EGU24-16778, updated on 14 Jan 2025
https://doi.org/10.5194/egusphere-egu24-16778
EGU General Assembly 2024

Probability distributions as indicators of dissipative dynamics in river chemistry

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The chemistry of rivers plays a crucial role in comprehending the evolution of weathering processes, especially in the context of climate change and human activities. As weathering proceeds within river catchments, chemical concentrations tend to move towards saturation, or thermodynamic equilibrium. However, thermodynamic equilibrium is extremely difficult to achieve in an open system where matter and energy are continuously exchanged.

The speed of weathering processes and the associated probability distributions of concentrations values differ among geochemical species. We demonstrate that these differences are characterized by the rate of entropy production associated with the mixing of groundwater enriched with weathering products with the less saturated river water.

Based on river chemistry and discharge data observations in the Arno River basin in central Italy, we distinguish two groups of chemical variables, reflecting different levels of dissipative behavior. We show that Calcium (Ca^{2+}) and Bicarbonate (HCO_3^-) concentrations are close to saturation along most of the downstream length of the Arno River, with decreasing dissipation rates and a (log)normal distribution, while Sodium (Na^+) and Chlorine (Cl^-) concentrations increase substantially downstream, showing increased dissipation rates and being power-law distributed. This supports our hypothesis that power law distributions appear to be indicative of dissipative systems far from thermodynamic equilibrium, while (log)normal distributions indicate weakly dissipative systems close to equilibrium. This suggests that the frequency distributions of environmental variables are intricately connected to their thermodynamic state, and the degree of disequilibrium constrains the range over which power-law scaling can be observed. These results should contribute to a more comprehensive understanding of the characteristics and underlying mechanisms that lead to these types of distributions, allowing to better classify variability in systems based on how dissipative they are.