



1 **Preferential Pathways for Fluid and Solutes in Heterogeneous**
2 **Groundwater Systems: Self-Organization, Entropy, Work**

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8

9 **Abstract**

10 Patterns of distinct preferential pathways for fluid flow and solute transport are ubiquitous in
11 heterogeneous, saturated and partially saturated porous media. Yet, the underlying reasons for
12 their emergence, and their characterization and quantification, remain enigmatic. Here we
13 analyze simulations of steady state fluid flow and solute transport in two-dimensional,
14 heterogeneous saturated porous media with a relatively short correlation length. We
15 demonstrate that the downstream concentration of solutes in preferential pathways implies a
16 downstream declining entropy in the transverse distribution of solute transport pathways. This
17 reflects the associated formation and downstream steepening of a concentration gradient
18 transversal to the main flow direction. With an increasing variance of the hydraulic conductivity
19 field, stronger transversal concentration gradients emerge, which is reflected in an even smaller
20 entropy of the transversal distribution of transport pathways. By defining “self-organization”
21 through a reduction in entropy (compared to its maximum), our findings suggest that a higher
22 variance and thus randomness of the hydraulic conductivity coincides with stronger macroscale
23 self-organization of transport pathways. While this finding appears at first sight striking, it can
24 be explained by recognizing that emergence of spatial self-organization requires, in light of the
25 second law of thermodynamics, that work be performed to establish transversal concentration
26 gradients. The emergence of steeper concentration gradients requires that even more work be
27 performed, with an even higher energy input into an open system. Consistently, we find that
28 the energy input necessary to sustain steady-state fluid flow and tracer transport grows with the
29 variance of the hydraulic conductivity field as well. Solute particles prefer to move through
30 pathways of very high power, and these pathways pass through bottlenecks of low hydraulic
31 conductivity. This is because power depends on the squared spatial head gradient, which is in
32 these simulations largest in regions of low hydraulic conductivity.



33 **1 Introduction**

34 **1.1 Preferential flow phenomena – fast, furious and enigmatic**

35 Distinct patterns of preferential movement of water, dissolved and suspended matter are
36 ubiquitous in fully-saturated aquifer systems (e.g., LaBolle and Fogg, 2001; Bianchi et al.,
37 2011; Berkowitz et al., 2006), partially saturated soils (e.g., Beven and Germann, 1982) and at
38 the land surface (e.g., Uhlenbrook, 2006). Preferential flow and solute transport in porous media
39 commonly leads to fast, localized early arrivals and/or long tailing in temporal breakthrough
40 curves (e.g., Berkowitz et al., 2006) and pronounced fingerprints in concentration patterns in
41 soils (Flury et al., 1994).

42 Preferential flow and transport often occur along connected highly conductive networks. Some
43 networks are formed by previous physical/chemical work performed by the fluid, as in the cases
44 of surface rill and river networks (Howard, 1990), subsurface pipe networks (Jackisch et al.,
45 2017), karst conduits (Groves and Howard, 1994), and fractured rock formations (Becker and
46 Shapiro, 2000; Berkowitz, 2002). Other networks are created by soil fauna and flora as earth
47 worm burrows (Zehe and Flühler, 2001; van Schaik et al., 2014) and plant roots (Wienhöfer et
48 al., 2009; Tietjen et al., 2009). Although it might appear unsurprising that flow and transport
49 through these networks dominates system behavior, effective ways to model flow and transport
50 in these networks have been debated for more than 30 years (Beven and Germann, 1981;
51 Šimůnek et al., 2003; Klaus and Zehe, 2011; Wienhöfer and Zehe, 2014; Berkowitz et al., 2006,
52 Sternagel et al., 2019, 2020). Preferential flow and transport occurs, however, also in porous
53 media without such “well-defined” networks, e.g., in coarse-grained soils due to fingering and
54 wetting front instabilities (Blume et al., 2009; Dekker and Ritsema, 2000; Ritsema et al., 1998)
55 and particularly in stochastically heterogeneous saturated porous media (Bianchi et al., 2011;
56 Edery et al. 2014).

57 The emergence of preferential pathways in systems without well-defined networks – and their
58 characterization – remains even more enigmatic. The numerical study of Edery et al. (2014),
59 for example, revealed that a higher variance in the hydraulic conductivity (K) field coincided
60 with a stronger concentration of solutes within a smaller number of preferential flow paths. If
61 the emergence of preferential flow is indeed manifested self-organization, as argued by
62 Berkowitz and Zehe (2020), this key finding of Edery et al. (2014) suggests that macroscale
63 steady states of stronger organization (or higher order) emerge and persist despite a greater



64 degree of subscale randomness. The related key questions we address here are (i) how spatial
65 organization in preferential fluid flow and solute transport can be quantified, and (ii) why a
66 larger subscale randomness might favor stronger macroscale organization.

67 **1.2 Attempts to characterize and predict preferential transport in groundwater**

68 The emergence of preferential pathways of fluid flow and solute transport in saturated porous
69 media has been explored in numerous simulation studies in heterogeneous conductivity fields,
70 to relate the spatial correlation structures of the hydraulic conductivity and velocity fields to
71 features of anomalous transport behavior (e.g., Cirpka and Kitanidis, 2000; Willmann et al.,
72 2008; Berkowitz and Scher, 2010; de Dreuzy et al., 2012; Morvillo et al., 2021). While velocity
73 correlation parameters have been successfully related to statistical moments of hydraulic
74 conductivity, it remains challenging or even impossible to a priori delineate preferential
75 pathways exclusively based on multivariate and topological characteristics of the hydraulic
76 conductivity field. Cirpka and Kitanidis (2000) and Willmann et al. (2008) report, for instance,
77 the emergence of preferential pathways in the distributions of tracer travel velocities and shapes
78 of solute plumes. These pathways were not apparent, however, from the analysis of the
79 stationary conductivity fields. Moreover, Edery et al. (2014) demonstrate that critical path
80 analysis (based on percolation theory), for example, does not determine the actual preferential
81 pathways in a system; the authors suggest that the operational preferential pathways become
82 fully apparent only when solving for fluid flow and solute transport through the domain.

83 Bianchi et al. (2011) explored the link between connectivity and the emergence of preferential
84 flow paths at the MADE site, using three-dimensional, conditional, geostatistical realizations
85 of the hydraulic conductivity field. Their simulations of flow and transport under permeameter-
86 like boundary revealed that the first 5% of particles, arriving at the downstream domain outlet,
87 moved through preferential flow paths carrying 40% of the flow. Fiori and Jankovic (2012)
88 reported similar findings and stressed the rather small probability that solute particles visit
89 highly conductive blocks particularly in case of a high variance in K . Bianchi et al. (2011)
90 highlighted that the fraction of particle paths passing the high-conductivity regions was between
91 43% and 69%, while the most rapid transport passed through low-conductivity bottle necks.
92 This is in line with the findings of Edery et al. (2014), who concluded that connectivity of rapid
93 preferential pathways need not require connected zones of continuously high hydraulic
94 conductivity. Along a different avenue, Bianchi and Pedretti (2017) characterized spatial



95 disorder in two-dimensional conductivity fields by means of the Shannon entropy (Shannon,
96 1948) and related this to moments of solute breakthrough curves. Dispersion in travel times and
97 the probability of solutes to pass through low conductivity regions were found to increase with
98 lower order expressed by a higher geological entropy.

99 **1.3 Preferential flow, self-organization, entropy, work – where is the connection?**

100 The results of the studies mentioned above all underpin that (a) preferential flow and transport
101 in heterogeneous, saturated porous media remains a largely enigmatic and emergent
102 phenomenon, and (b) efforts to represent this behavior by means of effective transfer functions,
103 inferred from volume-averaging based scaling of the hydraulic conductivity field, appear
104 virtually impossible. This is why, we propose to shift the attention from the question of “where”
105 preferential pathways emerge, to questions regarding their “macroscale organization and
106 strength”, and “the necessary physical work” to establish their self-organized emergence.

107 Haken (1983) defined self-organization as the emergence of ordered macroscale states, or the
108 dynamic behavior of an open system far from thermodynamic equilibrium (TE), that arises from
109 a synergetic interplay of microscale, irreversible processes. An ordered state is characterized
110 by the deviation of its entropy from the entropy maximum at TE (Kondepudi and Prigogine,
111 1998, see section 3). This reduction in entropy, and any additional entropy produced by the
112 internal irreversible processes, must be exported from the open system to establish order. This
113 is turn requires physical work, and thus an input of free energy into the system, that is large
114 enough to create and maintain the self-organized state. A classical example to illustrate that
115 self-organization in open systems requires free energy and work, which inspired also Haken’s
116 theory of “synergetics”, is a gas laser. Laser light results from coherent stimulated light
117 emissions from all molecules in the system. Stimulated emission emerges when the energy input
118 into the gas laser becomes sufficiently large that the number of stimulated molecules exceeds
119 the number of molecules in the basic state. This “energetic pumping” establishes a state very
120 far from thermodynamic equilibrium, corresponding to an even apparently negative absolute
121 temperature in Boltzmann statistics, at which coherent emission from all individual emissions
122 emerges. Haken (1983) postulated that a higher-order, non-local “enslavement principle” forces
123 the individual molecules into a coherent and thus ordered behavior. This example of a critical
124 pumping rate to establish organization of laser light will be shown below (section 4) to be
125 analogous to fluid flow through porous media.



126 Several researchers have suggested that self-organization and the formation of complex
127 organisms and patterns in biological and environmental systems are governed by non-
128 local/global energetic extremal principles, in analogy to the Haken (1983) enslavement
129 principle. Pioneering studies in this context proposed that species maximize their energy
130 throughput (i.e., power) during evolution (Lotka, 1922 a & b) or showed that steady-state
131 planetary heat transport may be modeled successfully with a very simple two-box model, when
132 assuming that this state maximizes entropy production (Paltridge, 1979). This work motivated
133 several studies that explored the possibility that energetically optimized model setups allow
134 hydrological prediction of the land surface energy balance and evaporation (Kleidon et al.,
135 2014; Zehe et al., 2013), rainfall runoff behavior (Zehe et al., 2013) and groundwater flow and
136 spring discharge (Hergarten et al., 2014). These and other studies generally showed that
137 preferential flow in connected networks allows for a more energy efficient throughput of water
138 and matter through the system. This is because they reduce flow-weighted dissipative losses
139 due to an increased hydraulic radius in the rill or river network compared to sheet overland flow
140 (Howard, 1990; Kleidon et al., 2013) or in subsurface connected preferential pathways
141 compared to matrix flow (Hergarten et al., 2014; Zehe et al., 2010).

142 While the second law of thermodynamic refers to physical entropy (introduced by Clausius
143 (1857), section 3.1), information entropy (introduced by Shannon (1948)) is closely related and
144 well suited for diagnosing spatial organization (section 3.3). The concepts of information and
145 Shannon entropy have been used widely to characterize irreversible mixing and reaction
146 processes and their predictability (Chiogna and Rolle, 2017), the emergence of order in
147 distributed time series (Malicke et al., 2020), information in multiscale permeability data
148 (Dell'Oca et al., 2020) and the role of spatial variability of rainfall and topography in distributed
149 hydrological modelling (Loritz et al., 2018, 2021). Woodbury and Ulrych (1993) and Kitanidis
150 (1994) used the Shannon entropy to describe the spatial-time development and dilution of tracer
151 plumes in groundwater systems. Chiogna and Rolle (2017) expanded the dilution index for the
152 case of reactive solute mixing in groundwater and found a critical value that indicated the
153 complete consumption of a reactant, which was independent of advection and dispersion.
154 Bianchi and Pedretti (2017) used the Shannon entropy to quantify spatial disorder in
155 stochastically generated alluvial aquifers and explored its relation to the first three moments of
156 simulated tracer breakthrough curves. They found the average breakthrough time and its



157 variance to increase with increasing geological entropy, while the skewness in travel times
158 declined with increasing geological entropy increasing disorder.

159 **1.4 Objectives**

160 We thus suggest that the concepts of entropy, free energy and work hold the key to better
161 understand why preferential flow and transport in unstructured heterogeneous, saturated porous
162 media actually emerge. To this end, we analyze simulations of fluid flow and solute transport
163 through stochastically heterogeneous aquifers with different degrees of randomness (variance
164 in hydraulic conductivity), based on the results and insights of Edery et al. (2014). Specifically,
165 we show that macroscale self-organization due to the emergence of preferential solute transport
166 can be quantified based on the downstream decline of the Shannon entropy of the transversal
167 concentration pattern. We also find that preferential patterns of higher order, expressed through
168 lower entropies, emerge in case of larger variances of hydraulic conductivity. What appears
169 almost as a paradox at first sight – in the sense that a higher subscale randomness of the medium
170 causes a stronger spatial organization – can be explained by the fact that the power required to
171 maintain the driving head difference in steady state increases with increasing variance of the
172 hydraulic conductivity field. Due to this higher energy input, the fluid and solutes may perform
173 the necessary work to form preferential transport pathways that pass rapidly through low
174 conductivity bottlenecks and form preferential flow paths by steepening transversal
175 concentration gradients. We show, finally, that the entropy in the corresponding breakthrough
176 curve (BTC) increases with the variance of the hydraulic conductivity. This can be explained
177 by recognizing that entropy cannot be consumed, due to the second law of thermodynamics.
178 Hence, the downstream declining entropy in the transversal distribution of solute needs to be
179 exported from the system, and this export is reflected in the higher entropy of the corresponding
180 BTC.

181 **2 Underlying simulations of fluid flow and transport**

182 **2.1 Media generation and numerical simulations of fluid flow**

183 Here, we partially revisit and expand upon the numerical simulations of Edery et al. (2014),
184 which were employed to provide insight on fluid flow and anomalous solute transport behavior.
185 Edery et al. (2014) considered steady-state fluid flow within a two-dimensional, stochastic
186 heterogeneous system. The flow domain measured 300 by 120 space units as discretized into



187 grid cells of uniform size $\Delta x = 0.2$, $\Delta y = 0.2$, while all quantities are expressed using the same
188 space-time units. We consider a deterministic head difference of 100, from the left (vertical)
189 upstream boundary to the right downstream boundary; no-flow conditions are assigned to the
190 two horizontal domain boundaries.

191 We generated random realizations of statistically homogeneous, isotropic Gaussian fields for
192 the natural logarithm of the hydraulic conductivity $\ln(K)$, with exponential covariance and mean
193 $\ln(K) = 0$, using the sequential Gaussian simulator GCOSIM3D (Gómez-Hernández et al., 1997).
194 Edery et al. (2014) considered fields associated with a unit correlation length, $l = 1$, exploring
195 the impact of different values of the variance of $\ln(K)$, i.e., $1 < \sigma^2 < 5$, on the emergence of
196 preferential solute transport.

197 Figure 1a shows a realization for $\sigma^2 = 3$, corresponding to mild and strong randomness for
198 distances larger than $3l$. The deterministic flow problem for each realization was solved using
199 a code that is based on finite elements with Galerkin weighting functions (Guadagnini and
200 Neuman, 1999). The corresponding hydraulic head values throughout the domain were
201 converted to local velocities, and thus streamlines (Fig. 1b), which were in turn used for
202 transport simulations using particle tracking. For the system considered here, we used a porosity
203 of 0.3 (e.g., Levy and Berkowitz, 2003).

204 **2.2 Simulated solute transport with particle tracking**

205 Solute movement in each domain realization was simulated using the calculated streamlines,
206 with a standard Lagrangian particle tracking method. For all domains, values of Δ and l were
207 chosen such that $l/\Delta = 5$, to enable capture of small-scale fluctuations and advective transport
208 features (Ababou et al., 1989; Riva et al., 2009). Along the left upstream boundary, particles
209 are injected, by flux-weighting, and advance by advection and diffusion. The Langevin equation
210 defines the particle displacement vector \mathbf{r} , starting from given particle locations at time t_k :

211

212

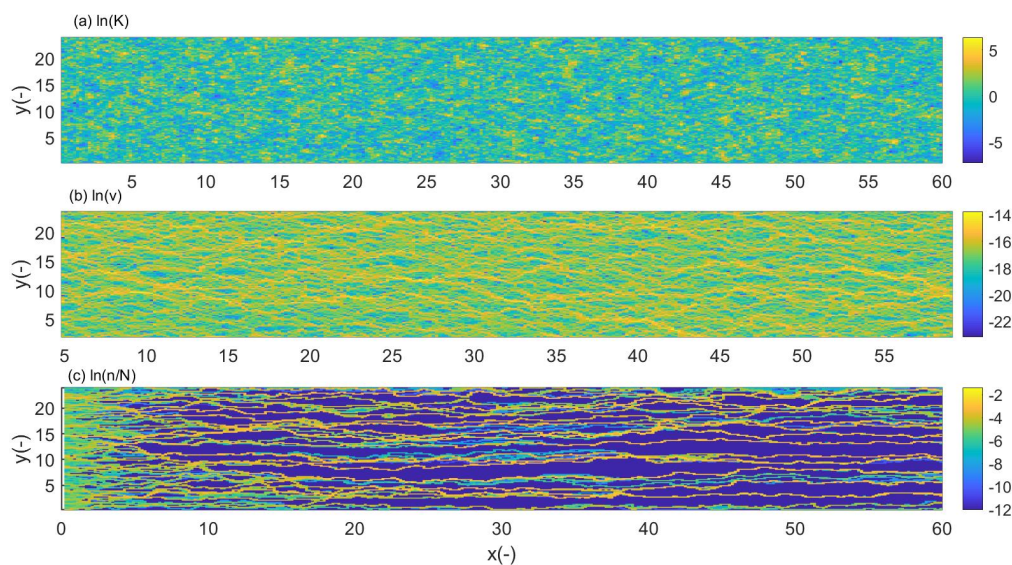
$$\mathbf{r} = \mathbf{v}[\mathbf{x}(t_k)]\delta t + \mathbf{d}_o \quad (\text{Eq. 1})$$

213

214 where \mathbf{v} is the fluid velocity vector, δt is the time step magnitude, and \mathbf{d}_o denotes the diffusive
215 displacement, with a modulus of \mathbf{d}_o given by $\xi\sqrt{2D_{\text{mol}}\delta t}$; ξ is a random number drawn the from



216 standard normal distribution $N[0, 1]$. A representative molecular diffusion coefficient of
217 $D_{\text{mol}} = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was prescribed (Domenico and Schwartz, 1990). The advective
218 displacements in Equation 1 are computed using the local velocities at \mathbf{x} with a fixed, uniform
219 spatial step δs . In Equation 1, the time step δt is given by $\delta t = \delta s/v$, where v is the modulus of
220 \mathbf{v} . Reflection conditions are prescribed along the two horizontal no-flow boundaries to avoid
221 particle leakage. As in Edery et al. (2014), we used 10^5 particles, with $\delta s = \Delta/10$.



222

223 Figure 1: Examples of (a) $\ln(K)$, (b) $\ln(v)$, and (c) the cumulative number of particles that visited
224 a grid cell in the simulation domain, normalized with the total number of particles N , on a
225 logarithmic scale. The variance of $\ln(K)$ is $\sigma^2 = 3$.

226 3 Free energy, entropy and work

227 3.1 Thermodynamics in a nutshell: the first and the second law

228 We start very generally with the first law of thermodynamics, which relates the variation in
229 internal energy U ($\text{J} = \text{kg m}^2 \text{ s}^{-2}$) of a system to a variation of work E_{free} (J) and a variation of
230 heat Q_h (J), while overall energy is conserved:

$$231 \quad \delta U = \delta E_{\text{free}} + \delta Q_h \quad (\text{Eq. 2})$$

232



233 Note that the capacity of a system to perform work is equivalent to “free energy”, while a
234 variation in heat is equal to the product of a variation of physical entropy S (J K^{-1}) and the
235 absolute temperature T (K): $\delta Q_h = T \delta S$ as introduced by Clausius (1857). The second law of
236 thermodynamics states that entropy is produced during irreversible processes, while it cannot
237 be consumed. The second law implies that isolated systems, which neither exchange mass, nor
238 energy, nor entropy with their environment, reach a dead state of maximum entropy called
239 thermodynamic equilibrium in which all gradients have been depleted. Kleidon (2016)
240 distinguishes three types of physical entropy: thermal entropy produced by friction and
241 depletion of temperature gradients, molar entropy produced by mixing and depletion of
242 chemical potential/concentration gradients, and radiation entropy produced by radiative cooling
243 and depletion of radiation temperature differences.

244 From Eq. 2 and the second law, we can conclude that free energy is not a conserved property,
245 as it corresponds to the variation in internal energy minus the variation in heat, during which
246 entropy is produced. Free energy dissipation and entropy production are thus inseparable, and
247 maximization of the entropy of an isolated system occurs due to conservation of energy at the
248 expense of minimizing its free energy. An open system may nevertheless persist in steady states
249 of lower entropy, if it is exposed to a sufficient influx of free energy to sustain the necessary
250 physical work that needs to be performed to act against the natural depletion of the internal
251 gradients, or even to steepen them and further reduce the entropy (as discussed for the gas laser).
252 Order in an open system thus manifests through persistent gradients and an entropy lower than
253 the maximum. Steps to higher order and lower entropies imply a steepening of internal
254 gradients. This is exactly what occurs when preferential transport of solutes emerges in our
255 transport simulations: solute particles tend to concentrate in localized pathways, thereby
256 forming a transversal concentration gradient (according to the domain geometry shown in Fig.
257 1). The Shannon entropy (Shannon, 1948) is ideally suited to quantify the related entropy
258 reduction, as detailed in section 3.3.

259 **3.2 The free energy balance of saturated porous media**

260 To determine the work that is performed by the fluid when flowing through heterogeneous
261 media, we derive the free energy balance of the fluid by relating changes in hydraulic head and
262 fluid flux to their energetic counterparts. The local formulation of the free energy balance of a
263 groundwater system, seen as an open thermodynamic system, is determined by the



264 difference/divergence of the free energy fluxes \mathbf{J}_{free}^E ($\text{J s}^{-1} \text{m}^{-2}$) per unit area and the amount of
265 dissipated energy per volume D ($\text{J s}^{-1} \text{m}^{-3}$):

$$266 \quad \frac{de_{free}}{dt} = -\nabla \cdot \mathbf{J}_{free}^E - D \quad (\text{Eq. 3})$$

267 where e_{free} ($\text{J s}^{-1} \text{m}^{-3}$) is the volumetric free energy density. Advective fluxes of relevant free
268 energy forms are generally determined by multiplying the Darcy flux with the corresponding
269 form of energy per unit volume. Here we account for advection of mechanical energy \mathbf{J}_H^E
270 (named power hereafter), gravitational potential energy \mathbf{J}_{pot}^E , and kinetic energy of the flowing
271 fluid \mathbf{J}_{kin}^E . As energy is additive, the term \mathbf{J}_{free}^E corresponds hence to the sum of the following
272 free energy fluxes:

$$273 \quad \mathbf{J}_H^E = \mathbf{q} \rho g H$$

$$274 \quad \mathbf{J}_{pot}^E = \mathbf{q} \rho g z \quad (\text{Eq. 4})$$

$$275 \quad \mathbf{J}_{kin}^E = \mathbf{q} \frac{1}{2} \rho v^2$$

276 where ρ (kg m^{-3}) is the density of water, g (m s^{-2}) the gravitational acceleration, \mathbf{q} (m s^{-1}) the
277 Darcy flux, v (m s^{-1}) the absolute value of the fluid velocity, H (m) the pressure head, and z (m)
278 the geodetic elevation. Note that while kinetic energy is proportional to v^2 , the kinetic energy
279 flux corresponds to the product of the volumetric water flux \mathbf{q} and its kinetic energy density
280 $\frac{1}{2} \rho v^2$. Thus, kinetic energy is in fact proportional to v^3 and is usually very small. By inserting
281 Eq. 4 into Eq. 3, we obtain:

$$282 \quad \frac{de_{free}}{dt} = -\rho g \nabla [\mathbf{q}(H + z)] - \frac{1}{2} \rho \nabla [\mathbf{q} v^2] - D \quad (\text{Eq. 5})$$

283 The left hand side of Eq. 5 corresponds to the change in Gibbs free energy of a fluid volume
284 under isothermal conditions (Bolt and Frissel, 1960). This change in free energy storage on the
285 left hand side can be decomposed into the sum of three terms as well (Zehe et al., 2019): (i) the
286 change in storage of gravitational potential energy reflecting soil water storage changes in
287 partially saturated soils or density changes in groundwater; (ii) the change in storage of
288 mechanical energy reflecting changes in pressure head in groundwater or changing matric
289 potentials in partially saturated soils; and (iii) the change in kinetic energy stored in the system,
290 due to acceleration of the fluid. The latter is usually very small and can be neglected.



291 In the case of steady-state groundwater flow, the variables H , z , ρ and v are constant in time, so
292 that the change in free energy storage at the left hand side of Eq. 5 is zero. As we assume z to
293 be constant along the system and neglect density changes of the fluid, the divergence in the flux
294 of gravitational potential energy at the right hand side is zero, as well. The system under
295 investigation hence receives solely steady-state inflow of high mechanical energy,
296 corresponding to the upstream inflow of water at a high pressure head, and it exports water at
297 a much lower mechanical energy at the lower downstream pressure head. The corresponding
298 energy difference is partly dissipated and partly converted into kinetic energy of flowing fluid
299 and dissolved solute masses. The latter is, however, usually neglected, as dissolved solute mass
300 is much smaller. As steady-state fluid flow further implies that the divergence of \mathbf{q} is zero as
301 well, the free energy (Eq. 4) becomes hence:

$$302 \quad \rho g \mathbf{q} \cdot \nabla H = -\rho v \mathbf{q} \cdot \nabla v - D \quad (\text{Eq. 6}).$$

303 The left hand side is the available power per unit volume P ($\text{J s}^{-1} \text{m}^{-3}$) in the groundwater flux,
304 which is partly converted into a spatial change in kinetic energy of the fluid and partly
305 dissipated. In contrast to overland flow systems (Loritz et al., 2019; Schroers et al., 2021), the
306 change in kinetic energy can be neglected for groundwater as it is proportional to the cube of
307 the fluid velocity (as noted before Eq. 5). In fact, the use of Darcy's law implies that kinetic
308 energy can be neglected.

309 The total available power P in the groundwater flux during steady-state flow is hence nearly
310 completely dissipated:

$$311 \quad P = \rho g \mathbf{q} \cdot \nabla H = -D \quad (\text{Eq. 7}).$$

312 By inserting Darcy's law into Eq. 7 and recalling that we focus on a two-dimensional domain,
313 we obtain an equation that relates power and dissipation to the squared head gradient (in sense
314 of a scalar product):

$$315 \quad P = -\rho g K \left[\frac{\partial H}{\partial x} \frac{\partial H}{\partial x} + \frac{\partial H}{\partial y} \frac{\partial H}{\partial y} \right] = -D \quad (\text{Eq. 8}).$$

316 The physical mechanism that causes dissipation relates to the shear and frictional losses the
317 fluid experiences when passing through the porous medium. As hydraulic conductivity relates
318 to the ratio of intrinsic permeability k (m^2) and viscosity of the fluid η (N sm^{-1}), the inverse of



319 K is a measure of the flow resistance and related dissipative losses. One would thus expect that
320 the dissipative losses grow with fluid viscosity (declining K , increasing resistance) and
321 declining permeability (declining k). To better underpin this, we simplify Eq. 8 for steady-state
322 flow through an heterogeneous, one-dimensional system, which means that $\frac{\partial H}{\partial y}=0$:

$$323 \quad P = \rho g(K(x)d_x H)d_x H = D(x) \text{ (Eq. 9).}$$

324 where d_x denotes the gradient with respect to x . Steady-state flow in one dimension implies a
325 constant flux q in the x direction, which means that the total spatial variation of dq is zero. As
326 K is spatially variable, this implies that local spatial variations of conductivity denoted by
327 $d(K(x))$ must be compensated by opposite spatial variations of the pressure head gradient,
328 $d(d_x H)$:

$$329 \quad dq = 0 \rightarrow$$
$$330 \quad d(-K(x)d_x H) = 0 \rightarrow$$
$$331 \quad -d(K(x)) d_x H = K(x) d(d_x H) \text{ Eq. (10)}$$

332 As a consequence, power P is not constant (Eq. 7) but instead grows with the magnitude of
333 local spatial variations of the head gradient $d(\nabla_x H)$:

$$334 \quad dP = \rho g q d(d_x H) \text{ (Eq. 11).}$$

335 Due to Eq. 10 (constant Darcy flux), we can express the spatial variation in the head gradient
336 $d(d_x H)$ in Eq. 11 as follows:

$$337 \quad -d_x H d(\ln(K(x))) = d(d_x H) \quad \text{(Eq. 12).}$$

338 Combining Eq. 12 with Eq. 11, together with the definition of power in Eq. 9, yields:

$$339 \quad dP = -P(x) d(\ln(K(x))) \rightarrow d(\ln(P(x))) = -d(\ln(K(x))) \text{ (Eq. 13).}$$

340 As a consequence, we expect an anti-proportionality between $\ln(P(x))$ and $\ln(K(x))$ for the one-
341 dimensional case. In conclusion, we propose that the necessary power to push the fluid through
342 an heterogeneous medium grows also in the two-dimensional case with the variance of the $\ln(K)$
343 field. Local areas of high power coincide with large positive deviations from the overall average
344 head gradient, and these in turn peak across regions of low conductivity. This makes sense, as



345 dissipation peaks in those areas as flow resistance reach a maximum and the required work to
346 push fluid through these bottlenecks grows as well. This potentially explains the finding of
347 Edery et al. (2014) that the preferential flow paths also pass through areas of low conductivity.
348 We discuss this idea further in section 5.

349 **3.3 Characterizing emergent spatial organization in solute transport using information** 350 **entropy**

351 We now address the connection between physical entropy and information entropy, and explain
352 how we use the latter to quantify ordered states due to the emergence of preferential flow paths
353 and the associated formation of a concentration gradient transversal to the main flow direction.
354 The Shannon entropy S_H (bit) is defined as the expected value of information (Shannon, 1948).
355 Here we defined S_H using the discrete probability distribution to find particles at a distinct
356 transversal position y at a given x coordinate, as detailed below.

357 The field of information theory, originally developed within the context of communication
358 engineering, deals with the quantification of information with respect to a concept called
359 “surprise” of an event (Applebaum, 1996). For a discrete random variable Y that can take on
360 several values y_i with associated prior probabilities $p(y_i)$ the surprise or information content of
361 receiving/observing a specific value $Y = y_i$ is defined as:

$$362 \quad I = -\log_b(p(y)) \quad (\text{Eq. 14})$$

363 where I is the information content, b is the base of the logarithm and $p(y_i)$ the prior probability
364 that Y can be observed in the state y . Due to the use of the logarithm in Eq. 14, information is
365 an additive quantity, similar to physical entropy, energy, and mass. The expected information
366 content associated with the probability distribution of the random variable Y is the Shannon
367 entropy S_H :

$$368 \quad S_H(Y) = -\sum_{y \in Y} p(y_i) \log_2 p(y_i) \quad (\text{Eq. 15})$$

369 The definition of the Shannon entropy is equivalent to Gibb’s definition of physical entropy in
370 statistical mechanics (Ben-Naim, 2008). The latter is obtained when using the natural logarithm
371 in Eq. 15 and by multiplying the sum with the Boltzmann constant ($k_B = 1.30640 \times 10^{-23} \text{ J K}^{-1}$).
372 Physical entropy describes, in terms of statistical mechanics, the number of microstates that



373 correspond to the same macro-state at a given internal energy. In the state of maximum entropy
374 where all gradients are depleted, each microstate is equally likely (Kondepudi and Prigogine,
375 1998). The probability p of a single state is in this case, hence, simply the inverse of the number
376 of microstates. This implies a maximum uncertainty about the microstates and corresponds to
377 a minimum order in the system. Jaynes (1957) transferred this fundamental insight into a
378 method of statistical inference, stating “*when making inferences based on incomplete*
379 *information, the best estimate for the probabilities is the distribution that is consistent with all*
380 *information, but maximizes uncertainty*”. We emphasize that a maximum in information
381 entropy and physical entropy commonly implies a zero gradient either in probability (from the
382 information perspective) or in an intensive state variable such temperature, concentration or
383 pressure (from the thermodynamic perspective).

384 Its straightforward implementation makes Shannon entropy a flexible means (i) for the
385 optimization of observation networks (Fahle et al., 2015; Nowak et al., 2012), (ii) for the
386 characterization of mixing and dilution of solute plumes (e.g., Woodbury and Urych, 1993;
387 Kitanidis, 1994), or (iii) to illuminate how spatial disorder in hydraulic conductivity relates to
388 statistical moments of solute breakthrough curves (Bianchi and Pedretti, 2017). Here we adopt
389 a straightforward use of the Shannon entropy to characterize simulated solute transport, as
390 introduced by Loritz et al. (2018) to characterize redundancy in a distributed hydrological
391 model ensemble. We suggest that the maximum uncertainty corresponds to the case where each
392 flow path through the domain is equally likely, and the probability distribution to find particles
393 in a position in the y -direction is, hence, uniform. Deviations from this entropy maximum reflect
394 spatial order due to the concentration of particles in preferred flow paths and the associated
395 persistence of a transversal concentration gradient. This can be analyzed by computing the
396 Shannon entropy of the particle density distributions along y , $S_H(x)$, at a fixed position x along
397 the main flow direction, using the particle density matrix. A state of maximum entropy implies
398 that the same number of particles has visited each of the 120 grid cells at a given x coordinate
399 i.e. $S_H^{max} = \log_2(120) = 6.9$ bits. A state of perfect spatial organization and zero entropy
400 arises, on the other hand, when all particles move through a single grid cell at a distinct
401 coordinate x .

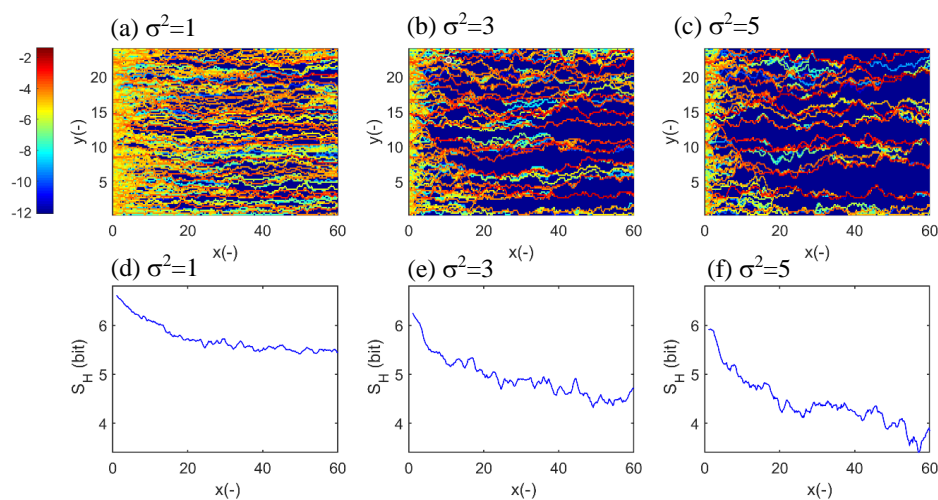


402 **4 Results**

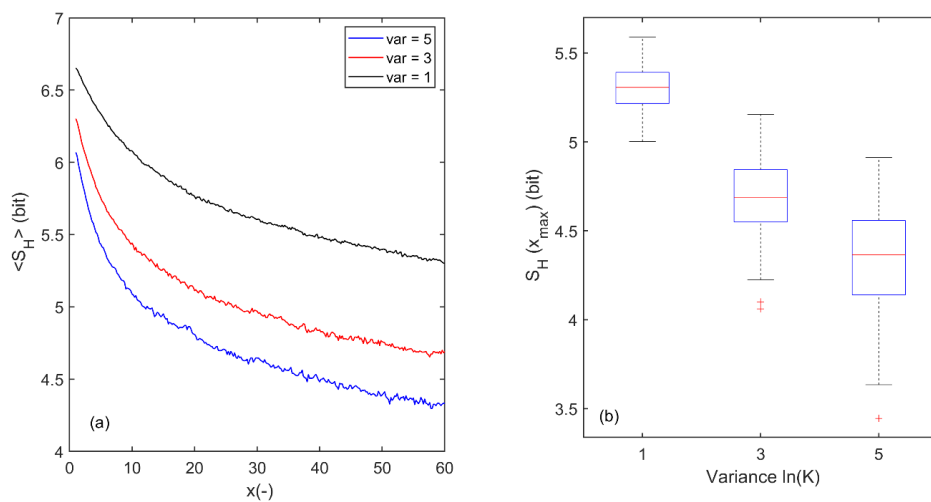
403 In the following, we demonstrate that preferential transport is indeed manifested self-
404 organization and showcase that a stronger self-organization requires indeed more physical
405 work. To this end, we calculated the Shannon entropy of transversal flow paths distribution and
406 relate this to power in fluid flow across the range of the variances in $\ln(K)$ as detailed below.
407 For this purpose, we set the dimensionless length and time units to meters and seconds,
408 respectively.

409 **4.1 Preferential flow paths and flow path entropy as function of the variance in $\ln(K)$**

410 Figures 2a-c compare the accumulated particle densities that passed through grid cells in the
411 domain as a function of the variance, σ^2 , for a randomly selected realization. The solute
412 transport pathways extend in a largely parallel form and share rather similar particle densities
413 for $\sigma^2=1$. However, the number of pathways clearly declines with increasing variance, and they
414 exhibit a stronger meandering and a larger visitation of particles in a smaller transversal number
415 of grids on their downstream course. The Shannon entropy S_H of the flow paths (flow path
416 entropy hereafter) exhibits, in general, and for all three variance cases, a clear decline with
417 increasing downstream transport distance (Figs. 2d-f). This reflects the increasing order in the
418 flow path distribution, corresponding to the emerging and increasing transversal concentration
419 gradients. A comparison of S_H among the variance cases clearly corroborates the visual
420 impression that the number preferential flow paths declines with increasing subscale
421 randomness, while the concentration of solutes therein increases. The analysis of flow path
422 entropy within the entire set of 100 realizations revealed that this behavior is not an artefact of
423 single realization. The flow path entropy average across all realization of a variance case
424 exhibits a steady downstream decline (Fig. 3 a), and the curves are clearly shifted to lower
425 values with increasing variance of $\ln(K)$. The boxplots in Fig. 3b characterize the distribution
426 of $S_H(x)$ at the downstream outlet among the realizations. While the spreading and the skewness
427 of the distribution clearly increases with increasing variance in $\ln(K)$, we also observe that flow
428 path entropy at the outlet declines clearly and statistically significantly with increasing variance.



429
 430 Figure 2: Accumulated, normalized number of particles that passed a distinct point in the
 431 domain as function of the variance in $\ln(K)$, σ^2 , ((a), (b), (c)) and the corresponding Shannon
 432 entropy of the transversal concentration, S_H , as a function of the main flow direction ((d), (e),
 433 (f)).



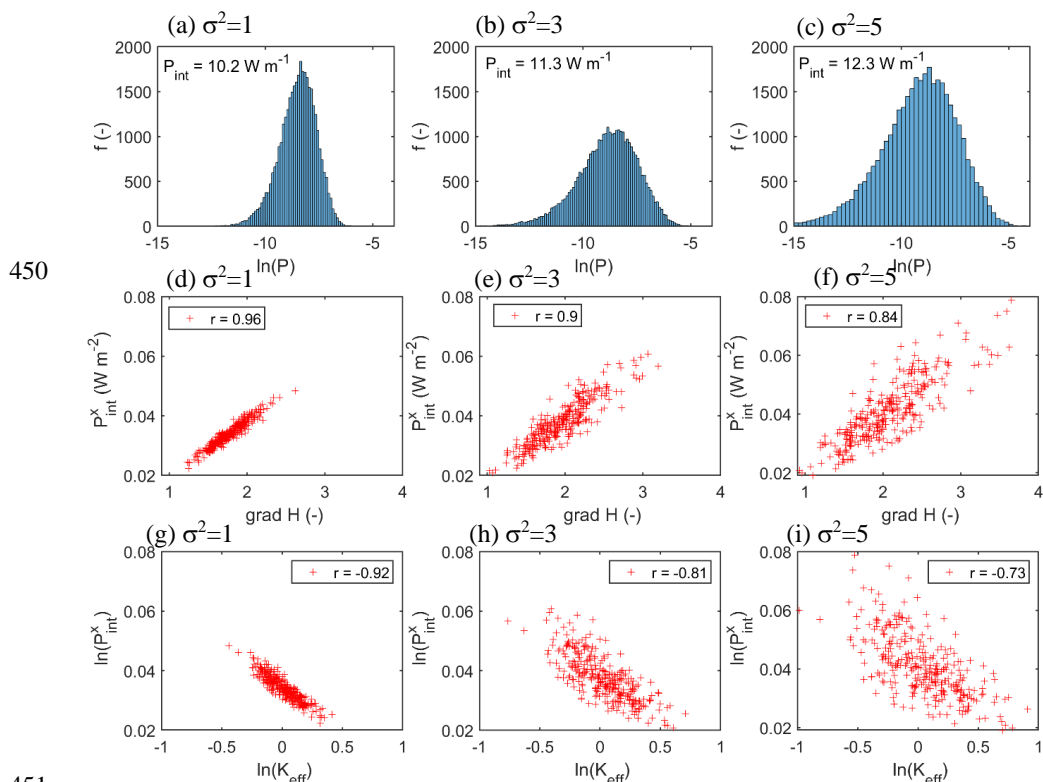
434
 435 Figure 3: Flow path entropy averaged across all 100 ensemble realizations $\langle S_H \rangle$ as function of
 436 downstream transport distance (a). Boxplot of flow path flow path entropy at the domain outlet
 437 for all realizations of the three variance cases (b); note this corresponds to the asymptotic values
 438 in (a) at $x(-) = 60$.



439 We thus state that a higher variance – and thus randomness – in hydraulic conductivity
 440 coincides, for all realizations, with stronger a downstream reduction of the flow path entropy.
 441 This corresponds to a macrostate of higher order due to a more efficient self-organization into
 442 a state of stronger preferential transport.

443 **4.2 Power in fluid flow as function of the variance in $\ln(K)$**

444 Figures 4a-c compare the distribution of power in the fluid flow calculated according to Eq. 7,
 445 as a function of the variance of $\ln(K)$ in the different domains, using a logarithmic scale. For
 446 consistency, we used the same ensemble as for Fig. 2. The distributions of power in the fluid
 447 generally spread across a wide range of magnitudes and are skewed to the left. However, the
 448 distributions clearly shift to larger values and their spread becomes wider when moving to larger
 449 variances.



451 Figure 4: Histogram of $\ln(P)$ as function of the variance σ^2 ((a), (b) (c)), integral power P_{int}^x in
 452 the total downstream water flux, plotted against the laterally averaged head gradient ((d), (e),
 453 (f)), and $\ln(P_{int}^x)$ as function of the \ln of transversally averaged $\ln(K_{eff})$ ((g),(j), (h)).



455 This is underpinned when comparing the integrated power in fluid flow across the entire two-
456 dimensional domain. An increase in variance by two orders of magnitude in the log-normal
457 scale corresponds to an increase in power of 2 W per unit width of the domain. To further
458 illuminate whether the above postulate of a strong linear relation between power and variation
459 in the head gradient exists, we integrated power in fluid flow across the transversal extent of
460 the domain (P_{int}^x hereafter) and plotted it against the laterally averaged head gradient (Fig. 3d-
461 f). In the case of unit variance, this indeed yields a strongly linear relation, with an almost
462 perfectly linear growth of P_{int}^x with the head gradient, as indicated by the correlation coefficient
463 of 0.96. While this the correlation becomes weaker with increasing variance, it remains
464 significant with a correlation coefficient of 0.84 even for the case of $\sigma^2 = 5$. The decline in
465 correlation is plausible as a higher variability in K , in two-dimensional domains, causes stronger
466 transversal flow components and thus a larger deviation from the one-dimensional
467 heterogeneous case for which Eqs. 9 -12 are valid. As expected, the head gradients show also a
468 wider spread with increasing variance (Figs. 3d-f); the same holds true for power in the total
469 downstream fluid flow.

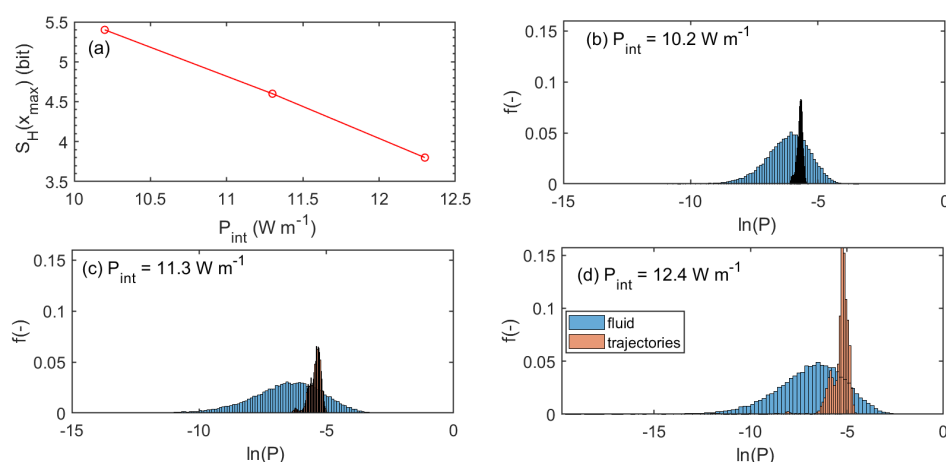
470 To check the inverse-linear relationship between $\ln(P)$ and $\ln(K)$, which was derived for the
471 one-dimensional approximation as well (recall Eqs. 11 - 13), we related $\ln(P_{int}^x)$ to the logarithm
472 of laterally averaged conductivity $\ln(K_{eff})$ (Figs. 3g-i). For the unit variance case, we observe
473 an almost perfect linear increase of $\ln(P_{int}^x)$ with a decline in $\ln(K_{eff})$, as underpinned by the
474 correlation coefficient of -0.92. This negative correlation declined with increasing variance to
475 a value of -0.81 and -0.72 for $\sigma^2 = 3$ and $\sigma^2 = 5$, respectively. Yet it is still significant, hence the
476 system behaves also in case of the highest variance largely similar to a heterogeneous one-
477 dimensional system. This is because of the confining upper and lower no-flow boundary
478 condition.

479 We thus argue that the power required to maintain the driving head difference and fluid flow in
480 steady state increases with increasing variance of the hydraulic conductivity field. Regions of
481 high power coincide with large positive deviations of the hydraulic head from its mean, and
482 also with “bottlenecks” of low hydraulic conductivity along the preferential pathways.



483 4.3 Entropy as a function of power and power along solute transport trajectories

484 Figure 5a shows the Shannon entropy at the downstream outlet $S_H(x_{max})$ as a function of the
485 power in fluid flow integrated over the entire domain P_{int} for all variance cases. The almost
486 perfect linear decline of $S_H(x_{max})$ with P_{int} reveals, in line with the gas laser example given in
487 the introduction, that a larger power input due to a higher pumping rate leads to a higher order
488 in the macroscale preferential transport pattern. We return to this point in section 5.3.



489 Figure 5: (a) Shannon entropy at the downstream outlet $S_H(x_{max})$ as function of the power in
490 fluid flow integrated over the entire domain P_{int} (a), cumulative distributions of $\ln(P)$ in the flow
491 domain (blue) and of $\ln(P)$ averaged along the particle trajectories (brown) for the variance
492 cases (b) $\sigma^2 = 1$, (c) $\sigma^2 = 3$, and (d) $\sigma^2 = 5$.
493

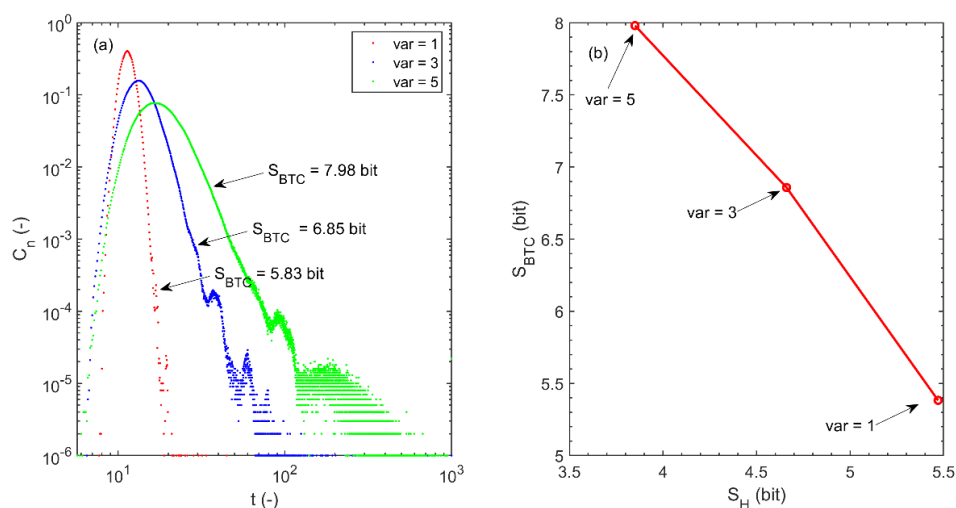
494 Figures 5b, c, d compare the probability density distributions (pdfs) of $\ln(P)$ within the entire
495 flow domain (blue), against the power averaged along the actual particle trajectories (in brown,
496 again on a log scale). While in the case of perfectly mixed flow and transport, both pdfs should
497 be rather similar, they actually are remarkably different. The particles clearly prefer pathways
498 of high power, as the pdfs are clearly shifted towards higher power (Fig. 5 d).

499 4.4 Space-time asymmetry and entropy export into the breakthrough

500 To switch the observing perspective, we determined the particle breakthrough curves (BTC) for
501 the different variance cases (Fig. 6a) and calculated their Shannon entropy as means of
502 uncertainty and order in the arrival times, using the time step width of 0.1 dimensionless time
503 units as bin width. The width of the breakthrough curves clearly increases with increasing



504 variance, indicating an earlier breakthrough, a longer tailing and a more even distribution of
 505 normalized concentrations in time (Fig. 6 a). This implies that the Shannon entropy in arrival
 506 times grows with increasing variance of $\ln(K)$ reflecting a larger uncertainty and a declining
 507 order in the temporal distribution of travel times. In this context, it is important to recall that
 508 entropy cannot be consumed, due to the second law. This that means that the declining flow
 509 path entropy needs to be exported from the system.



510

511 Figure 6: Breakthrough curves and their Shannon entropies S_{BTC} (a); S_{BTC} plotted against the
 512 flow path entropy of the downstream outlet $S_H(x_{max})$, before particles leave the domain, for all
 513 variance cases (b).

514 Figure 6b) visualizes this space-time asymmetry in entropies, the growing spatial organization
 515 with increasing variance of $\ln(K)$ translates due to the associated entropy export into a declining
 516 organization in arrival times. Please note that due to the different binning in space and time,
 517 changes in S_{BTC} and S_H with changing variance cannot be exactly the same. In fact, also the
 518 entropy, which is produced due to energy dissipation, must be exported, but this is much more
 519 difficult to quantify. The opposite of the Shannon entropy monotonies corroborate nevertheless
 520 that reduced flow path entropy is indeed exported into the BTC. One might hence wonder
 521 whether a perfect spatial organization due to preferential transport of the entire solute particles
 522 through a single preferential flow path would, in the case of a step input, translate into a BTC



523 of maximum entropy/disorder, i.e. rectangular BTC (and vice versa). We return to this issue in
524 sections 5.1 and 6.

525 **5 Discussion**

526 **5.1 An energy and entropy centered framework to characterize and explain preferential** 527 **flow**

528 This study proposes an alternative framework to quantify and explain the enigmatic emergence
529 of preferential flow and transport in heterogeneous saturated porous media, using concepts from
530 thermodynamics and information theory. We examined simulations of two-dimensional fluid
531 flow and solute transport based on the methods of Edery et al. (2014), and characterized the
532 discrete probability distribution associated with finding solute particles crossing a distinct
533 transversal position in a plane normal to the direction of the mean flow by means of the Shannon
534 entropy. In general, we found a declining entropy with increasing downstream transport
535 distance, reflecting a growing downstream self-organization due to the increasing concentration
536 of particles in preferential flow paths. Strikingly, preferential flow patterns with lower entropies
537 emerged when analyzing simulations in media with larger variances in hydraulic conductivity.
538 This implies that macro-states of higher order established, despite the higher subscale
539 randomness of $\ln(K)$. The key to explain this almost paradoxical behavior is the finding that
540 the required power to maintain the driving head difference, in steady-state flow, grows with the
541 variance of the hydraulic conductivity field. Due to this larger energy input, the fluid and solutes
542 may perform more work to increase the order in the flow path distribution, through steepening
543 transversal concentration gradients as reflected in lower entropies.

544 Notwithstanding these findings, we of course recognize that the concepts of entropy, free
545 energy and work are, per se, not new in hydrology. We thus place our findings in context
546 relative to related studies, in the sections below.

547 **5.2 Measuring irreversibility and macroscale organization using the Shannon entropy**

548 Here we show that the Shannon entropy of the transversal distribution of solutes is suited to
549 quantify the downstream emergence of preferential solute movement, as reflected in a declining
550 “flow path entropy”. Lower flow path entropies and thus a stronger spatial order in preferential
551 transport are established when solutes are transported through stronger heterogeneous hydraulic



552 conductivity fields. In this context, we recall that Edery et al. (2014) analyzed breakthrough
553 curves using the continuous time domain random walk framework (Berkowitz et al., 2006).
554 When fitting an inverse power law to the breakthrough curves, the corresponding β parameter
555 (which is a measure of the degree of anomalous transport, with β increasing to 2 indicating
556 Fickian transport) increased with increasing variance of $\ln(K)$. Here we analyzed the Shannon
557 entropy of the breakthrough curves in time, and contrary to the flow path entropies, they grow
558 with increasing variance of $\ln(K)$. This means that higher degrees in spatial order in solute
559 transport that emerges at larger variances in $\ln(K)$, expressed by lower flow path entropies,
560 translate into a higher entropy and thus a higher disorder and thus uncertainty in arrival times.
561 This is reflected by an earlier first breakthrough, a retarded appearance of the peak
562 concentration, and a longer tailing in the breakthrough curves and higher similarity of the BTC
563 to a uniform, rectangular pulse. This finding coincides well with the illustrative case that
564 Bianchi and Pedretti (2017) used to compare solute breakthrough through ordered and
565 disordered alluvial aquifers.

566 This space-time asymmetry in entropy and organization can, however, only be explained using
567 the physical perspective of entropy and the second law. The emergence of spatially organized
568 preferential transport and the related decline in flow path entropy essentially requires an export
569 of the entropy from the system into the BTC. We thus conclude that the β parameter of the
570 CTRW framework, is also two-fold measure for spatial organization of solute transport through
571 the system and temporal organization in arrival times and their asymmetry.

572 **5.3 Preferred flow and transport pathways as maximum power structures?**

573 The idea that preferential flow coincides with a larger power in fluid flow has been discussed
574 widely in hydrology. Howard (1971, cited in Howard, 1990) proposed that angles of river
575 junctions are arranged in such way that they minimize stream power; later he postulated that
576 the topology of river networks reflects an energetic optimum, formulated as a minimum in total
577 energy dissipation in the network (Howard, 1990). This work inspired Rinaldo et al. (1996) to
578 propose the concept of minimum energy expenditure as an enslavement principle for the self-
579 organized development of river networks. Hergarten et al. (2014) transferred this concept to
580 groundwater systems. They derived preferential flow paths that minimize the total energy
581 dissipation at a given recharge, under the constraint of a given total porosity and showed that
582 these setups allowed predictions of spring discharge at several locations. Minimum energy



583 expenditure in the river network implies that power therein is maximized. In this light, Kleidon
584 et al. (2013) showed that directed structural growth in the topology of connected river networks
585 can be explained through a maximization of kinetic energy transfer to transported suspended
586 sediments.

587 Our findings are in line with but step beyond these studies, which commonly refer to
588 preferential flow in connected, highly conductive networks. Here we find that solute particles
589 prefer to move through pathways of very high power, even when they are not connected by a
590 continuous set of cells of relatively high hydraulic conductivity. On the contrary, these
591 pathways incorporate regions of low hydraulic conductivity. This finding reflects the squared
592 dependence of power on the spatial head gradient, which in turn becomes largest in regions of
593 low hydraulic conductivity. We stress that this result, and our finding that a larger power input
594 (due to a higher pumping rate) leads to a higher order in the macroscale preferential transport
595 pattern, is a consequence of the imposed boundary condition. A steady-state head difference
596 implies a positive energetic feedback: in a real-world experiment, the pump provides this
597 feedback, as otherwise the gradient is depleted by the flowing fluid. Although such a positive
598 feedback is straightforwardly established in a numerical model by assigning the desired
599 constant head difference, it is important that this choice implies that such a positive feedback
600 exists. Due to this virtual energy input, the fluid and solutes may perform the necessary work
601 to rapidly pass through low conductivity bottlenecks and form an ordered preferential flow
602 pattern at the macroscale. The higher necessary pumping rate and energy input into the domains
603 with a larger variance in K explain, furthermore, why preferential flow patterns of higher order
604 emerge with growing subscale randomness.

605 **6 Conclusions and outlook**

606 Based on the presented findings, we conclude that the combined use of free energy and entropy
607 holds the key to characterize and quantify the self-organized emergence of preferential flow
608 phenomena and to explain the underlying cause of their emergence. Information entropy is an
609 excellent, straightforward concept to diagnose self-organization in space and time: Here, the
610 formation of preferential transport is reflected in the downstream decline in the entropy of the
611 transversal flow path distribution and that this decline becomes stronger with increasing
612 variance of hydraulic conductivity. The concepts of free energy and physical entropy, however,



613 provide the underlying cause: steepening of transversal concentration gradients requires work,
614 the formation of even steeper gradients and lower flow path entropies needs even more work
615 and thus a higher free energy input into the open system. The higher necessary pumping rate
616 and energy input into the domains is the reason, why spatial organization in preferential solute
617 movement increased with growing subscale randomness of hydraulic conductivity. This is
618 behavior is very much in line with what we discussed for the gas laser in the introduction.

619 Entropy can, however, due to the second law not be consumed, and the declining flow path
620 entropy is in fact be exported from the system into the breakthrough curve. Shannon entropy
621 allows again for the straightforward diagnosis, while physical entropy provides the reason for
622 this space-time asymmetry in entropy, organization and uncertainty. Transport of all solute
623 particles through a single preferential flow paths implied a maximum spatial organization and
624 maximum/knowledge certainty about the transversal spreading of solute. However, this would,
625 due to the entropy export, into a maximum disorder of and thus uncertainty about the arrival
626 times, as the BTC would correspond to rectangular pulse of uniform concentration. Advective
627 diffusive transport through a homogeneous flow field implied, in case of a spatially
628 homogeneous step input, maximum uncertainty about transversal position of solute molecules,
629 while the BTC would be perfectly certain and providing minimum uncertainty about arrival
630 times. This space-time asymmetry in entropy implies that perfect organization and certainty
631 about both flow paths and travel times can never simultaneously occur. This required
632 consummation of entropy and thus violation of the second law of thermodynamics. However,
633 we wonder whether effective predictions of the entropies in the BTC and the flow path
634 distributions based on the knowledge driving head differences and the variance and correlation
635 lengths of hydraulic conductivity might be achievable in the future. This will of course not tell
636 us where solutes move and when they breakthrough, but predict the related uncertainty as an
637 important constraint of transversal distribution of transport pathways and travel times.

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