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UNIVERSITÀ DEGLI STUDI FIRENZE

INNOVATIVE GRAPHICAL-NUMERICAL METHODS TO INVESTIGATE COMPOSITIONAL CHANGES IN GROUNDWATER SYSTEMS

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State of art

Geochemical and hydrological processes are often characterized by random components mixed with intermittency and presence of positive feedbacks between fluid transport and mineral dissolution. Large fluctuations in intermittent processes are no so rare as in normal and log-normal processes and significantly contribute to the statistical moments, thus moving data from the Euclidean geometry to the fractal and multifractal ones.

Aim

From this point of view, the study focuses on the development of tools to investigate the compositional changes in groundwater systems, with the aim of finding out different behaviors related to the water-rock interaction dynamics, not always explained by Normal/Lognormal Gaussian model.

Data

GEOBASI project, 1519 groundwaters samples from Tuscany (HCO_3, Ca, Cl, Mg, K, Na, SO_4, NO_3). Available here http://www506.regione.toscana.it/geobasi/index.html.

Statistical Approach

Compositional Data Analysis (CoDA, Aitchison, 1982), particularly suitable to look into the whole composition and the relationships between its parts.

CoDA APPROACH

THEORY

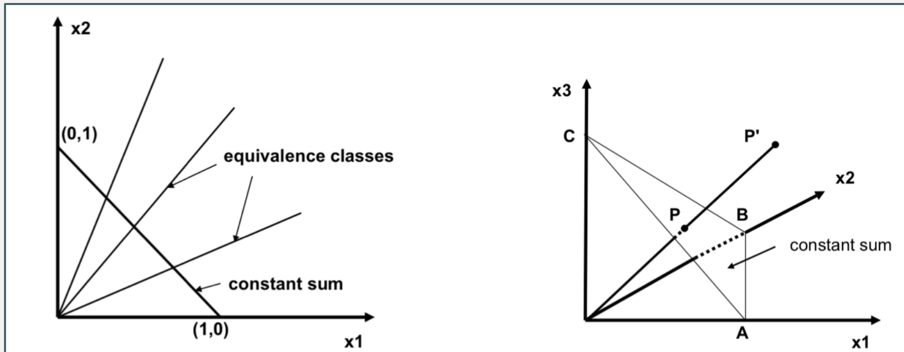
Geochemical data, as concentrations, express part of a composition and so they are frequently positive proportions (percentages, ppm, ppb..) of a total. As consequence of their nature, compositional data have a peculiar geometry and belong to a constrained sample space known as **simplex** of D-parts (S^D), which is the set of real positive vectors closed to a constant summa k.

$$S^D = \{(x_1, x_2, \dots, x_D): x_1 > 0, x_2 > 0, \dots, x_D > 0; x_1 + x_2 + \dots + x_D = k\}$$

Compositional data are:

- **parts of some whole which only carry relative information (ratios of components);**
- **always positive.**

The usual Euclidean geometry in real space is not a proper geometry for compositional data (Aitchison, 1982; Pawlowsky-Glahn & Buccianti, 2011).



compositional data in $\mathbb{R}^2$ compositional data in $\mathbb{R}^3$

HOW TO OVERCOME THIS ISSUE?

1) **By staying in the simplex** and using a new mathematical language, the Aitchison geometry.

2) By using an appropriate transformation in order to **transfer data from the simplex to the real space** (Euclidean geometry).

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PERTURBATION OPERATOR
(STAYING IN THE SIMPLEX)

Basic operations in the simplex

Let x and y be compositions of S^D, and $\alpha \in \mathbb{R}$.

- **perturbation** of x by y:

$$x \oplus y = C[x_1 y_1, x_2 y_2, \ldots, x_D y_D]$$

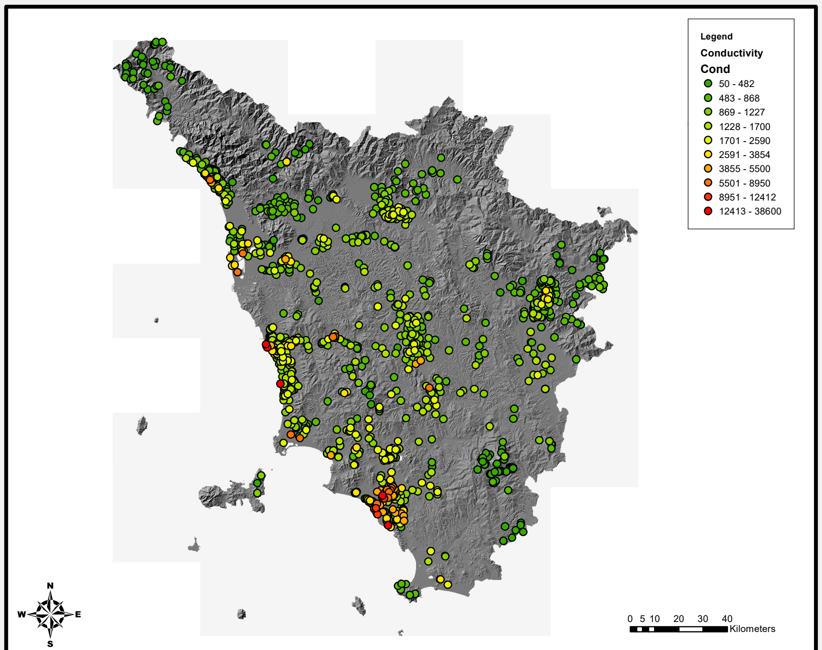
- **powering** of x by α:

$$\alpha \odot x = C[x_1^{\alpha}, x_2^{\alpha}, \ldots, x_D^{\alpha}]$$

By ranking data matrix according to increasing of conductivity (related to water rock-interaction), the perturbation values matrix has been calculated.

$$x_{i+1} \ominus x_i = \text{Perturbation matrix}$$

GROUNDWATER SAMPLES



For each sample, perturbation values express the **COMPOSITIONAL CHANGE** from the water immediately previous considering the criterion of ascending conductivity.

In other words, in order to go from a starting water x_i (**Initial composition**) to the following water x_{i+1} (**pertubed composition**) it is necessary the work of a perturbing agent (Geo-environmental forcing agents, **perturbing composition**) that represents the change.

An easy way to visualize the result of perturbation operator is as multiplicative (not closed) factor.

Since this is unclosed, it could be used in statistical modeling inside the Euclidean space.→ PERTURBATION FACTORS

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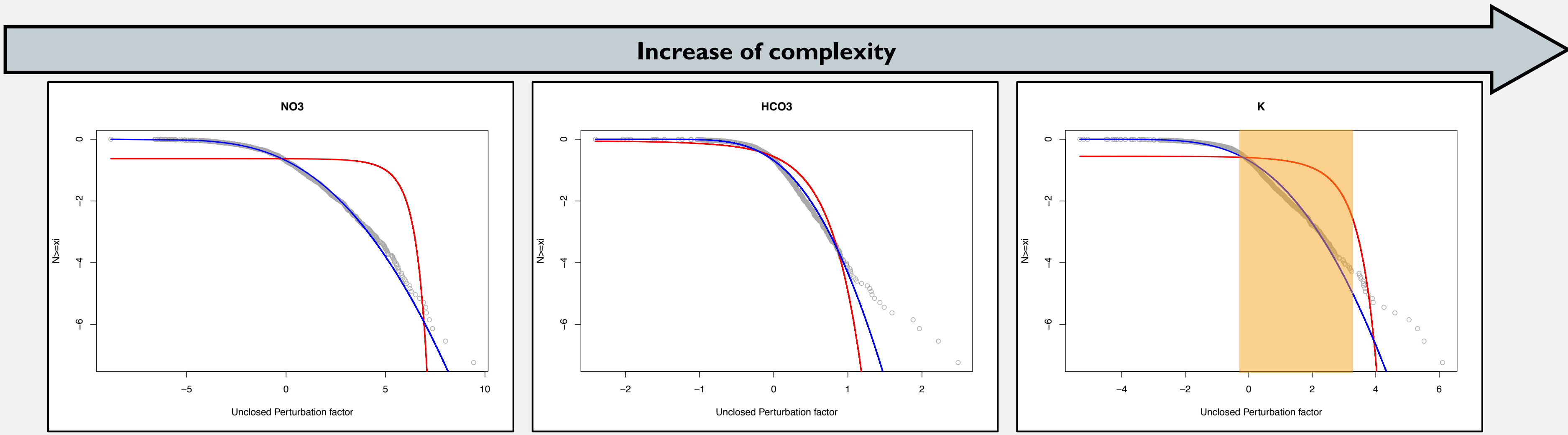
PERTURBATION FACTOR

Here, we report the case of 3 variables, chosen for their different geochemical source: 1) HCO_3 – carbon cycle, calcite dissolution; 2) K – silicates weathering, fertilizers in agriculture; 3) NO_3 – strongly affected from use of Nitrogen compounds in agriculture and from redox conditions.

By plotting the cumulative number $N \geq x$ versus x in log-log coordinates, it is possible to discriminate different behaviors among chemical species and obtain indications about the increase of their complexity. In this plot, a straight line indicates the emergence of a power law (fractality).



- No variables follow the normal Gaussian model (red lines), suggesting **additive processes** are not those driving these chemical species.
- Furthermore, moving from NO3 to HCO3 and K case, we pass trough variables showing a greater adaptability to the lognormal model (blue lines, **multiplicative processes,** NO3), variables partially explained by multiplicative processes (HCO_3, evidence of slight straightness), and variables with a more segmented pattern, typical of fractal/multifractal dynamics (orange box, **multiplicative + feedback mechanisms**, K).

CONCLUSION

Perturbation operator can be an useful statistical tool to investigate the compositional changes due to the geo-environmental forcing agents. In other words, the perturbator operator allows us to look inside the dynamics of the groundwater system, related to interactions between components.

In addition, perturbation values are a sensible probe to highlight the degree of complexity in the geochemical variables, identifying the different components (additive, multiplicative, fractal) contributing to the variability of the geochemical data.

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