## A thermodynamic framework to link process, structure and function.

This study proposes a theoretical framework that links hydrological dynamics to thermodynamics, with emphasis on dynamics and dissipation of free energy and production of entropy in the critical zone. Based on this theory we may shed light on the dynamics and dissipation of free energy and production of entropy in the critical zone by analysing simulated dynamics from physically based hydrological models. This is exemplified in the Weiherbach and the Malalcahuello catchment which are located in strongly different hydroclimactic and hydro-pedological settings. The application to the Weiherbach catchment suggests the existence of thermodynamic optimal hillslope structures as a result of coevolution of biotic patterns and the soil catena. These optima allow acceptable uncalibrated reproduction of observed rainfall-runoff behaviour when being used in a catchment model: in fact they come close to the best fit. Application showed furthermore that connected networks like structure, vertical preferential pathways and the river net, act as dissipative structures by accelerating flow against driving gradients, which implies an elevated entropy production. This seems to be "a key instrument in this concert". For the Malalcahuello catchment we found that maximum drainage is the functional optimum hillslope structure. This is explained by the very wet, energy limited climate, the presence non-cohesive highly permeable ash soils and the different mechanism causing preferential flow. This theory makes a substantial contribution to the understanding of the omnipresence of preferential flow and the functional advantage of this phenomenon; which seems to be independent of scale and nature of the flow paths. We conclude further that the presented findings are promising for predictions in ungauged catchments (PUB). The thermodynamic optimal model structure can, if existent, be used as first guess for an uncalibrated simulation of rainfall runoff.