

Dissipative dynamics in river catchments: insights from probability distributions

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Geochemical elements typically exhibit characteristic frequency distributions (e.g., normal, log-normal, or power-law distributions). Extensive literature aims to relate these types of distributions to the underlying natural processes that generate them. However, the link between the dissipative behavior of a process and the frequency distribution of the involved variables remains unclear. As weathering progresses within river catchments, chemical concentrations tend to approach saturation or thermodynamic equilibrium. However, achieving thermodynamic equilibrium is extremely difficult in an open system such as a river catchment, where matter and energy are continuously exchanged. In this framework, the speed of weathering processes and the associated probability distributions of concentration values can vary among geochemical species.

Based on water chemical and discharge data from the Arno River Basin in central Italy, we distinguish two groups of geochemical variables, reflecting different levels of dissipative behavior. We show that Ca^{2+} and HCO_3^- concentrations are close to saturation along most of the downstream length of the Arno River, exhibiting decreasing dissipation rates and a (log)normal distribution. In contrast, Na^+ and Cl^- concentrations increase substantially downstream, showing increased dissipation rates and a power-law distribution. In this work, we demonstrate, using a simple model, that these differences are characterized by the rate of entropy production associated with the mixing of groundwater enriched with weathering products and the less saturated river water.

Hence, is the frequency distribution of concentrations reflective of the thermodynamics of the system? Our results indicate that power-law distributions appear to be indicative of dissipative systems far from thermodynamic equilibrium, while (log)normal distributions suggest weakly dissipative systems close to equilibrium. This implies that the frequency distributions of environmental variables are intricately connected to their thermodynamic state [1]. These results should contribute to a more comprehensive understanding of the characteristics and underlying mechanisms that lead to these types of distributions, allowing for a better classification of variability in systems based on their dissipative behavior.

[1] Kleidon, A., Gozzi, C., Buccianti, A., & Sauro Graziano, R. (2024). Type of probability distribution reflects how close mixing dynamics in river chemistry are to thermodynamic equilibrium. *Science of The Total Environment*, 941(173409).