

Dear Editor and Associate Editor,

thank you for your constructive comments and suggestions. Please find below the detailed responses to the reviewers comments and suggestions. The manuscript was revised accordingly. In my opinion, adding the numerical results will overwhelm the reader and distract from the central message of the manuscript, which I consider a useful contribution to the field of *theoretical hydrology*. The proposed framework provides a thermodynamic perspective of inference of macroscale variables and already a new set of equations for simple problems of variably saturated flow. Follow-up studies will reveal, whether the proposed framework is also applicable in conjunction with in-situ and remotely sensed observations.

I do understand that the manuscript, in its current form, may not be considered a full research paper. Therefore, I suggest handling the manuscript as a technical note, which I indicated in the modified title "Technical note: Inference in hydrology from entropy balance considerations".

Thank you for your consideration.

Sincerely,

Stefan Kollet

## Response to the Reviewers

Thank you again for our comments and suggestions, which helped considerably in improving the manuscript. In the following, comments by Referee#1 are indicated with [R#1] in italic and replies by the author are indicated by [K].

### Reviewer 1

*[R#1] This paper has been revised significantly (like a new paper). To me, this paper proposes entropy balance to link macroscale entropy current and microscale entropy production. My understanding is that the macroscale entropy current is the net entropy across the boundary of a control volume; and the microscale entropy production is the total entropy production within the control volume.*

[K] The entropy balance states that the increase/decrease of entropy of an open system with time equals the internal entropy production (always positive) inside minus the divergence of the entropy current i.e. the exchange with the outside.

*[R#1] The utility of the entropy balance method is not clear to me. Does this method can help us build a model, estimate parameters or quantify fluxes? The author argued that the advantage of the entropy balance method is that the macroscale variables (e.g., conductance coefficient) can be estimated by computing the internal entropy production when the macroscale chemical potential is unknown. In order to compute the internal entropy production, the spatial domain needs to be discretized and Darcy's law is applied. That requires a lot of efforts. Then what's the purpose to estimate the macroscale conductance coefficient? What's the relationship between the microscale conductance coefficient and macroscale coefficient? For example, if the hydraulic conductivity in the cross-section of example 1 is homogeneous, does the macroscale conductance coefficient equal to the microscale ones?*

[K] The paragraph below was added to the conclusions sections in order to clarify the utility of the proposed approach. If the hydraulic cross section of example 1 is homogeneous, then the macroscale conductance equals the microscale ones.

Added to the conclusion section: "The study is a contribution to the field of theoretical hydrology and proposes an inference approach of effective, macroscopic exchange coefficients, and thermodynamics forces and potentials. The approach is founded on the two-scale nature of the entropy balance unifying the micro- and macroscale. In this study, Darcy's law served as the movement equation at the microscale, which may be replaced by models of e.g. multi-phase, multi-component fluid flow and reactive transport (in this case, the entropy balance equation contains additional terms). At the macroscale, the linear conductance equation served as the movement equation, which may be replaced by more complex, non-linear equations. While inference of macroscale variables necessitates explicit calculation of the entropy production and thus considerable computational resources, these resources are well-invested. Obtaining previously unknown macroscale parameters is at the center of the ubiquitous challenge of upscaling and applying the proposed framework may help in finding general upscaling relationships over a hierarchy of scales."

Reviewer 2

[R#2] *Although this is officially a revised manuscript, the content is so different from the initial one that I will review it as being a first submission.*

*In this paper the author shows how the entropy balance can be used for inference of macroscopic fluxes and forces by knowing the microscopic fluxes and forces. This has been illustrated by a couple of examples of increased complexity for groundwater flow of which the boundary conditions are known. This is an interesting approach, but I do have some doubts about the usefulness of the method, which have to be clarified before publication:*

*The main approach of the author is basically that in steady state, the internal entropy production  $\sigma$  equals the entropy current. Here is  $\sigma = \sum qf$  and the entropy current is given as  $JM$  where  $q$  and  $f$  are the microscopic flux and force and  $J$  and  $M$  the macroscopic flux and force. In the whole analysis, the author assumes that  $q$  and  $f$  are known (and/or retrieved) for each 'grid cell' by running a detailed groundwater model. This may be true for homogenous lab setups, but in the field this is not true at all. First of all, there are only limited measurements of the soils permeability, while macroscopic structures such as macropores or other preferential flow paths are not included in the permeability measurements. I would even argue that in practice, the macroscopic force and macroscopic flux are measured, which can subsequently be used to infer the microscopic parameters (which is done by calibrating a model). Since this is generally an ill-posed problem, I do not immediately see how the method described in this manuscript is useful.*

[K] I would like to thank the Reviewer for his constructive comments and suggestions, which helped considerably improving the manuscript. The original manuscript underwent a complete rewrite with the focus on the theory resulting in a technical note highlighting a new approach in theoretical hydrology. The approach is a contribution to theoretical hydrology and provides a thermodynamic point of view of matter (water) flow from the micro- to the macroscale. The equations cast the problem of variably saturated groundwater flow in terms of the entropy balance (equivalent to the internal energy balance, because temperature is constant in the derivations), demonstrating how macroscopic variables may be assembled via integration/summation of the internal entropy production (dissipation) over volumes or hierarchy of scales. This is true for all kinds of setups, which can be modeled explicitly at the microscale in order to interrogate scaling behavior of the entropy production and macroscale variables and different macroscale movement equations. As such I consider this a contribution that is interesting and useful to a wide range of hydrologist. The applicability to measurements needs to be shown in future applications, however with the advent of high-resolution (soil moisture) sensing networks, there may be potential for applications of the theory in the field beyond calibration of a macroscopic model.

[R#2] For the following, I assume – just as the author – that  $q$  and  $f$  are known everywhere in the model domain. I remain with mainly some suggestions to clarify the manuscript a bit more:

1) I fully agree with the statement in line 303-308. However, I suggest to move this part to the end of example 1 (personally, I was a bit annoyed after reading example 1 (and before I read the statement in line 303-308) because  $\lambda$  could be obtained in a much easier way here).

[K] Example 1 is not meant to annoy the reader but to illustrate how the well-known problem of variably saturated flow may be cast in thermodynamic terms at two different scales. While discussions of the

results should be part of the discussion section, a short explanation is now provided with the derivations of example 1 following the suggestion of Reviewer 2.

[R#3] 2) *It may be helpful for the reader to add next to each example (figure) another one to show the macroscopic model concept.*

[K] I generated figures for the different examples and found that they may suggest only a single macroscopic model, while each domain may be subdivided into different numbers of subdomains resulting in a hierarchy of scales. Therefore I decided not to include the figures.

[R#3] *Due to the many different parameters, the formulas are sometimes difficult to follow.*

- *I suggest to repeat the meaning of the parameters every now and then*

- *Is it possible to skip a couple of parameters? E.g. instead of using  $S_i$ , always use  $\int \sigma$  or  $\int \Sigma qf$ ?*

- *use  $1/x$  instead of  $x^{-1}$ ?*

- *is the macroscopic mass change rate  $\Theta'$  the change of mass over time? And what does  $\Theta$  represent in Eq. 36a?*

[K] Parameters meanings are now repeated more often. The full expression of  $S_i$  is repeated on purpose to remind the reader that the calculation of the microscopic flux-force relationships is required. I would like to leave use of  $1/x$  instead of  $x^{-1}$  to the type setting experts.  $\Theta'$  is the mass change rate.  $\Theta$  was corrected to  $\Theta'$  in equation 36a.

[R#3] *Line 279: "S' and can be": a symbol is missing.*

[K] corrected.

[R#3] *Line 59-61: I wouldn't say it is interestingly that those studies calculated the entropy exchange with the outside instead of calculating the internal entropy production. They rather used a different approach to obtain an effective macroscopic conductance, namely, assuming that entropy production is maximum.*

[K] Those studies did not calculate the internal entropy production explicitly but used the entropy exchange with the outside in their approach. Therefore the statement is correct and the sentence was not changed.

Reviewer 4, Stan Schymanski

[R#3] *This revised manuscript does not have much in common with the original manuscript, offering substantial additional thoughts and theory, but also missing substantial points of the previous manuscript, as described below. Again, the paper is very thought-provoking and I hope that my comments will help to improve its utility and appeal for the scientific community. The new manuscript provides a detailed theory for the calculation of thermodynamic forces and fluxes in different hydrological settings and points to potential for deducing macroscopic "effective" hydraulic conductances from microscopic simulations. The approach is very promising and may open the way to a range of new insights. Unfortunately, the author has removed any numerical simulations from the manuscript, so the new version remains entirely theoretical and hypothetical. I do not know if this was done willingly or if a*

*section of the manuscript went missing, but I feel that some meaningful numerical analysis would be very beneficial for the manuscript and the readers, as it could be used to test some very fundamental and often implicit assumptions in physically based hydrological models. Without such analysis, I am afraid that further use of the paper would rely too much on a leap of faith that the approach is actually useful. I also found a few other shortcomings that should be considered or at least discussed.*

[K] I would like to thank the reviewer for the constructive comments and the kind words. The original manuscript underwent a complete rewrite with the focus on the theory resulting in a technical note highlighting a new approach in theoretical hydrology. As such no applications are provided. In order to judge whether the approach is useful and in which aspects of hydrology, a large variety of studies need to be performed ranging from numerical experiments to field studies utilizing sensor networks. This is beyond the scope of this manuscript. However, the usefulness of the theory is not hypothetical, because from the derivations new insights were already obtained and discussed in the manuscript. I suggested to the Editor to change the manuscript from a full research paper to a technical note, which is also reflected in the new title.

[R#3] *The manuscript derives equations for the calculation of entropy production by water fluxes for a range of different idealised hillslope or catchment geometries and proposes to use these equations in order to deduce macroscopic conductances from microscopic analysis in a way that would result in consistent entropy balance across scales. However, no test of the utility or even justification of the approach has been presented. For example, the different idealised configurations could be used to answer two questions:*

- 1. Are the deduced macroscopic properties robust under different soil moisture distributions or forcing? For example, such an analysis might reveal that the macroscopic conductance depends on heterogeneity in moisture, which would invalidate the approach. A numerical analysis along these lines could give valuable insights into general laws in using effective macro-scale parameters in conjunction with equations derived for the micro-scale, e.g. Richards equation.*
- 2. Does the tracking of entropy production and exchange across scales reveal inconsistencies in common physically based hydrological formulations? Analysis of a model similar to that used in the previous version of the manuscript could reveal that entropy production and exchange at the large (macroscopic) scale does not match the sum of entropy production in all sub-domains, pointing to omissions in the original model or in the formulations used in the present manuscript.*

[K] It is correct that no numerical experiment has been provided in the revised manuscript, yet the utility of the theory is justified in the manuscript by a rigorous derivation and discussion, which was revised additionally in this revision.

In the response to 1), the derivations show how the effective conductances depend on the variance and covariance of the forcing. Thus, they are not necessarily constant but there may be some universal scaling that can be extracted with the proposed theory. Also the dependence on heterogeneity does not mean directly that the approach is invalid; it will be interesting to explore how entropy production behaves in a hierarchy of scales for different types of heterogeneity i.e. the approach again provides new avenues of research, which are beyond the scope of this manuscript.

In the response to 2), if the entropy balance is violated in the simulations then the mass balance, and entropy/energy balance must be incorrect. This may be the case due to numerical issues etc. However, if

all processes are accounted for, the entropy/energy balance must close. In the presented case, only the equations of transport of matter need to be considered, because the generation/transport of heat is not considered.

[R#3] *I also noticed that the revised paper does not mention evaporation at all. This would have a large effect on both the mass and entropy balance of the system, and cannot be neglected under any relevant natural conditions I can think of. Therefore, I believe that root water uptake and evapotranspiration should be included in the analysis or at least the author should provide discussion of how it could be included or why and under what conditions it can be left out. In the specific comments below, I included thoughts that I had while reading the paper, some of which reflect the above comments and others relate to technical corrections or unclear formulations.*

[K] Evaporation and transpiration were implicitly mentioned in the periodic source/sink in example 3, where the sink is evapotranspiration. This was clarified in the revision.

[R#3] 1. L13: *"explicit calculation"*

[K] corrected

[R#3] 2. L44: *"demonstrating how" (remove comma)*

[K] corrected

[R#3] 3. L45: *This sentence is unclear. Do you mean how the exchange coefficient can be optimised to maximise entropy production?*

[K] The sentence was revised.

[R#3] 4. L63: *"a simple microscale Klausmeier model" sounds odd. "A simple distributed model of the water and carbon balance"?*

[K] Revised following the reviewers comments

[R#3] 5. L62{65: *This sentence is convoluted. Please consider splitting it in two.*

[K] Sentence was revised.

[R#3] 6. L68: *may be*

[K] corrected

[R#3] 7. L84: *The "entropy current per unit volume" should have the same dimensions as change in entropy density, but here they are given as  $[M T^{-3} K^{-1}]$ , so I assume it is simply missing a  $L^{-1}$ . Also, consider using  $\theta$  for temperature instead of  $K$ , as  $K$  is an actual unit, not a dimension.*

[K] The missing  $L^{-1}$  is contained in the nabla operator. I choose  $T$  as a symbol for temperature  $\theta$  for the macroscopic soil water content.

[R#3] 8. L89: *I would refer to Eq. 5 for the definition of chemical potential and maybe mention here that it is equivalent to the sum of matrix and gravitational potentials, to make it more intuitive to hydrologists.*

[K] Followed Reviewer's recommendation.

[R#3] 9. L90: *The switch from macroscale to microscale here should be emphasized clearer, perhaps by an additional sub-heading? Also, it would be good to clarify that  $f$  is not a mechanical force (which would have dimensions of  $M L T^{-2}$ ), but a thermodynamic force, having units of chemical potential, which is defined using units of energy per mass here.*

[K] The sentence was revised and the forces were termed thermodynamic forces to distinguish clearly from mechanical forces.

[R#3] 10. L98: *"true steady state" is a bit unclear. Why not: "...at steady state (assuming  $s_0 = 0$ )..."*

[K] "true" was removed

[R#3] 11. L110: *Thermodynamic force*

[K] revised

[R#3] 12. L133: *It would be good to point out that a good consistency test would be whether the sum of the sub-domains equals the entropy balance of the whole domain.*

[K] This was not done here, because from the derivation follows that the entropy balance must hold at all scales.

[R#3] 13. L140: *Eq. 7 seems to be the wrong equation to get macroscopic fluxes from.*

[K] corrected

[R#3] 14. L161: *What is meant by "true" effective conductance?*

[K] True in the sense of thermodynamic consistent; was removed.

[R#3] 15. L238: *Why  $Q_s = 0$ ? This made me realise that there is no evaporation mentioned in the paper. How would that affect the energy and entropy balances?*

[K]  $Q_s = 0$  because the example deals with a periodic source/sink (infiltration/evaporation) which holds at dynamic equilibrium. This was clarified in the text.

[R#3] 16. L242: *It would be good to provide intermediate steps to allow the reader to follow the derivation of Eq. 35b.*

[K] I am not providing intermediate steps because the equation is based on the well-known definition of the covariance.

[R#3] 17. L253-257: *What is the benefit of calculating the macroscopic  $S'$  using microscale variables?*

[K] With  $S'$  in hand one can calculate the effective macroscopic potential, force and conductance. A short explanation was added to the manuscript.

[R#3] 18. L279: *Either the "and" is redundant or something is missing.*

[K] revised

[R#3] 19. L300-302: *Does the macroscopic conductance depend on heterogeneity in moisture, i.e. in the Richards Equation case? This would possibly invalidate the approach.*

[K] It probably depends on the moisture heterogeneity, though I don't see why this possibly invalidates the approach. First a potential dependence needs to be explored also considering different types of (non-linear) macroscopic movement equations instead of the simple linear conductance equation.

[R#3] 20. L325-326: *This would have been a great thing to do as part of this paper.*

[K] This is extremely involved and beyond the scope of the current manuscript.

[R#3] 21. L344: *Should be  $\overline{J^2}$  instead of  $\overline{J}$*

[K] corrected

[R#3] 22. L357-359: *This is misleading, as 'thus' implies that all macroscopic variables that are functions of entropy production are 'thermodynamically consistent'. I think the point is that the macroscopic variables derived in this way promise a thermodynamically consistent link between different scales. However, it would be good to discuss what this actually means. Would we obtain different macroscopic properties for different forcing, even if the microscopic parameters were the same? Would we obtain different values for different scales? Is this approach only useful if we are able to obtain reliable microscopic parameterisations?*

[K] The sentence was revised following the Reviewer's suggestion. The Reviewer posed a number of valid questions; answering these questions will require a significant number of additional studies utilizing high-resolution numerical experiments to explicitly resolve the internal entropy production and performing the required analysis.



1 | [Technical note](#): Inference in hydrology from entropy balance considerations

2

3 | Stefan J. Kollet

4

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7

8 | Correspondence to: S. Kollet (s.kollet@fz-juelich.de)

9

10 | **Abstract**

11 | In this study, the method of inference of macroscale [thermodynamic](#) potentials, forces and exchange  
12 | coefficients for variably saturated [groundwater](#) flow is outlined based on the entropy balance. The  
13 | theoretical basis of the method of inference is the explicitly calculation of the internal entropy  
14 | production from microscale, [thermodynamic](#) flux-force relationships using e.g. hyper-resolution variably  
15 | saturated groundwater flow models. Emphasis is placed on the two-scale nature of the entropy balance  
16 | equation that allows incorporating simultaneously movement equations at the micro- and macroscale.

17 | The method is ~~demonstrated~~ [illustrated](#) with simple hydrologic cross-sections at steady state and [cyclic](#)  
18 | [periodic](#) sources/sinks at dynamic equilibrium, and provides a thermodynamic point of view of upscaling  
19 | in variably saturated groundwater flow. The current limitations in the connection with observable  
20 | variables and predictive capabilities are discussed, and some perspectives for future research are  
21 | provided.

22

23

## 24 Introduction

25 The current earth sciences literature ~~indicates~~~~suggests~~ that entropy balance considerations ~~were~~~~have~~  
26 ~~been~~ mainly applied in the context of optimality and self-organization. ~~This is because t~~Theories of  
27 optimality and self-organization are appealing when dealing with complex non-linear systems, because  
28 of their apparent usefulness in interpreting interactions of gradients and fluxes and in quantifying  
29 (predicting) systems' states and uncertainties. In this context, the entropy ~~and energy~~ balance received  
30 attention, because of its physics-based foundation in non-equilibrium thermodynamics and potential  
31 connection with information theory (e.g., Dewar 2003, Koutsoyiannis 2014). The entropy balance  
32 appears to be useful in applications to hydrologic (e.g., Zehe et al. 2013, Ehret et al. 2014), ecohydrologic  
33 (e.g., Dewar 2010, Miedziejko and Kedziora 2014, del Jesus et al. 2012), and atmospheric sciences (e.g.,  
34 Paillard and Herbert 2013), and in general to open complex nonlinear thermodynamic systems (Abe and  
35 Okuyama 2011).

36 The entropy balance states that in an open system, the change in entropy equals the internal production  
37 of entropy minus the divergence of the entropy current. A dynamic equilibrium or steady state is  
38 obtained, when entropy production inside (due to e.g. flow processes of heat ~~and or matter~~~~water~~)  
39 equals the divergence of the entropy current i.e. the entropy exchange with the outside. Note also,  
40 dynamic equilibrium refers to a state of stationarity in the statistical sense. Optimality of the dynamic  
41 equilibrium may be achieved, because the gradient, which drives the flux and, thus the production of  
42 entropy, is reciprocally depleted by the same flux (Kleidon et al. 2013).

43 In hydrology, the entropy balance has been applied to conceptual problems based on the overarching  
44 rationale that entropy production is maximized (maximum entropy production, MEP) in obtaining a state  
45 of dynamic equilibrium by optimizing the fluxes and gradients in competition via an adjustment of some  
46 (non-)linear exchange coefficient. There have been some studies demonstrating, how entropy  
47 production can be ~~maximized by~~-optimiz~~ing as a function of~~ an exchange coefficient to obtain an an

48 | ~~optimal~~ system's state ~~at which entropy production is indeed at its maximum~~. In hydrology, there are  
49 | quite a few examples of the application and discussion of the MEP principle (e.g., Ehret et al. 2014,  
50 | Westhoff et al. 2014, Kleidon and Schymanski 2008) also in connection with data (e.g., Zehe et al. 2013).  
51 | However, its validity and applicability to hydrologic systems is still in question (Westhoff and Zehe 2013).

52 |  
53 | Often the entropy balance has been applied at steady state with simple bucket models, which are well-  
54 | mixed (i.e. without internal gradients). For example, Porada et al. (2011) performed a detailed entropy  
55 | production analysis of the land surface hydrologic cycle including the shallow vadose zone assuming  
56 | vertical equilibrium of the soil bucket model. Applying linear bucket models without considering internal  
57 | gradients, Kleidon and Schymanski (2008) showed that if the natural system possesses enough degrees  
58 | of freedom, in case of steady state, the system will tend towards a certain exchange coefficient, when  
59 | entropy production is maximized. For similar bucket models, Westhoff et al. (2014) demonstrated the  
60 | impact of periodic boundary forcing on entropy production, which may result in more than one  
61 | maximum for unique values of the exchange coefficient at dynamic equilibrium. Interestingly, these  
62 | studies did not calculate the internal entropy production explicitly; ~~Instead,~~ entropy production was  
63 | estimated indirectly from the exchange with the outside (i.e. the divergence of the entropy current).

64 | ~~In order to optimize effective values of a simple two-box model,~~ Schymanski et al. (2010) recognized the  
65 | potential ~~of~~ explicitly estimating the internal entropy production using a simple ~~distributed model of~~  
66 | ~~the water and carbon balance microscale Klausmeier model~~ (Klausmeier 1999), which is based on  
67 | coupled equations of moisture and biomass and is able to produce vegetation patterns; ~~in order to~~  
68 | ~~optimize effective values of a simple two-box model~~. This study highlights an interesting aspect of  
69 | entropy balance considerations ~~that is related to~~ the inference of upscaled effective parameters and  
70 | state variables to represent subgrid scale variability in coarse scale (macroscale) models. Thus,  
71 | ultimately, the appeal of the entropy balance maybe the inference of upscaled or effective exchange

72 coefficients and forces/gradients, which may be used to quantitatively describe the complex system  
73 without the explicit knowledge about microscopic details (Dewar 2009). In this context, a popular  
74 example is gas diffusion, which can be captured by an inferred, macroscopic diffusion coefficient and  
75 gradient instead of honoring the motion and interactions of individual molecules.

76 In this study, the method of inference of effective hydrologic exchange coefficients, potentials and forces  
77 is outlined using the entropy balance equation in applications to simple hydrologic cross-sections. The  
78 purpose of this study is to direct attention to the potential insights gained from a new branch of  
79 theoretical hydrology combining modern thermodynamic principles with numerical experiments. While  
80 the thermodynamic principles constitute the link between different spatial scales that may be useful in  
81 upscaling hydrologic process across a hierarchy of scales, the numerical experiments constitute the  
82 methodological pillar to obtain explicitly the internal entropy production or dissipation required in the  
83 upscaling, equivalent to *ab initio* simulations in molecular dynamics (Kresse and Hafner 1994). The

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84 following sections provide the basic theory with an emphasis on the two-scale nature of the entropy  
85 balance, and the application to the hydrologic cross-sections with ensuing discussion and conclusions.

86

## 87 **Basic theory and the two-scale nature of the entropy balance**

88 The theory outlined in Kondepudi and Prigogine (2015) is applied to the problem of variably saturated  
89 groundwater flow at constant temperature. Based on conservation of energy (and the balance equation  
90 for concentrations, which is not required in this analysis) Kondepudi and Prigogine (2015) write the  
91 entropy balance as follows

$$92 \quad s' + \nabla \cdot J_s = \sigma \quad (1),$$

93 where  $s'$  ( $\text{ML}^{-1}\text{T}^{-3}\text{K}^{-1}$ ) is the change in the entropy density with time;  $J_s$  ( $\text{MT}^{-3}\text{K}^{-1}$ ) is the entropy current per  
94 unit volume; and  $\sigma$  ( $\text{ML}^{-1}\text{T}^{-3}\text{K}^{-1}$ ) is the internal entropy production per unit volume, which is always

95 positive by definition. Thus, the change of entropy density with time of a macroscopic volume depends  
96 on the divergence of the entropy current and the internal entropy production.

97 In the considered case of variably saturated groundwater flow,  $J_s = JM/T$ , where  $J(\text{ML}^{-2}\text{T}^{-1})$  is the mass  
98 flow per unit area,  $M(\text{L}^2\text{T}^{-2})$  is the chemical potential (i.e. the sum of pressure and gravitational potential,  
99 equation 5) at the macroscale and  $T$  (K) is the temperature. At the microscale, defining  $q(\text{ML}^{-3}\text{T}^{-1})$  and  $f$   
100 ( $\text{L}^2\text{T}^{-2}$ ) as the fluxes and thermodynamics forces at the microscale per unit volume, the divergence of the  
101 entropy current and the internal entropy production can be expanded as follows

$$102 \quad s' + (M/T)(\nabla \cdot J) + J \cdot (\nabla(M/T)) = \sum qf/T \quad (2).$$

103 For the derivations below it is important to recognize that Equation (2) exhibits the unique  
104 characteristics of incorporating two scales: the entropy density change with time and divergence of the  
105 entropy current at the macroscale (all terms on the left hand side), and the entropy production at the  
106 microscale i.e. the sum of all products of the internal microscopic fluxes and forces (term on the right  
107 hand side). Note, in the following, the temperature  $T$ (K) is omitted in the equations and units, because  
108  $T = \text{constant}$  in the following derivations.

109 Performing an entropy balance at true-steady state leads to

$$110 \quad M(\nabla \cdot J) + J \cdot (\nabla M) = \sigma \quad (3)$$

111 because  $s' = 0$ . In contrast, performing an entropy balance under the influence of periodic external  
112 forcing requires integration over one full forcing cycle at dynamic equilibrium of equation 2 indicated by  
113 overbars

$$114 \quad \overline{M(\nabla \cdot J)} + \overline{J \cdot (\nabla M)} = \bar{\sigma} \quad (4).$$

115 with  $\bar{s}' = 0$  over one full cycle. Both approaches will be applied in the following sections, in order to  
116 arrive at effective variables at the macroscale.

117 | ~~In order to further emphasize~~Because of the two-scale nature of equations 1 and 2, movement  
 118 | equations are introduced at the macroscale- and microscale. At the macroscale,  $M$  ( $L^2T^{-2}$ ) is defined as  
 119 | the sum of the macroscopic pressure potential  $\Psi$  ( $L^2T^{-2}$ ), and gravitational potential  $gz$  ( $L^2T^{-2}$ ), leading to

$$120 \quad M = \Psi + gz \quad (5);$$

121 | and is, thus, equivalent to the hydraulic head;  $(\nabla M)$  symbolizes a macroscopic thermodynamic force  $F$   
 122 | ( $L^2T^{-2}$ ) being the difference in the macroscopic chemical potentials

$$123 \quad (\nabla M) = F = M_{high} - M_{low} \quad (6);$$

124 | and, at the moment,  $J$  is defined as a conductance concept

$$125 \quad J = \lambda F \quad (7),$$

126 | where  $\lambda$  ( $ML^{-4}T$ ) is a conductance coefficient ( $\lambda = \rho r_s$ , with water density  $\rho$  ( $ML^{-3}$ ) and resistance  $r_s$  ( $TL^{-1}$ ))  
 127 | relating the flux with the force at the macroscale.

128 | At the microscale, the chemical potential  $\mu$ , ( $L^2T^{-2}$ ), the mass flux  $q$  ( $ML^{-3}T^{-1}$ ) per unit volume and the  
 129 | thermodynamic force  $f$  ( $L^2T^{-2}$ ) are

$$130 \quad \mu = \psi + gz \quad (8),$$

131 | where  $\psi$  ( $L^2T^{-2}$ ) is the microscale pressure potential;

$$132 \quad q = \frac{1}{\alpha} \rho \frac{K}{\nu} k_r(\psi) (\mu_{high} - \mu_{low}) \quad (9),$$

133 | where  $\rho$  ( $ML^{-3}$ ) is the density;  $\nu$  ( $L^2T^{-1}$ ) is the kinematic viscosity;  $K$  is the permeability ( $L^2$ ),  $k_r(\psi)$  (-) is the  
 134 | relative permeability, and  $\alpha$  ( $L^{-2}$ ) is the unit microscopic flow-through area; and the microscale force

$$135 \quad f = (\mu_{high} - \mu_{low}) \quad (10).$$

136 | Technically,  $\sum qf$  is the sum of all fluxes and forces (~~both~~ always positive, because any flux produces  
137 | entropy) between all neighboring cells or elements in a microscale, numerical, variably saturated  
138 | groundwater flow model including ~~any~~ Dirichlet and ~~/or~~ Neumann boundary conditions.  
139 | Thus, the two-scale nature of equation 2 allows to apply different thermodynamic flux-force  
140 | relationships at the different scales that are the conductance concept at the macroscale (equation 7) and  
141 | essentially Darcy's law or Richards equation (equation ~~79~~) at the microscale. In equation 2, the entropy  
142 | production serves as an "automatic" spatial and also temporal integrator of the microscale fluctuations.  
143 | These two characteristics are remarkable. Note, the calculation (integration) of the entropy balance may  
144 | be performed over the global domain of volume  $V$  ( $L^3$ ) or any subdomain  $V_i$  ( $L^3$ ) thereof.

145

#### 146 | **Method of Inference**

147 | The basis of the method of inference is that the internal, microscopic entropy production  $\sigma$  and also the  
148 | complete entropy balance can be calculated from support scale simulations by implementing the  
149 | microscale equations 9 and 10 in combination with a continuity equation over the macroscopic domain.

150 | In obtaining  $\sigma$  explicitly, one is able to estimate effective potentials, forces and conductance coefficients  
151 | of equation 7, at the macroscale (~~equation 7~~) from the explicitly resolved fluctuations at the microscale,  
152 | which are thermodynamically consistent. In order to illustrate the method of inference of macroscale  
153 | potentials, conductances and forces, a number of illustrative examples based on simple hydrologic  
154 | profiles are presented applying different boundary conditions and source/sink terms.

155

156 | *Example 1:*

157 Directed at a heat flow example in Kondepudi and Prigogine (2015), a simple cross-section is considered  
 158 (figure 1) with steady-state, variably saturated groundwater flow,  $J$ , from left to right due to Dirichlet  
 159 boundary conditions on the left  $M_l$  and right  $M_r$ , with  $M_l > M_r$ . Because  $\nabla \cdot J = 0$ , and  $s' = 0$  at steady  
 160 state, integration of the entropy balance over the cross-section leads to

$$161 \quad S'_i = \int_0^{L_z} \int_0^{L_x} \sigma(x, z) dx dz = L_z \int_0^{L_x} J_x (\nabla_x M) dx \quad (11a)$$

$$162 \quad S'_i = L_z J_x (M_l - M_r) = L_z J_x F \quad (11b),$$

163 where  $L_z$  and  $L_x$  (L) are the constant vertical and horizontal extents of the cross-section, respectively;  $S'_i$   
 164 is the total internal entropy production; and  $F = (M_l - M_r)$  is the macroscopic force. Note, in the  
 165 following, the entropy production integral is simply written as  $S'_i = \int \sigma$ , and  $L_z$  is lumped into the flux  
 166  $L_z J_x = J$  for convenience.

167 In case of this simple example, applying  $J = \lambda(M_l - M_r)$  from equation 5, one obtains the expression for  
 168 the effective conductance

$$169 \quad \lambda = S'_i (M_l - M_r)^{-2} = S'_i F^{-2} \quad (12)$$

170 and the effective force

$$171 \quad F = S'_i J^{-1} \quad (13).$$

172 | Thus, one may obtain the ~~true~~ effective conductance for any kind of heterogeneity (i.e. microscale  
 173 fluctuations) by explicitly calculating  $\sigma$  and  $S'_i$  based on equations 6 and 7 and the macroscopic  
 174 boundary conditions  $M_l$  and  $M_r$ . Note, entropy production is simply the sum of the product of the steady  
 175 state fluxes and incremental forces over the cross-section

$$176 \quad S'_i = \int \sigma = \int (\sum qf) = \int \left( \sum \frac{1}{\alpha} \rho \frac{K}{v} k_r(\psi) (\mu_{high} - \mu_{low})^2 \right), \text{ where individual values of } qf \text{ are calculated}$$

177 with equations 9 and 10 between two adjacent microscale elements in support scale numerical



178 simulations. While  $\lambda$  could have been obtained directly from the macroscopic flux and the applied  
179 boundary conditions similar to a numerical Darcy experiment, the example serves to illustrate the basic  
180 concept of inference arriving at a thermodynamic expression for  $\lambda$  and the force  $F$  (if a flux is prescribed  
181 at the boundaries).

182

183 *Example 2:*

184 This example expands example 1 to steady state groundwater flow including recharge represented by  
185 the mass rate  $Q_s$

$$186 \quad Q_s = \int_0^L (\nabla \cdot J) dx \quad (14),$$

187 and integration leading to

$$188 \quad MQ_s + J_l M_l - J_r M_r = S'_i \quad (15).$$

189 where  $M$  is the macroscopic potential of the cross-section.

190 The general expression for the macroscopic potential of the cross-section is

$$191 \quad M = Q_s^{-1} (S'_i - (J_l M_l - J_r M_r)) \quad (16).$$

192 In this example, three special cases are considered, namely  $J_l = 0$ ,  $J_l < 0$ , and  $J_l > 0$ . In case of  $J_l = 0$   
193 (figure 2), there is a no-flow boundary condition on the left side resulting in  $J_r = Q_s$  and, thus

$$194 \quad M = S'_{i, J_l=0} Q_s^{-1} + M_r \quad (17)$$

$$195 \quad F = (M - M_r) = S'_{i, J_l=0} Q_s^{-1} \quad (18)$$

196 where the subscript indicates the respective case for the left boundary flux.

197 With equation 7 and  $J_r = Q_s = J$  follows for the conductance coefficient

$$198 \quad \lambda = S'_{i,J_l=0} F^{-2} \quad (19).$$

199 For  $J_l < 0$  (figure 3), the symmetric case is considered, where the potentials at the boundaries are equal

200 ( $M_l = M_r = M_b$ ) and  $Q_s$  is uniform over the profile ( $-J_l = J_r = Q_s/2$ ) leading to

$$201 \quad M Q_s - 1/2 Q_s M_l - 1/2 Q_s M_r = S'_{i,J_l < 0} \quad (20a).$$

$$202 \quad Q_s (M - (M_l + M_r)/2) = S'_{i,J_l < 0} \quad (20b).$$

$$203 \quad Q_s (M - M_b) = S'_{i,J_l < 0} \quad (20c)$$

204 and ultimately for the macroscopic potential

$$205 \quad M = S'_{i,J_l < 0} Q_s^{-1} + M_b \quad (21).$$

$$206 \quad F = (M - M_b) = S'_{i,J_l < 0} Q_s^{-1} \quad (22)$$

207 and

$$208 \quad \lambda = S'_{i,J_l < 0} F^{-2} \quad (23)$$

209 Note,  $M$  and  $F$  reflect values for each of the two half-spaces separated by a no-flow boundary condition

210 e.g.  $F = (S'_{i,J_l < 0}/2)(Q_s/2)^{-1}$ , which is true for a homogeneous profile only and is equivalent to the case

211  $J_l < 0$  above. The entropy production is calculated also with

$$212 \quad S'_{i,J_l < 0} = \int \sigma = \int (\sum qf) = \int \left( \sum \frac{1}{\alpha} \rho \frac{K}{v} k_r(\psi) (\mu_{high} - \mu_{low})^2 \right).$$

213 For a heterogeneous profile and/or  $M_l > M_r$  (figure 4) i.e. when there is no symmetry

$$214 \quad M Q_s - J_l M_l - J_r M_r = S'_{i,J_l < 0} \quad (24).$$

215 | Thus, the effective potential  $M_e$  of the cross section may be obtained from

216  $M = Q_s^{-1}(S'_{i,J_l < 0} + J_l M_l + J_r M_r)$  (25)

217 Additionally, expressions can be obtain for the conductance coefficients in the exchange with the left

218 and right boundary conditions that are

219  $\lambda_l = (MQ_s - S'_{i,J_l < 0} - J_r M_r)(F_l M_l)^{-1}$  (26a)

220  $\lambda_r = (MQ_s - S'_{i,J_l < 0} - J_l M_l)(F_r M_r)^{-1}$  (26b).

221 where the macroscale forces  $F_r = M - M_r$  and  $F_l = M - M_l$  result from the differences between  $M$  and

222  $M_l, M_r$  with  $M$  following from equation 25. Again, entropy production is calculated with

223  $S'_{i,J_l < 0} = \int \sigma = \int (\sum qf) = \int \left( \sum \frac{1}{\alpha} \rho \frac{K}{v} k_r(\psi) (\mu_{high} - \mu_{low})^2 \right).$

224 For  $J_l > 0$  (figure 5), the entropy balance is

225  $MQ_s + J_l M_l - J_r M_r = S'_{i,J_l > 0}$  (27)

226 and the macroscopic potential is

227  $M = Q_s^{-1}(S'_{i,J_l > 0} - J_l M_l + J_r M_r)$  (28)

228 With  $Q_s = J_r - J_l$  follows

229  $J_l(M_l - M) + J_r(M - M_r) = S'_{i,J_l > 0}$  (29)

230 Thus, two conductances can be obtained, which are

231  $\lambda_l = (S'_{i,J_l > 0} - J_r(M - M_r)) F_l^{-2}$  (30)

232  $\lambda_r = (S'_{i,J_l > 0} - J_l(M_l - M)) F_r^{-2}$  (31)

233 with the macroscopic forces  $F_l = (M_l - M)$  and  $F_r = (M - M_r)$ . In this example, two additional  
 234 conductances can be obtained for the subdomains separated by the dividing streamline due to recharge  
 235 shown in figure 5 that are

$$236 \quad \lambda_{Q_s} = \left( S'_{i,J_l>0} - J_l(M_l - M_r) \right) F_{Q_s}^{-2} \quad (32)$$

$$237 \quad \lambda_{l,r} = \left( S'_{i,J_l>0} - Q_s(M - M_r) \right) F_{l,r}^{-2} \quad (33)$$

238 with  $J_r = J_l + Q_s$ , and the macroscale forces  $F_{Q_s} = (M - M_r)$  and  $F_{l,r} = (M_l - M_r)$ . In the domain, the  
 239 entropy production is calculated also with

$$240 \quad S'_{i,J_l>0} = \int \sigma = \int (\sum qf) = \int \left( \sum_{\alpha} \frac{1}{\alpha} \rho \frac{K}{v} k_r(\psi) (\mu_{high} - \mu_{low})^2 \right).$$

241

242 *Example 3:*

243 In this example, a no-flow boundary condition on the left is considered resembling a hillslope with a no-  
 244 flow boundary along a hypothetical ridge on the left side, and a Dirichlet boundary condition along a  
 245 hypothetical stream on the right side. Now, a source/sink  $Q_s(x,t)$  varies periodically in space and time  
 246 (periodically varying recharge/discharge). In this case, equation 2 needs to be solved for the different  
 247 variables and integrated over one complete cycle at dynamic equilibrium.

248 Note, again  $\int_0^L \nabla \cdot J dx = Q_s$ , because there is a macroscopic, transient source/sink in the domain,  
 249 therefore, after integration along the cross-section, the entropy balance reads

$$250 \quad S' + M Q_s - J_r M_r = S'_i \quad (34)$$

251 where  $S'$  is the entropy change rate. After time integration over one full cycle at dynamic equilibrium,  
 252  $\overline{Q_s} = 0$  and  $\overline{S'} = 0$ , the effective macroscopic potential of the cross-section due to the periodic varying  
 253 source/sink is

$$254 \quad \overline{M} = \overline{(S'_i + J_r M_r - S')} Q_s^{-1} \quad (35a)$$

255 or

$$256 \quad \overline{M} = \text{cov}(S'_i, Q_s^{-1}) + \overline{S'_i} \overline{Q_s^{-1}} + M_r (\text{cov}(J_r, Q_s^{-1}) + \overline{J_r} \overline{Q_s^{-1}}) + \text{cov}(S', Q_s^{-1}) \quad (35b)$$

257 based on the definition of the covariance.

258 Recognizing that  $J_r = \int_0^L (Q_s - \theta') dx$ , where  $\theta'$  is the macroscopic mass change rate of the cross-  
 259 section, one obtains for the effective force

$$260 \quad \overline{F} = \overline{(S'_i - \theta' M_r - S')} Q_s^{-1} \quad (36a)$$

261 or

$$262 \quad \overline{F} = \text{cov}(\sigma, Q_s^{-1}) + \overline{\sigma} \overline{Q_s^{-1}} - M_r \text{cov}(\theta', Q_s^{-1}) + \text{cov}(s', Q_s^{-1}) \quad (36b)$$

263 with  $\overline{\theta'} = 0$  due to dynamic equilibrium; and for the effective conductance

$$264 \quad \overline{\lambda} = \overline{(S'_i - \theta' M - S')} F^2 \quad (37a)$$

265 or

$$266 \quad \overline{\lambda} = \text{cov}(S'_i, F^2) + \overline{S'_i} \overline{F^2} - \text{cov}(\theta' M, F^2) + \overline{\theta' M} \overline{F^2} + \text{cov}(S', F^2) \quad (37b)$$

267 with  $J_r = \lambda F = \lambda(M - M_r)$ .

268 Apparently, on the right hand side of equations 35, 36, and 37 all terms may be calculated from the  
 269 numerical simulations except the entropy change rate  $S' = \int s'$  and therefore also  $\text{cov}(S', Q_s^{-1})$ , because

270 both,  $S'$  and  $M$  are not known in equation 34 (note,  $S'_i$  is calculated explicitly). However,  $S'$  is needed in  
 271 the estimation of  $\bar{F}$  and  $\bar{\lambda}$  and may actually be calculated from the microscale variables, which is  
 272 demonstrated with a discrete example depicted in the schematic in figure 6.

273 In this schematic, there are three microscale elements with sources/sinks in each individual element ( $q_l$ ,  
 274  $q_c$ ,  $q_r$ ) and a constant potential boundary condition on the right ( $\mu_b$ ). For each individual element the  
 275 entropy balance is

$$276 \quad s'_l + q_l \mu_l - q_{l,c} \mu_{l,c} = \sum q_l f_l = q_{l,c} (\mu_l - \mu_{l,c}) \quad (38a)$$

$$277 \quad s'_c + q_c \mu_c + q_{l,c} \mu_{l,c} - q_{c,r} \mu_{c,r} = \sum q_c f_c = q_{l,c} (\mu_{l,c} - \mu_c) + q_{c,r} (\mu_c - \mu_{c,r}) \quad (38b)$$

$$278 \quad s'_r + q_r \mu_r + q_{c,r} \mu_{c,r} - q_b \mu_b = \sum q_r f_r = q_{c,r} (\mu_{c,r} - \mu_r) + q_b (\mu_r - \mu_b) \quad (38c)$$

279 where the fluxes and potentials with the subscript  $l,c$  and  $c,r$  are valid at the element interfaces. The  
 280 terms on the right hand side i.e. the entropy production for each element encompass the fluctuations in  
 281 the flux-force relationships between the element's interior and the element boundaries. Summation of  
 282 the individual balance equations leads to the total balance

$$283 \quad s' + q_l \mu_l + q_c \mu_c + q_r \mu_r - q_b \mu_b = \sigma = q_{l,c} (\mu_l - \mu_c) + q_{c,r} (\mu_c - \mu_r) + q_b (\mu_r - \mu_b) \quad (39).$$

284 Note, on the left hand side, all the interface terms disappear and only the source and boundary terms  
 285 remain, equivalent to the macroscale balance in equation 34. Equation 38 is the entropy balance  
 286 equation for the system depicted in figure 6.

287 Any changes in the entropy of the system with time are due to transient effects that cancel out at  
 288 dynamic equilibrium  $\bar{s}' = 0$ . In order to demonstrate this, substitution of  $q_{l,c} = (q_l - \theta'_l)$ ,  $q_{c,r} =$   
 289  $(q_l - \theta'_l) + (q_c - \theta'_c)$ , and  $q_b = (q_l - \theta'_l) + (q_c - \theta'_c) + (q_r - \theta'_r)$  for the interface fluxes on the right  
 290 hand side in equation 38 leads to

$$s' + q_l \mu_l + q_c \mu_c + q_r \mu_r - q_b \mu_b =$$

$$(q_l - \theta'_l) \mu_l + (q_c - \theta'_c) \mu_c + (q_r - \theta'_r) \mu_r - q_b \mu_b \quad (40)$$

292 | which demonstrates continuity in case of ~~true~~ steady state  $\theta'_l = \theta'_c = \theta'_r = 0$ , and shows that any e.g.  
 293 | positive mass storage change  $\theta'$  over the microscopic volume leads to negative change in entropy and  
 294 | vice versa. Note, the entropy production is still always positive as required by definition. Thus,  $S'$  and  $M$   
 295 | can be evaluated by applying equation 39 to microscale simulations.

296 | A special case may be considered, in which the system depicted in figure 6 is also closed on the right side  
 297 | resulting in a sole exchange with the surroundings via the periodic source/sink (e.g.  
 298 | infiltration/evapotranspiration)  $Q_s(t)$ . This would be equivalent to a profile with a discharge area in the  
 299 | center and the assumption of symmetry shown in the schematic in figure 7. The requirement again is  
 300 | that  $\overline{Q_s} = 0$  over one full cycle at dynamic equilibrium. Then e.g. equation 35 simplifies to

$$301 \quad \bar{M} = \overline{(S'_l - S')} Q_s^{-1} \quad (41a)$$

302 | or

$$303 \quad \bar{M} = \text{cov}(\Delta S', Q_s^{-1}) + \overline{S'_l} \overline{Q_s^{-1}} \quad (41a)$$

304 | with  $\Delta S' = S'_l - S'$ .

305 |

306 |

### 307 | Discussion

308 | The major advantage of the proposed inference theory is the estimation of macroscopic variables that  
 309 | are thermodynamically consistent with the microscale fluctuations. This is discussed in the context of the  
 310 | simple example 1 interpreting the entropy current  $J_s = JM$  as an advective potential flux. -Because  $J$  is

311 constant and  $M_l > M_r$ , the entropy current leaving the domain on the right side is smaller than the  
312 entropy current entering the domain on the left side. This is due to dissipation in the interior of the  
313 domain resulting into the production of entropy  $S'_i$ . In hydrology, the dissipation is simulated using  
314 Darcy's law and Richards equation at the support (here microscopic) scale, where all dissipative  
315 processes are lumped in the hydraulic conductivity representing the flow resistance. Thus, at the  
316 macroscale the derived conductance  $\lambda$  is thermodynamically consistent if one accepts e.g., Darcy's law as  
317 a valid parameterization of the internal dissipative processes. Note, in this study,  $J_s$  is equivalent to the  
318 internal energy current in the energy balance equation, because temperature is constant.  
319 Equations 12 and 13 have not been applied before in the context of hydrology. While the equations  
320 illustrate the basic idea for the simplest case of a Darcy experiment, one may argue that the insight  
321 gained from this example is rather limited, because  $\lambda$  could have been obtained from the known flux-  
322 force relationship and the conductance equation (one unknown  $\lambda$  with one equation 7). Examples 2 and  
323 3, on the other hand, clearly illustrate the advantage, because the macroscale potential  $M$  (and  
324 therefore  $F$ ), which are needed to obtain  $\lambda$  are not known in these examples. Thus, one is left with two  
325 unknowns  $\lambda$  and  $F$ , and only one equation (the conductance equation 7). In the proposed theory, the  
326 entropy balance provides the second equation to solve for the two unknowns at the cost of explicitly  
327 calculating the internal entropy production  $S'_i = \int \sigma = \int (\sum qf) = \int \left( \sum \frac{1}{\alpha} \rho \frac{K}{v} k_r(\psi) (\mu_{high} - \mu_{low})^2 \right)$ ,  
328 and at the benefit of thermodynamic consistency. This is the central message of the proposed method of  
329 inference, which utilizes/exploits the internal entropy production  $S'_i$  as a spatial and also temporal  
330 integrator.

331 It is important to emphasize that one can also obtain, in an ad hoc fashion, the forces and conductance  
332 coefficients for any sub-domain  $V_i$  of the global domain with volume  $V$ . For example, in order to obtain  
333 the macroscale potential in the center of the profile of example 1, one arrives at



334  $M_c = M_l - J^{-1} \int_{V_i} \sigma dV_i$  (42).

335 Thus, from  $\int_{V_i} \sigma dV_i$  estimates, one is able to obtain macroscale variables over a hierarchy of scales for  
336 different hydrologic configurations similar to the simple examples provided above.

337 Under purely saturated groundwater flow conditions, the estimates of macroscale variables can be used  
338 directly for predictions, because  $\lambda$  is constant for the same flow geometries, which is trivial, but  
339 important to realize. In case of variably saturated flow and transient conditions (when the flow geometry  
340 changes),  $\lambda$  is of course not constant and  $S'_i$  will depend in an unknown, non-linearly fashion on the flux  $J$   
341 and its variability (example 3), which apparently limits the usefulness of the proposed approach.  
342 However, universal relationships of  $S'_i(J)$  and  $\text{cov}(S'_i, J^{-1})$  can perhaps be obtained from a series of  
343 numerical experiments under characteristic hydrologic configurations.

344 This also brings up the question, whether one is able to establish a connection of the proposed theory  
345 with observations of real-world systems. Obviously,  $S'_i$  ~~and  $S^L$~~  can not be measured directly in the field  
346 utilizing independent experiments, which could, in turn, be used to derive macroscopic thermodynamic  
347 forces from flux observations that are more readily available. Thus, utilizing the entropy balance for  
348 estimating macroscopic field variables and ensuing predictions appears limited at this point. Yet, this  
349 study suggests ~~to explore~~exploring relationships of measurable field variables and  $S'_i$  utilizing numerical  
350 experiments, in future. In turn, under certain conditions, estimates of  $S'_i$  from measurable quantities  
351 may be possible. With the help of the extended example 1, this is discussed below.

352 Assuming a time varying force i.e. Dirichlet boundary conditions, temporal integration of equation 11  
353 over one full cycle at dynamic equilibrium yields

354  $\bar{S}'_i = \bar{JF}$  (43)

355 Inserting the conductance equation into equation 43 under saturated, linear groundwater flow  
356 conditions with the assumption of only small changes in the flow geometry ( $\lambda$  is constant) leads to

$$357 \quad \bar{S}_i^* = \lambda^{-1} \bar{J}^2 = \lambda^{-1} [\text{var}(J) + \bar{J}^2] \quad (44).$$

358 Thus, entropy production is related inversely to  $\lambda$ , linearly to with  $\text{var}(J)$ , and power two with to  $\bar{J}$ . If an  
359 estimate of  $\lambda$  is available,  $\bar{S}_i^*$  can be calculated from observations of  $J$ . In the more realistic case of  
360 variably saturated groundwater flow and/or varying flow geometry, equation 44 changes to

$$361 \quad \bar{S}_i^* = \overline{\lambda^{-1} J^2} = \text{cov}(\lambda^{-1}, J^2) + \overline{\lambda^{-1} J^2} \quad (45).$$

362 illustrating the same dependence of  $\bar{S}_i^*$  on  $\bar{\lambda}$  and  $\bar{J}$  as before. The unknown covariance  $\text{cov}(\lambda^{-1}, J^2)$  may  
363 potentially be estimated from numerical experiments.

364

## 365 Summary and conclusions

366 In this study, the method of inference based on the entropy balance equation was introduced. The  
367 theoretical basis is the explicit calculation of the internal microscale entropy production, which is used in  
368 the balance equation to solve for macroscale potentials, and thermodynamic forces and fluxes. The  
369 proposed method was illustrated with simple hydrologic cross-sections of steady-state, variably saturated  
370 groundwater flow and a periodic source/sink (infiltration/evapotranspiration) at dynamic equilibrium.

371 The entropy balance equation is remarkable, because the equation unifies the macro- and microscale in  
372 one equation allowing the simultaneous application of two different movement equations that are the  
373 conductance equation at the macroscale and Darcy's law/Richards equation at the microscale, in this  
374 study. The derivations lead to expressions for macroscale variables that are a function of the entropy  
375 production (i.e. the internal fluctuations of the microscale flux-force relationships) and are provide a  
376 thermodynamically consistent link between the two different scales. - thus, thermodynamically

377 ~~consistent~~. Therefore, the derivation provides a different theoretical ~~perspective~~point of view of variably  
378 saturated groundwater flow and new approaches for obtaining effective macroscale variables. The  
379 discussion suggests that these may be derived consistently for a hierarchy of scales. With the advent of  
380 high-performance computing in hydrology, there is strong potential for additional insight from hyper-  
381 resolution numerical experiments to explicitly calculate the internal entropy production. For example,  
382 existing and new averaging and upscaling laws may be tested and derived using series of numerical  
383 experiments with e.g. varying subsurface heterogeneity configurations, and boundary conditions. These  
384 experiments may also be useful in deriving new movement equations at the macroscale replacing  
385 empirical, calibrated parameterizations and regionalization approaches.

386 The study is a contribution to the field of *theoretical hydrology*, providing a thermodynamic perspective  
387 of inference in hydrology. While inference of macroscale variables necessitates explicit calculation of the  
388 entropy production and thus considerable computational resources, these resources are well-invested:  
389 Obtaining previously unknown macroscale parameters is at the center of the ubiquitous challenge of  
390 upscaling and applying the proposed framework may help in finding general upscaling relationships over  
391 a hierarchy of scales. Thus, the appeal of the proposed method is mainly theoretical at this point,  
392 providing a thermodynamics perspective of inference in hydrology. The connection to real-world  
393 observations needs to be established in future, also with the help of numerical simulations. In the  
394 provided theoretical setting, the usefulness of the method for predictions is evident from the simple  
395 examples provide here, however, for real-world predictions this remains to be demonstrated.

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396

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402

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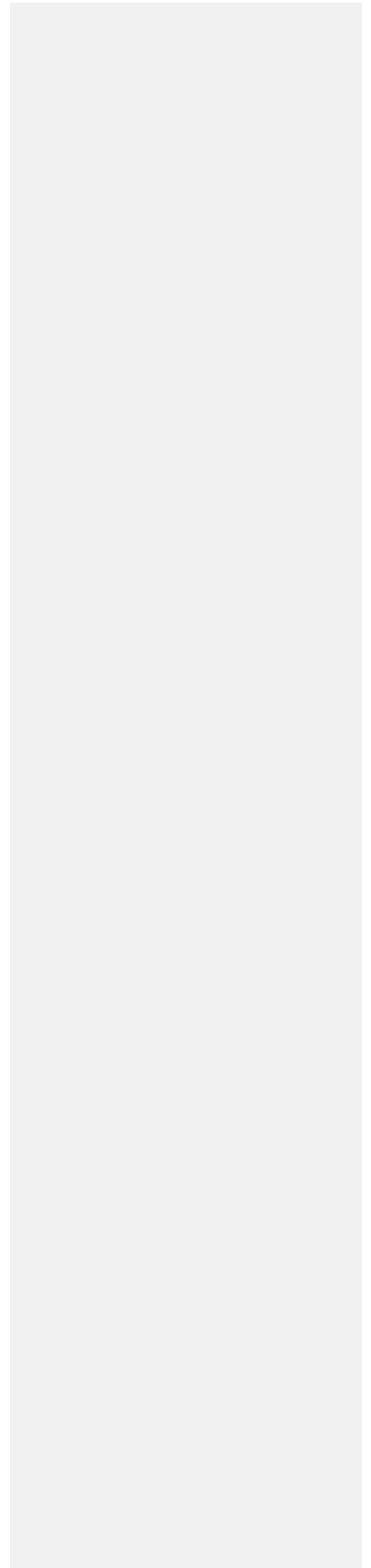
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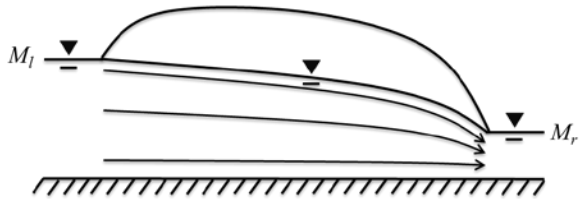
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453 **Figures**

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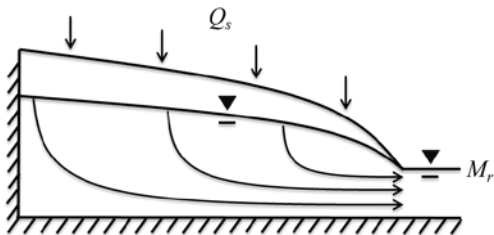


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456 Figure 1. Schematic of a simple profile with Dirichlet boundary conditions on the right and left ( $M_r, M_l$ )  
457 and steady state variably saturated flow. In the theory, the vertical and horizontal extents of the cross-  
458 section are assumed to be constant.

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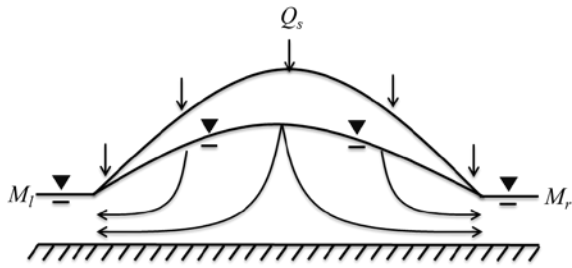


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462 Figure 2. Schematic of a simple profile with a Dirichlet boundary condition on the right ( $M_r$ ), a no-flow  
463 boundary condition on the left, a constant source ( $Q_s$ ), and steady state variably saturated groundwater  
464 flow. In the theory, the vertical and horizontal extents of the cross-section are assumed to be constant.

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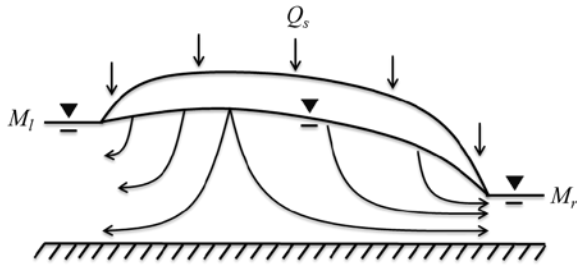
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468 Figure 3. Schematic of a simple profile with Dirichlet boundary conditions on the right and left ( $M_r, M_r$ ) a  
469 constant source ( $Q_s$ ), and steady state variably saturated groundwater flow. In this symmetric case,  
470 there exist a water divide in the center of the domain. In the theory, the vertical and horizontal extents  
471 of the cross-section are assumed to be constant.

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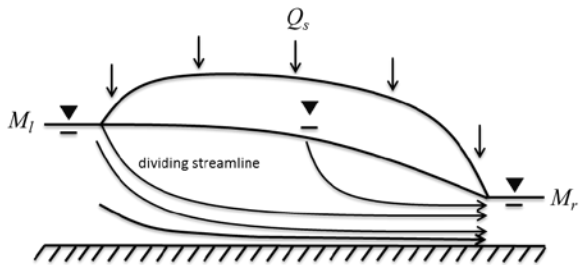


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474 Figure 4. Schematic of a simple profile with Dirichlet boundary conditions on the right and left ( $M_r, M_r$ ) a  
475 constant source ( $Q_s$ ), and steady state variably saturated flow. In this case there exist a water divide in  
476 the domain. In the theory, the vertical and horizontal extent of the cross-section is assumed to be  
477 constant.

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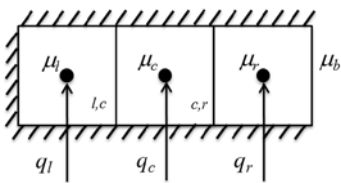
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480 Figure 5. Schematic of a simple profile with Dirichlet boundary conditions on the right and left ( $M_r, M_l$ ), a  
 481 constant source ( $Q_s$ ), and steady state variably saturated groundwater flow. Note the dividing streamline  
 482 in this example. In the theory, the vertical and horizontal extents of the cross-section are assumed to be  
 483 constant.

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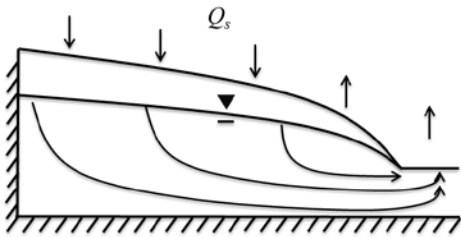


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488 Figure 6. Schematic of the discrete example consisting of three microscale elements with a Dirichlet  
 489 boundary condition on the right side ( $\mu_b$ ) and a source/sink in each element ( $q_l, q_c, q_r$ ).

490

491



492

493 Figure 7. Schematic of a simple profile with a no-flow boundary condition on the left and right (based on  
494 symmetry) and transient, spatially varying sources/sinks  $Q_s(x, t)$  resulting in a recharge and discharge  
495 area. In the theory, the vertical and horizontal extent of the cross-section is assumed to be constant.

496