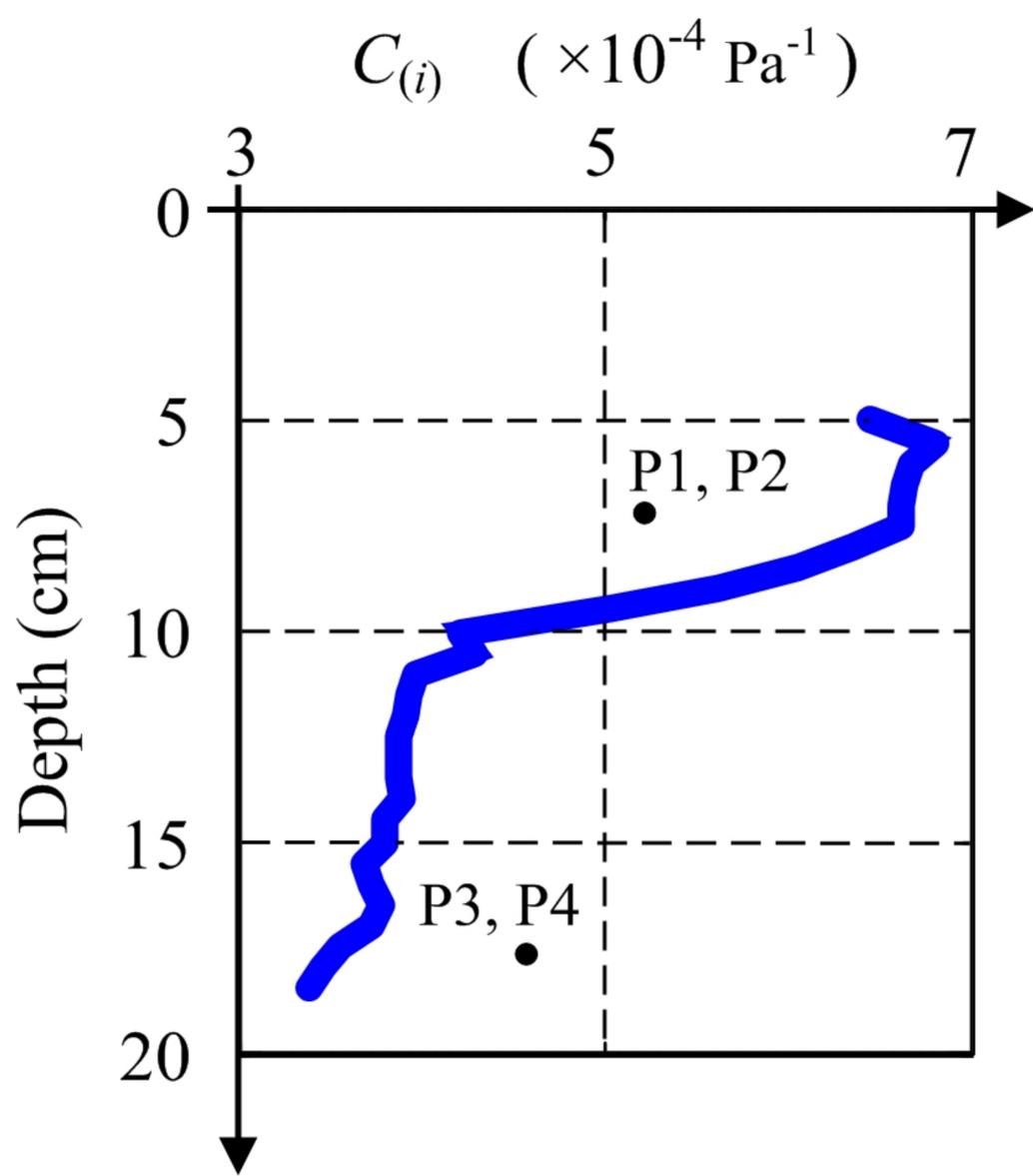
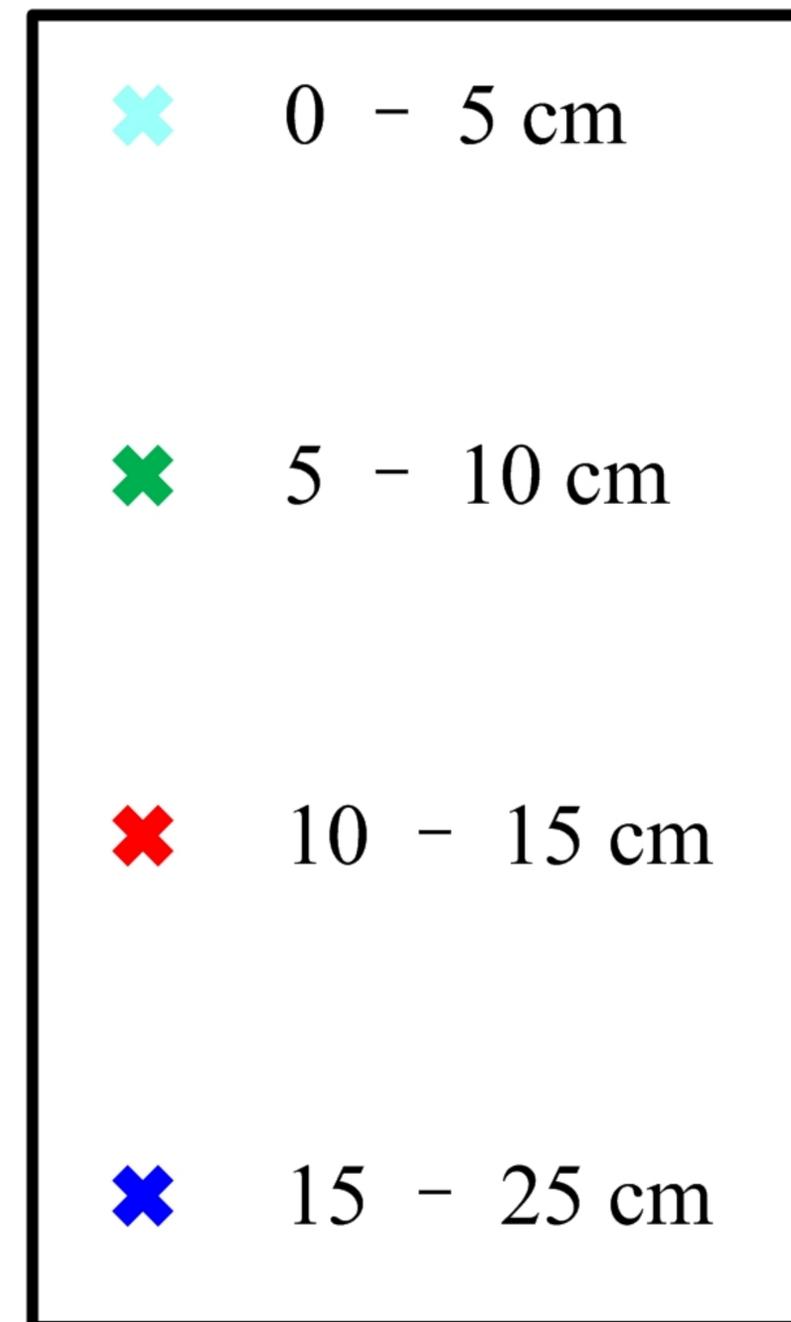
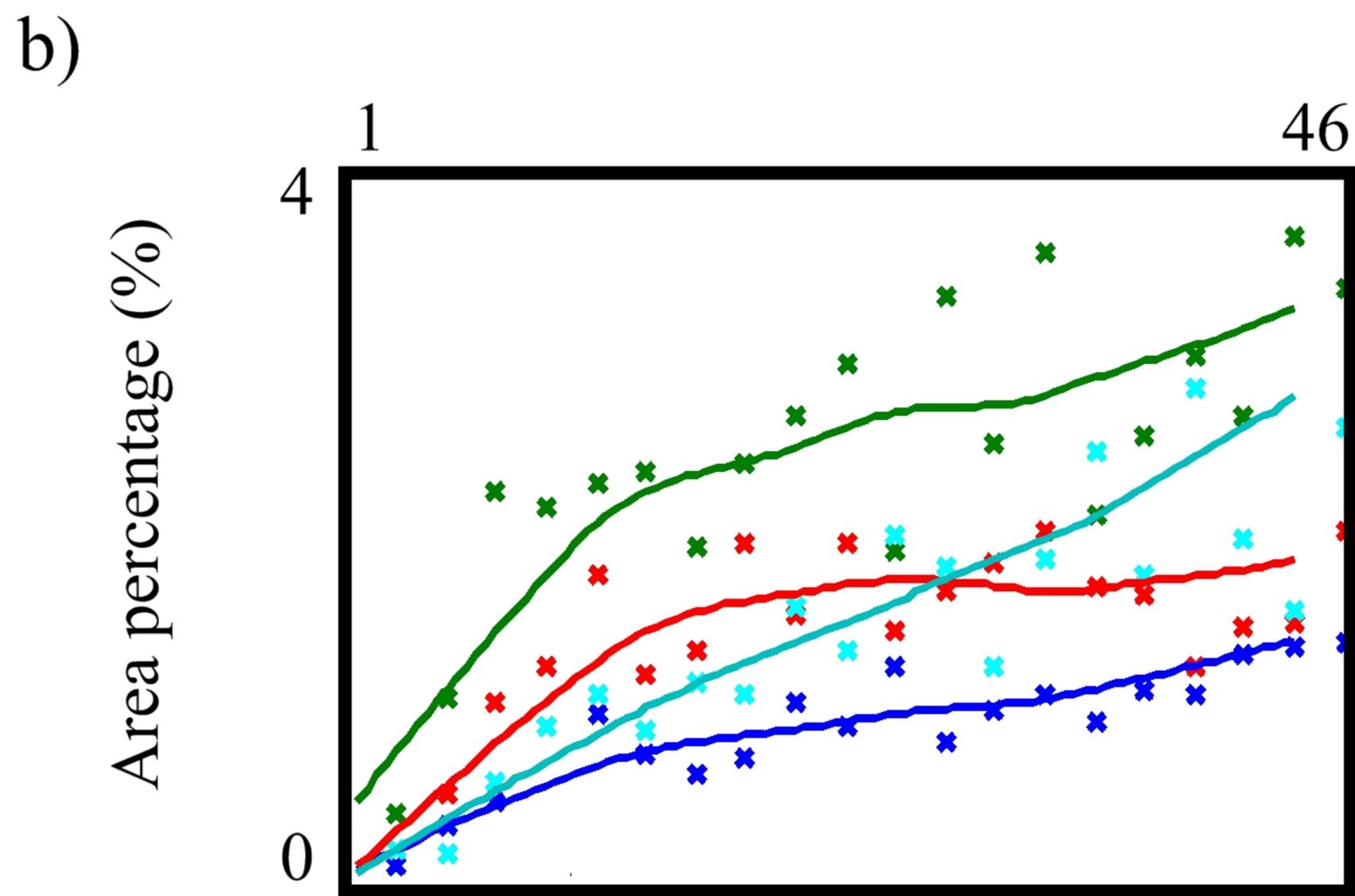
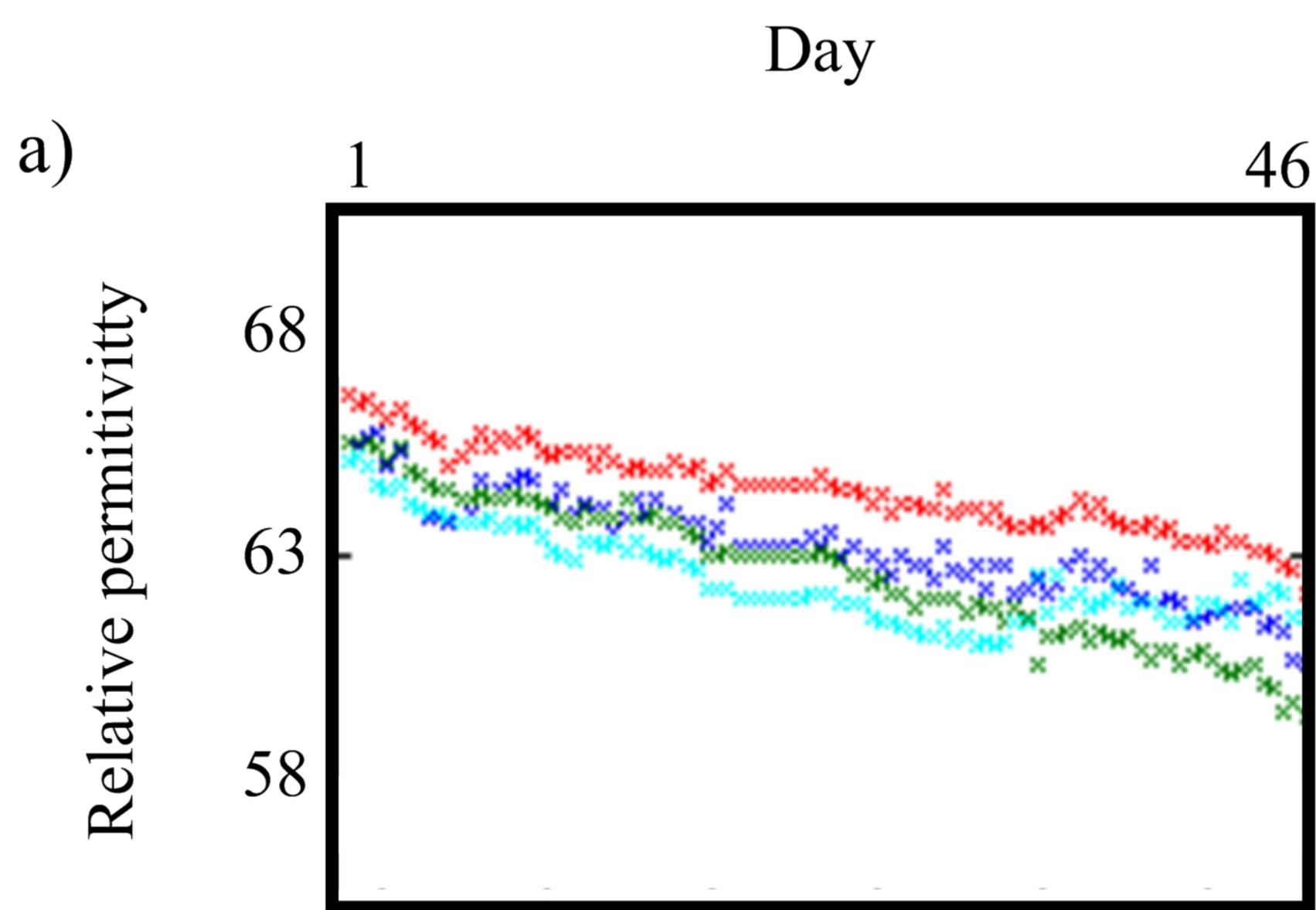
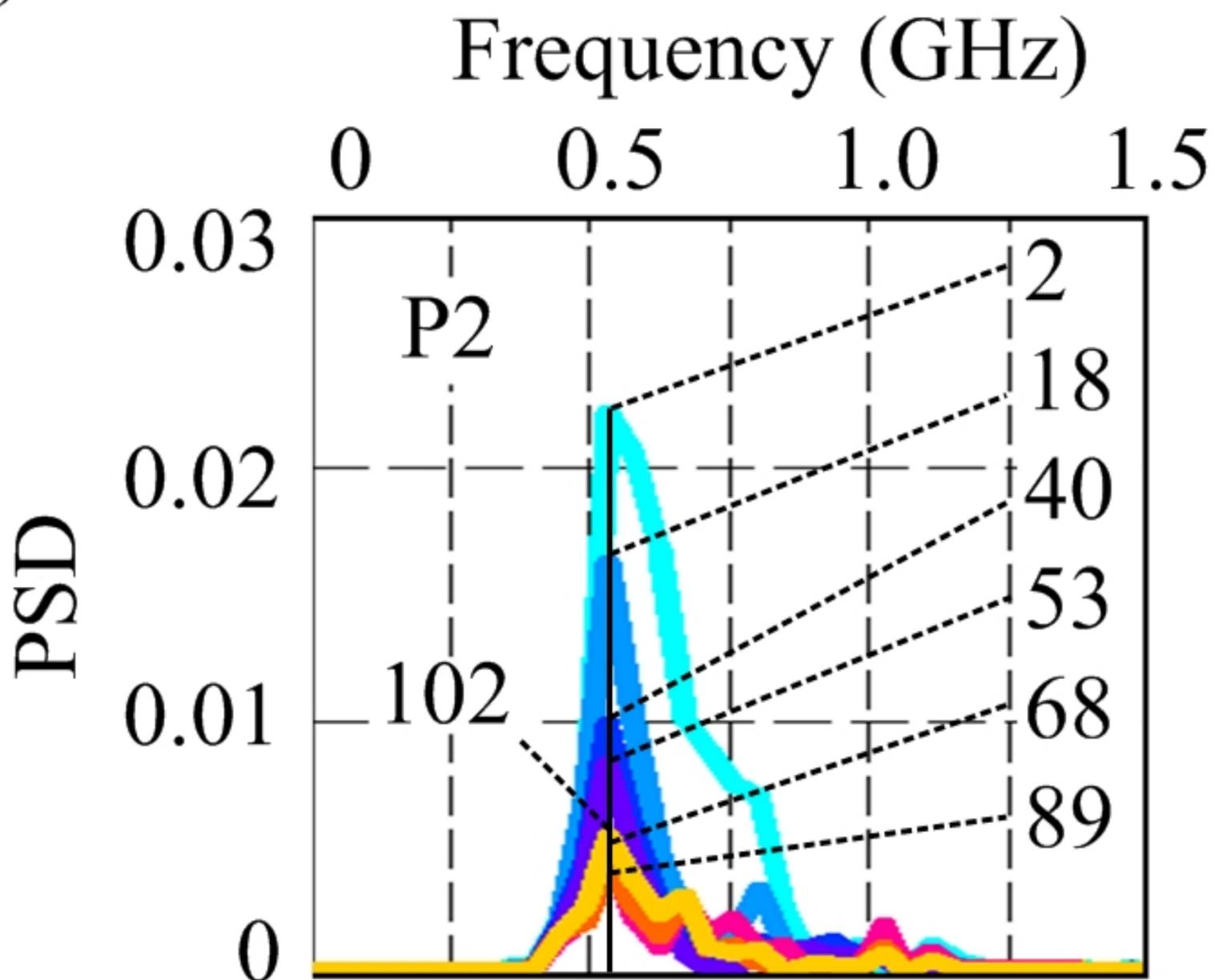


Figure 6.



**Figure 7.**

a)



b)

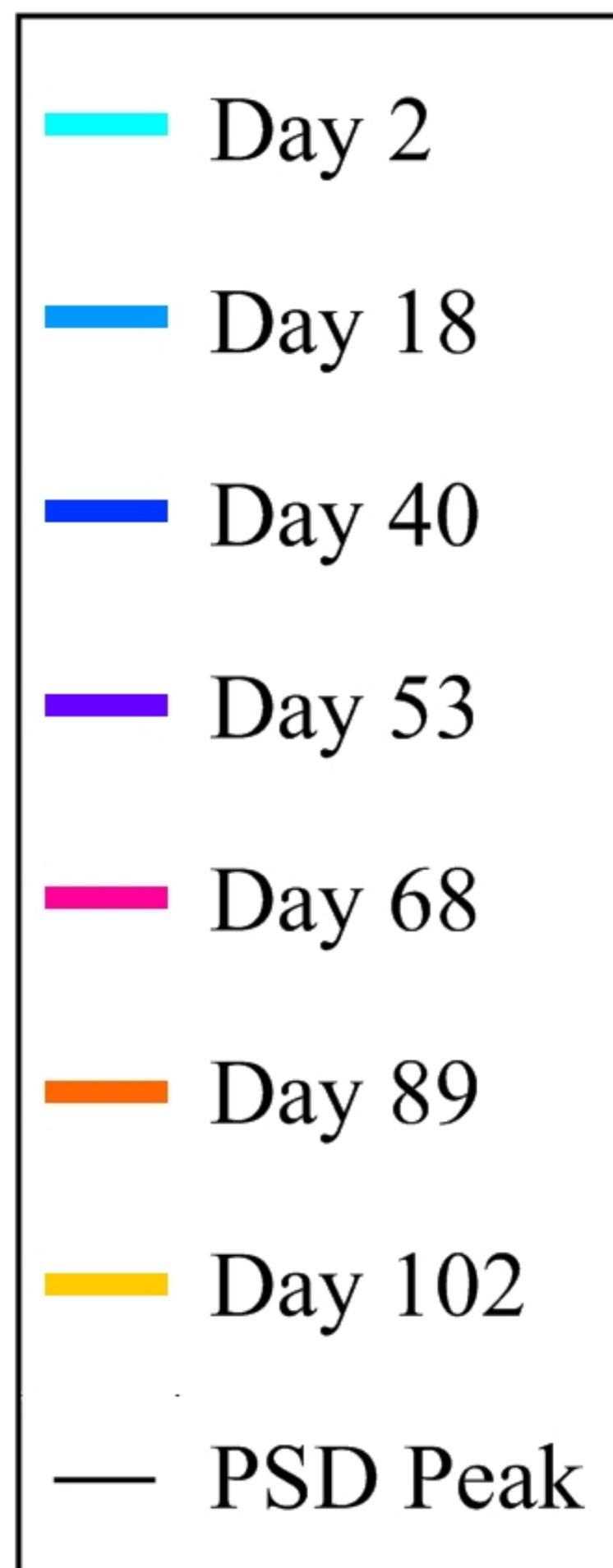
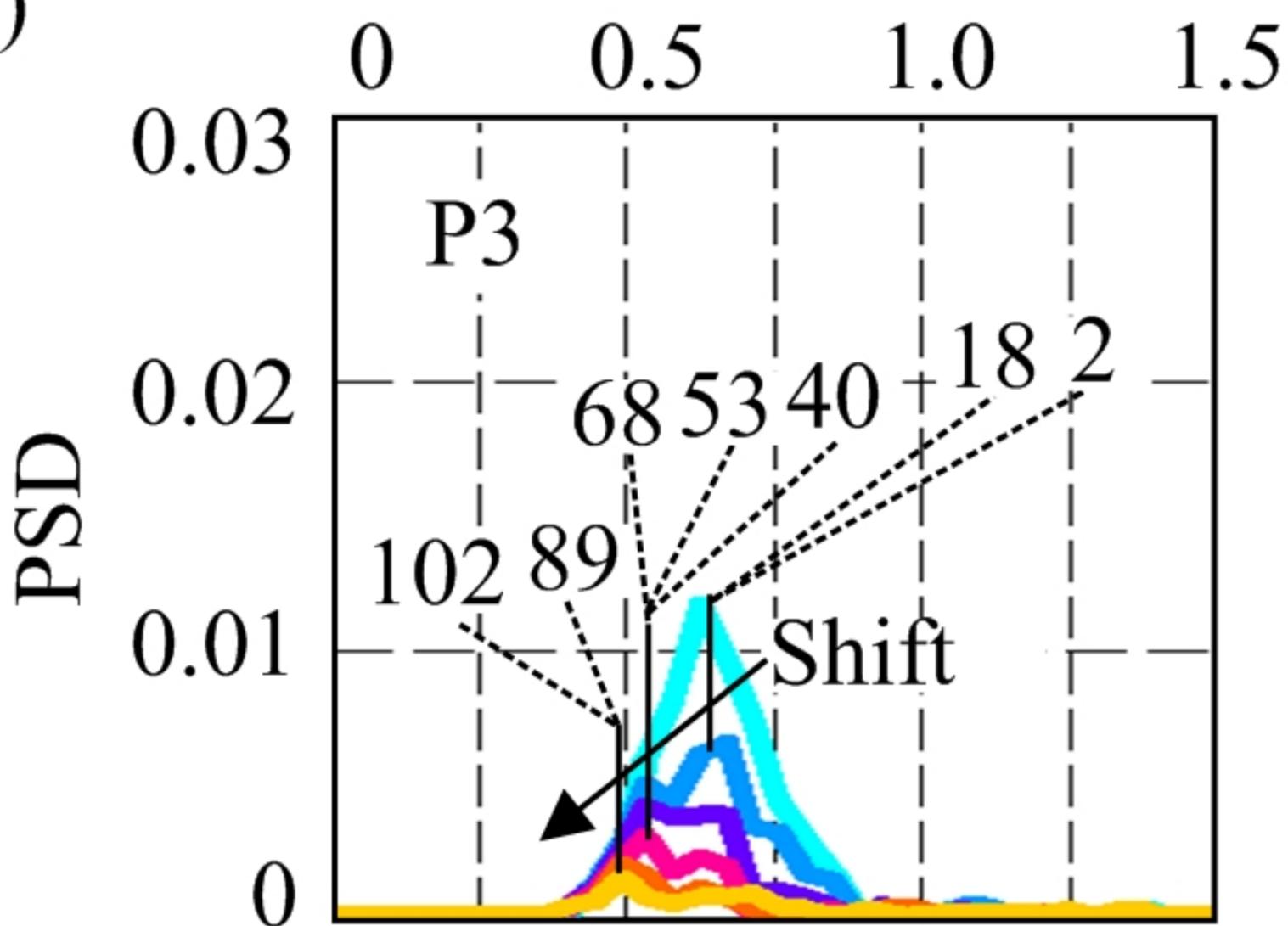


Figure 8.

