# Analyzing long-term streamwater chemistry with complexity measures

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## Introduction

Triggered by the "acid rain" debate and symptoms of forest decline, forests in the Bramke valley (Harz mountains, Lower Saxony, Germany) have been monitored since the 1970s. From three small catchments – Lange (LB), Steile (SB) and Dicke (DB) Bramke (Fig. 1) – stream chemistry time series are available at biweekly resolution. They show pronounced trends and differences between the catchments (Figs. 3, 4). We characterize the dynamics of the concentrations and fluxes with complexity measures based on ordinal patterns.

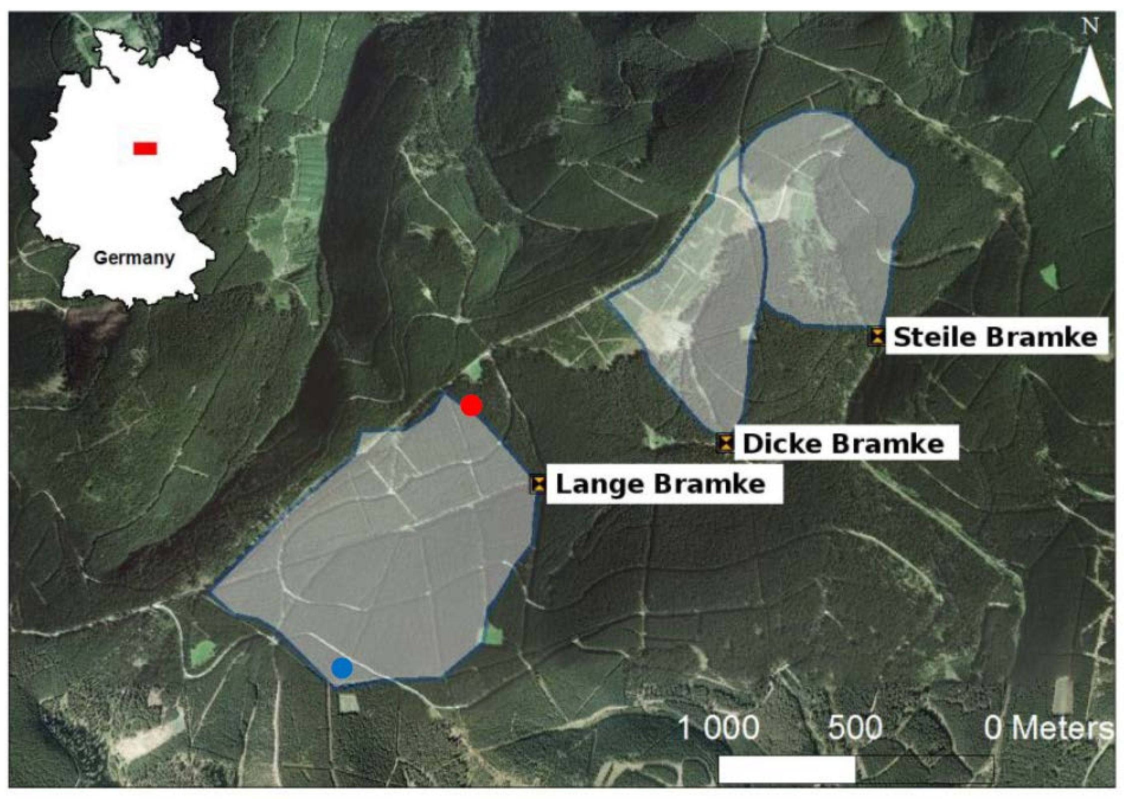


**Figure 1.** The three first-order catchments in the Bramke valley. Water samples are taken at the outlet of each; at Lange Bramke, also the spring is sampled (LBS). Streamflow at daily resolution is available from a gauged weir at the outlet of Lange Bramke (LBW).

## Analysis method: complexity measures

The information content and complexity of the ion concentrations are quantified using *ordinal patterns*: within each window of length $D$ ($D = 4$), values are sorted according to their rank, leading to $D!$ rank patterns. Their probabilities $p_i$ are used to calculate (permutation) entropy, complexity (based on the distance to the uniform distribution) and Fisher Information (Rosso et al. 2010). Recent extensions are the *q-entropy* and *q-complexity* (Ribeiro et al. 2017) based on the q-logarithm $\log_q(x) = (x^{1-q} - 1)/(1 - q)$ (Tsallis 2009; $0 \le q < \infty$ and $\log_1(x) = \log(x)$). Entropy, complexity and Fisher Information separate deterministic-chaotic from stochastic processes. Example: stochastic processes form closed loops in a q-entropy vs. q-complexity graph when q is varied, deterministic ones do not (Ribeiro et al. 2017). The three quantities classify time series (Fig. 2).

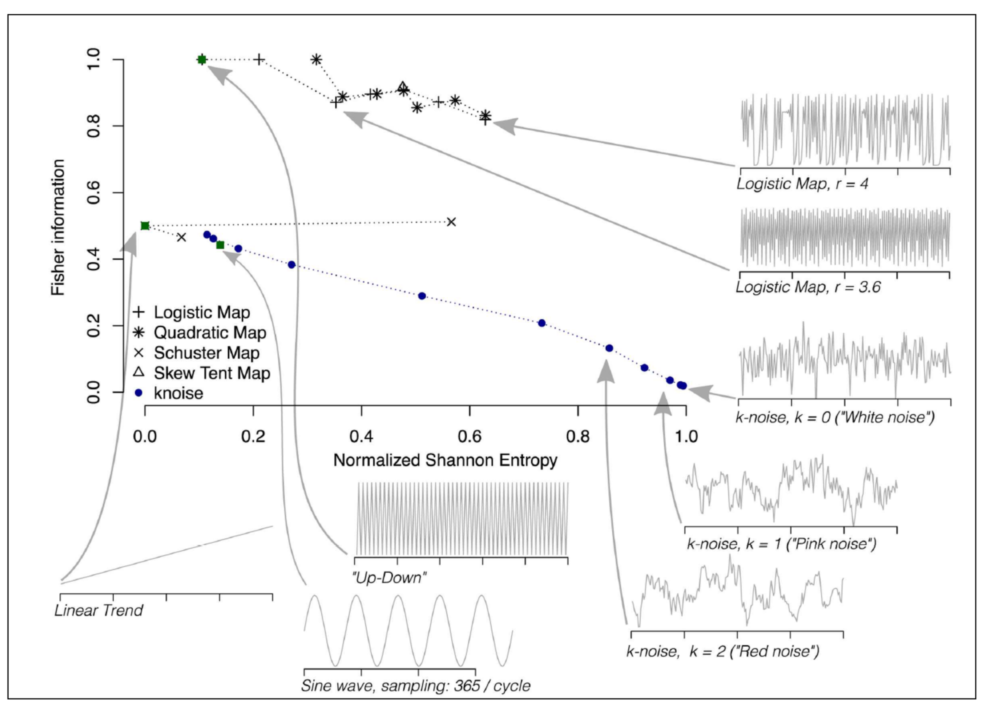


**Figure 2.** Position of artificially generated time series in the entropy – Fisher Information plane. Picture taken from Sippel et al. (2016).

Time series of $SO_4$–S concentrations

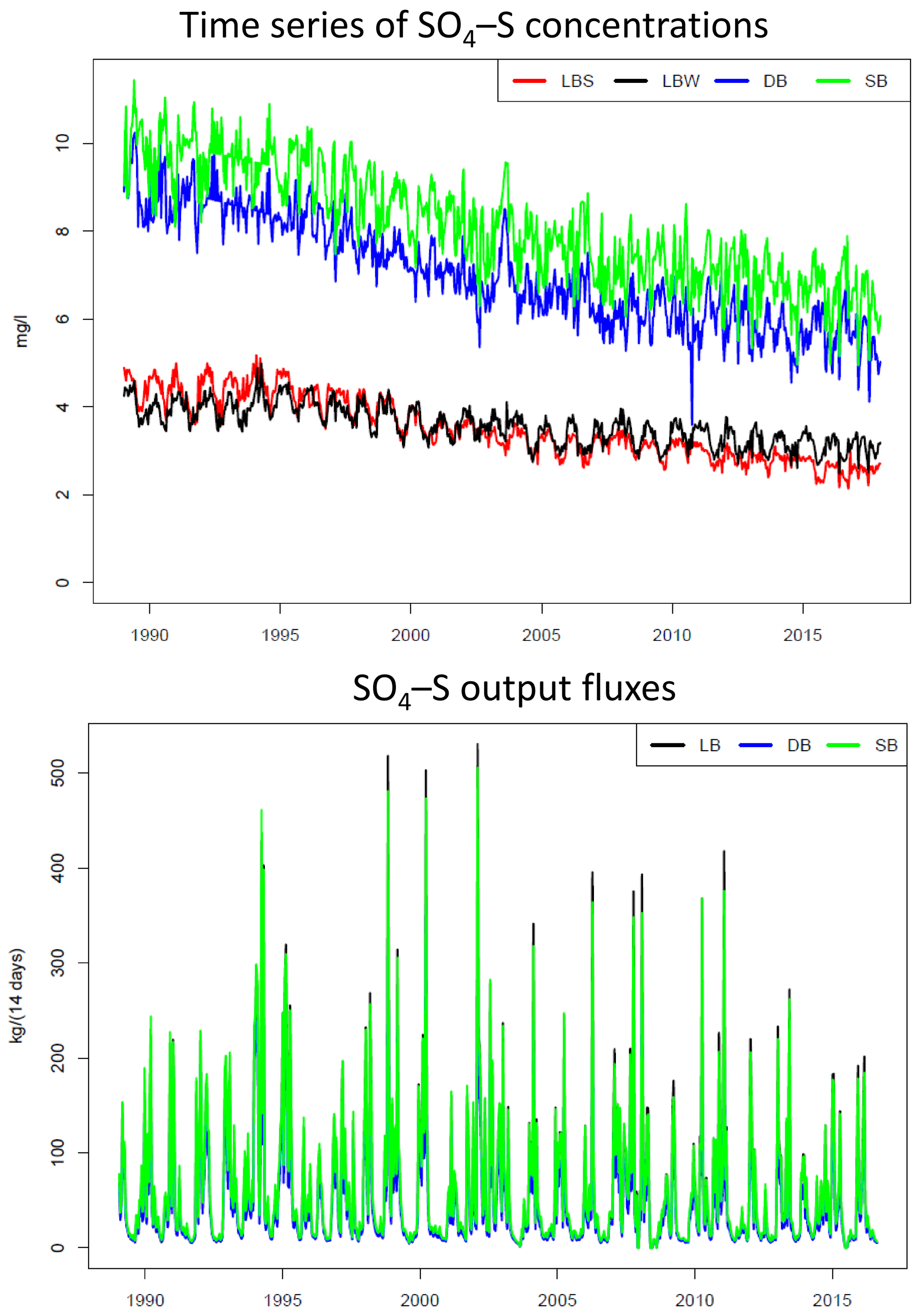


**Figure 3.** Upper panel: Concentrations of $SO_4$-S from the Bramke catchments. The declining trends are related to reductions in atmospheric deposition, but levels are quite different. When converted to output fluxes (lower panel), the three catchments show very similar values.

## Results

Only sulfate ($SO_4$) and nitrate ($NO_3$) measurements since 1989 are shown as examples. The $SO_4$ concentrations show declining trends, consistent with reductions in atmospheric Sulphur deposition, but differ between the catchments (Fig. 3). However, the area-corrected fluxes are quite similar. $NO_3$ concentrations at DB are declining after a peak in 1989, and separate from SB in 2000 (Fig. 4a). For the complexity analysis, these trends were removed nonlinearly using Singular System Analysis (Golyandina and Korobeynikov 2014). The complexity and Fisher Information (FI) in moving windows of 10 years (Fig. 4b,c) show large differences between the catchments, apart from a more recent convergence. The q versions for whole time series (Fig. 5) show closed loops, typical for stochastic processes with a fixed Hurst exponent.

The entropy– FI plot for 8 different ions (Fig. 6) shows that the time series are high-entropic, differ between catchments, and have systematically higher FI than a standard reference process, the fractional Brownian motion.

## Conclusions

Complexity analysis allows the classification of time series from constant to random, and from deterministic to stochastic. Concentrations from the three Bramke catchments have different dynamics, even after trends are removed. They are random and long-range correlated, but differ from reference stochastic processes.

Time series of $NO_3$–N concentrations

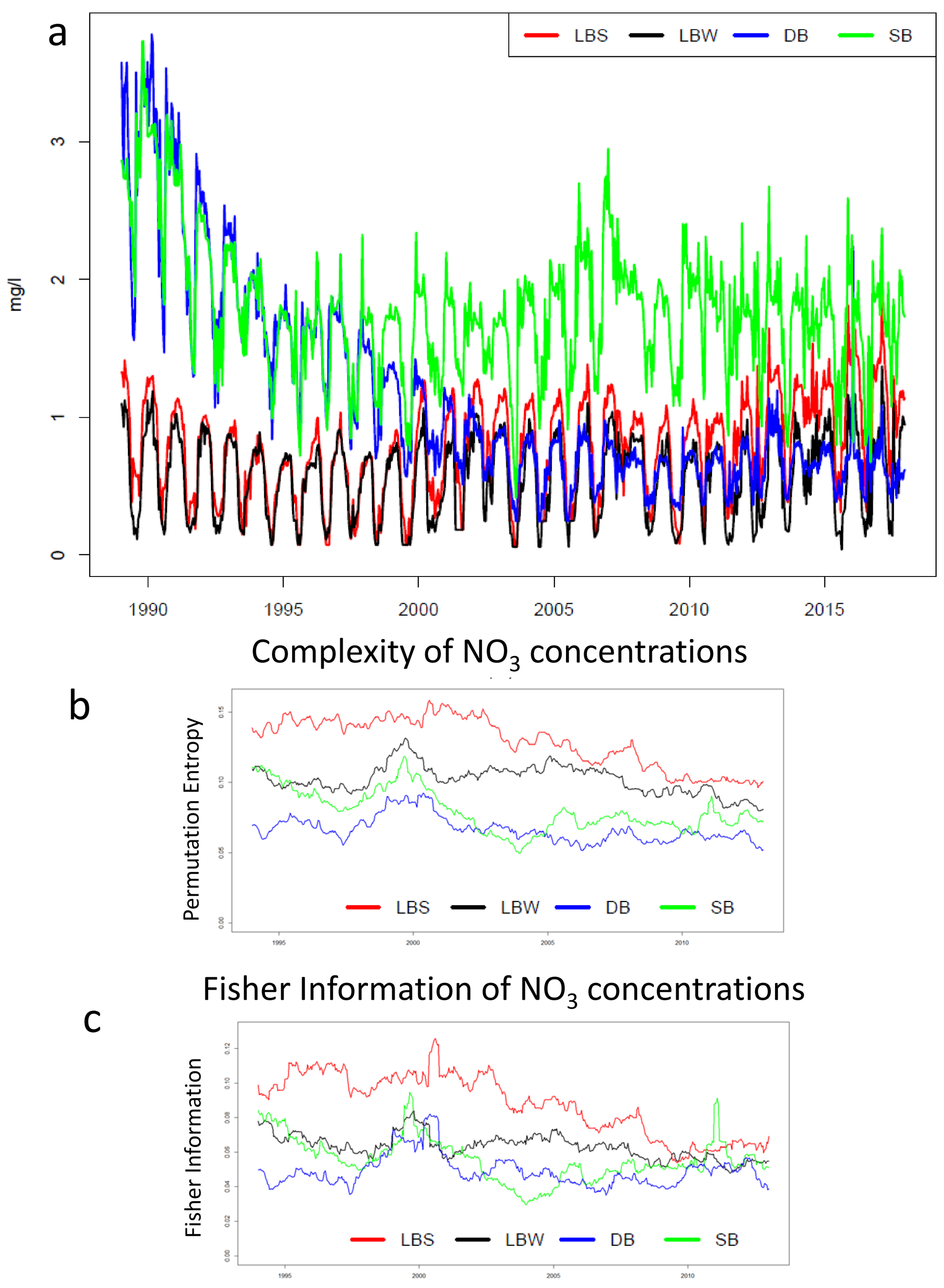


**Figure 4. a**: Time series of $NO_3$-N from the Bramke catchments. Note the strong annual cycle and the "decoupling of DB and SB around the year 2000. **b**: Complexity of these series in moving 10-year windows. Reference time is the midpoint of each interval. The weir at Lange Bramke has the highest complexity values. Up to around 2000, LBS and SB are very similar. **c**: Similar to b, but for the Fisher Information.

q-entropy and q-complexity of $NO_3$ concentrations

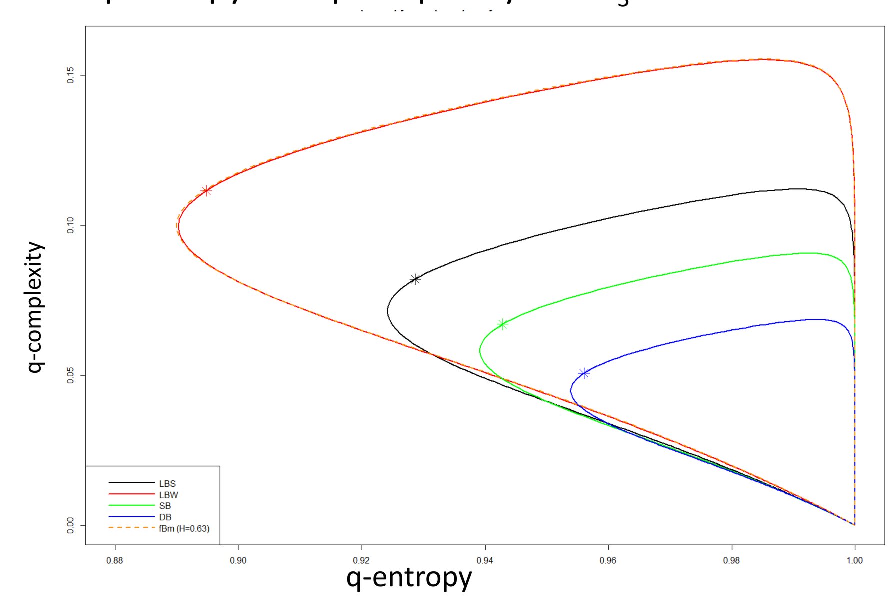


**Figure 5.** The q-variants of entropy and complexity. For each series, q runs from $10^{-3}$ to $10^{2}$. Closed loops indicate long-range stochastic processes. The dashed line is for fractional Brownian motion with a Hurst exponent H=0.63; in this representation it is hardly distinguishable from the loop for LBW. The conventional values (q=1) are marked.

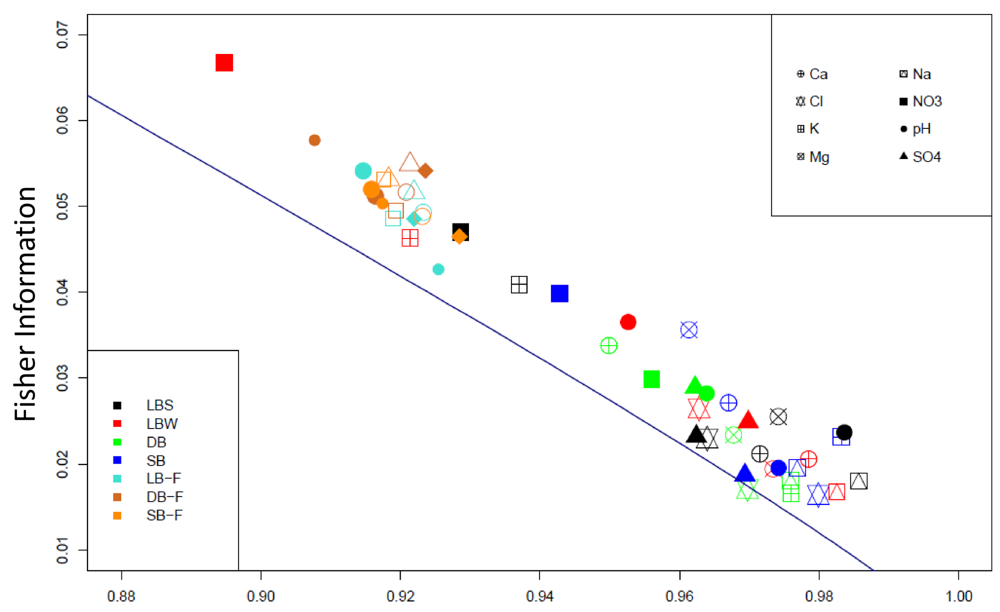


**Figure 6.** Entropy and Fisher Information for eight different ions from the Bramke. Colours indicate location and concentrations or fluxes (F), symbols the different ions. The solid line is for the fractional Brownian motion where the Hurst exponents varies.

**References**

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