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WEATHERING AND TRANSPORT PROCESSES INVESTIGATED THROUGH THE STATISTICAL PROPERTIES OF THE *GEOCHEMICAL LANDSCAPES*: THE CASE STUDY OF THE TIBER RIVER BASIN (CENTRAL ITALY)

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ABSTRACT

This article summarizes the results of a three-year PhD project concerning the study of the geochemical landscapes of the Tiber River basin (TRB), a catchment that has driven very little attention so far. During the research, a wide survey was carried out to characterize the chemical composition of river waters and stream sediments within the different geological and topographical settings of the basin. A combination of multidisciplinary approaches and geostatistical methods, such as Compositional Data Analysis (CoDA), pairwise robust Mahalanobis distance, ecological regime shift theory, and watersheds delineation, were applied to investigate catchment-scale processes. This research opens up new perspectives for the study of complex river systems from a holistic point of view, focusing on basin-wide responses to environmental changes.

INTRODUCTION

Water and sediment transported and distributed within a river catchment represent a sentinel variable able to monitor the interactions between litho-hydro-eco-atmospheric processes at various scales. Their composition change under the influence of a large variety of environmental factors and pressures (*e.g.*, topography, soil use, climatic and anthropic pressures) guided by the catchment properties (*e.g.*, connectivity, self-organization, fractality). These features make a river basin an extremely complex and dynamic geochemical environment that is challenging to be deciphered.

This work illustrates the results of a survey concerning the Tiber River basin (TRB), the largest river basin in central Italy, draining an area of 17,156 km^2. The Tiber River (TR) has its source in Mt. Fumaiolo (1,268 m) and flows towards the Tyrrhenian Sea for 405 km, receiving the water of Paglia-Chiani and Treia tributaries on the right bank and Chiascio-Topino, Nera-Velino and Aniene on the left one. In spite of the several data collected by different public or research bodies, comprehensive scientific works concerning the chemical characterization of TRB media are almost entirely absent. The basin is mainly featured by terrigenous deposits in its upper part, the carbonatic Apennine ridge towards South-East and potassic and ultra-potassic volcanic complexes in the South-western area (Boni *et al.*,1986). Its highly heterogeneous geological and morphological environment coupled with a noticeable presence of anthropic activities made the TRB the ideal area to evaluate the nature of the geochemical landscapes. The main aim of the PhD project was to investigate the variability and resilience of the TRB to natural and anthropic changes. Valuing rivers is critical to adaptation and understanding water system resilience to environmental variations represents a key point to define trajectories and boundaries for a sustainable future (Boltz *et al.*, 2019; WWF, 2019). The work looks into the spatio-temporal distribution of chemical species in the riverine media, identifying particle sources, weathering mechanisms and shifting patterns during the transmission of the chemical footprints from source to sink.

MATERIALS AND METHODS

Field Sampling Methods

In order to first obtain a comprehensive survey of the TRB surface waters, several sampling campaigns were carried out. The fieldwork was set from January to May (winter-spring) and from June to August (summer) 2017, during which the northern and the southern part of the basin were covered, respectively. Overall, 160 river waters were sampled. Among these, 19 were collected from the TR at a distance of about 20 km apart, starting from the source area and the remaining were taken from major (38), minor (94) tributaries and springs (4). TR samples were taken both upstream and downstream from each confluence with a major tributary to evaluate compositional changes on the main flow induced by inputs from different sub-basins. For the sake of clarity, the TRB was then grouped into four main sub-basins corresponding to the most significant lithological changes: High Tiber (HT), Middle Tiber (MT), Nera (NE) and Low Tiber (LT) and likewise the corresponding samples. Once obtained a general framework of the TRB water chemistry, new sampling campaigns were carried out during 2018 with the aim of assessing the influence of different hydrological regimes on the water composition. The monitoring campaigns involved 62 selected sites, which included all the sampling locations along TR, major tributaries and few minor streams. The sampling covered the southern part of the basin in spring season (March-April 2018) and the northern one in summer (August-September 2018), following exactly a reverse order by contrast to the first survey. River waters were sampled in mid-flow to avoid possible contamination due to riverbed or river bank processes. The geographical coordinates were measured on the field together with the water chemical-physical parameters. At each sampling point, the necessary aliquots for the determination of anionic, cationic species and trace elements were collected.

For a better comprehension of the interlinks between water composition and the underlying geological substratum, stream sediments were also collected alongside with water samples, for a total of 57 stream sediment samples. These samples were taken using a stainless steel hollow-core sampler from several spots on the river bank to obtain a representative composite sample. All sampling locations are shown in Fig. 1 jointly with the watersheds of the considered sub-basins.

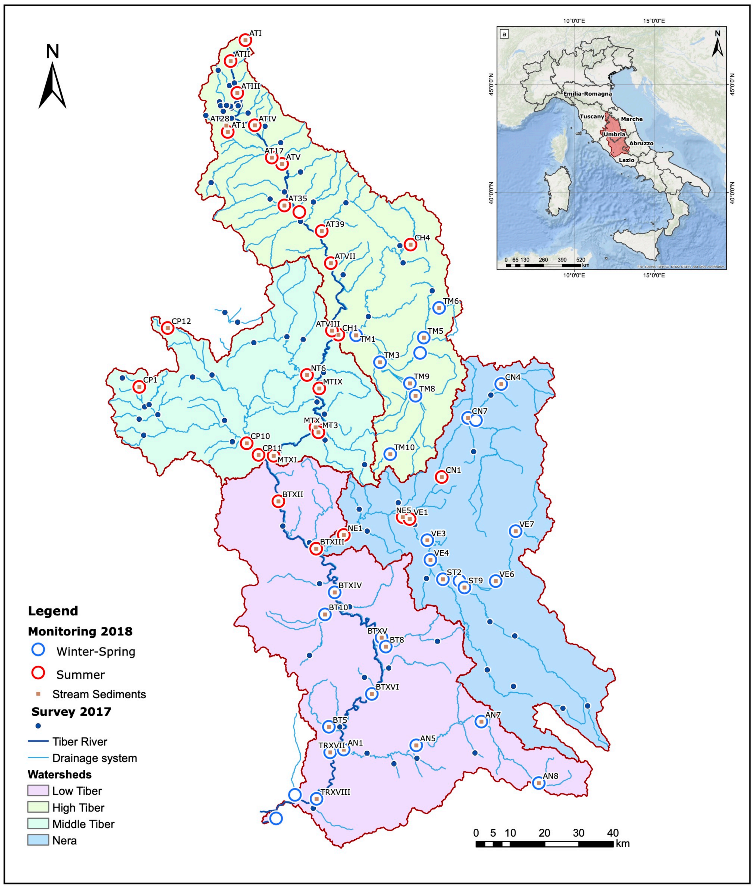

Fig. 1 - Map of the sampling sites related to the comprehensive survey and monitoring campaigns carried out during 2017-2018. The brown squares represent the sampling locations for the stream sediments.

Analytical Techniques

Dissolved major and trace species were analyzed in the Water Analysis Laboratory at the Department of Earth Sciences of the University of Florence. The chemical analysis of the stream sediment was performed by X-ray fluorescence (XRF) at the premises of the Montanuniversität in Leoben, Chair of Geology and Economic Geology (Austria). Magnetic susceptibility (MS) represents a valuable indicator for heavy metal contamination of river sediments yielding additional useful information to the chemical analysis at a low cost and in a short time (Scholger, 1998). For this reason, bulk MS of the stream sediments was also assessed at the Paleomagnetic Laboratory of the Institute for Geophysics of the Montanuniversität Leoben in Gams (Austria). Samples having high values of susceptibility were further investigated by separating the ferrimagnetic fraction from the sample powder. The magnetic particles were then verified by digital microscopy to check whether their shape and dimension could be helpful for discriminating between the anthropic or/and geogenic origin of the particles.

All measured chemical species/properties and technical details about instruments are summarized in Table 1.

Table 1 - Summary of the measured chemical species/properties and analytical instruments.

Environmental media	**Chemical species/Properties**	**Instruments**
River waters	F, Cl, Br, NO_3, PO_4, SO_4	Metrohm 761 Compact IC
	Ca, Mg, Na, K	Metrohm 861 Advanced Compact IC
	NH_4	Portable Datalogging Spectrophotometer HACH DR/2010
	HCO_3, CO_3	Metrohm 654 Multi-Dosimat
	Mn, Fe, Co, Ni, Cu, Zn, Si, Sr, Ba	ICP-OES; OptimaTM 8000 PerkinElmer
	Rb, B	ICP-MS, method EPA 6020B 2014
Stream sediments	SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Cu, Ce, Nb, Y, Sr, Rb, Th, Pb, Ga, Zn, Ni, C, La, Ba, Sc, Cr, Cs, Hf, Nd	Axio^{smAX}- Advanced wavelength dispersive XRF spectrometer (Malvern PANalytical).
	Magnetic susceptibility (MS)	Three Frequency Kappabridges (Agico MFK1-FA). Field intensity 200 A/m and frequency 976 Hz

Statistical and GIS Methods

The obtained data were processed using advanced statistical methods with respect to the compositional nature of geochemical data. Compositional data are known in geochemistry as closed data, since they represent a part of a given numerical total, carrying only relative information (Aitchison, 1986). They are always positive, not free to vary independently, and characterized by mathematical properties that may significantly affect their analysis (Buccianti *et al*., 2006; Pawlowsky-Glahn & Buccianti, 2011). To overcome these issues a series of transformations can be applied to move compositional data from the simplex to the usual real space such as the centered log-ratio (*clr*) and the isometric log-ratio (*ilr*) transformations (Egozcue *et al*., 2003). The resulting new coordinates enable the use of classical statistical methods for their analysis. Due to the limits of a non-compositional approach, new compositional graphical-numerical methods were proposed for the study of the river water composition as a whole. In particular, special attention was paid on the investigation of data variability structure and spatio-temporal changes as valuable sources of information about the dynamics of complex riverine systems. The main techniques applied for data processing are the following.

i) Cascade approach of robust compositional *clr*-biplots to unveil different scales in the variability structure of the data.

ii) Applications of the robust Mahalanobis distance (RMD) between pairs of multivariate observations (Filzmoser *et al*., 2014) to detect compositional changes in the water chemistry both through the TRB and along the main course (iterative method). RMD of all samples was computed using the compositional center and covariance matrix of HT surface waters, considered representative of a pristine unpolluted condition.

iii) Creation of a sequence of isometric log-ratio coordinates, called Principal Balances (PBs), which successively maximize the explained variance in the total database (Martín-Fernández *et al*., 2017).

iv) PBs application to the winter-spring and summer (2017-2018) data sets separately in order to evaluate the influence of flood and droughts conditions on the water composition.

v) Study of *ilr* density distributions to highlight the presence of basins of attraction and investigation of system resilience to seasonal changes in the light of the methods proposed by Scheffer *et al*. (2012) and Dakos *et al*. (2014) for the detection of early warning signals in ecology and climate science.

vi) Robust factor analysis (RFA) to examine water-sediment interaction processes.

Furthermore, for most of the sampling sites, the corresponding watersheds were delineated using a GIS-based elaboration from the Digital Terrain Model of the TRB. After calculating the watersheds and their drainage divides, landscape properties, such as mean elevation, drainage area and slope, were calculated for each of the contributing areas. This was done for the purpose of evaluating the mutual relationships between morphological attributes of the contributing areas and the Total Dissolved Solids (TDS) of river waters at the outlets.

RESULTS AND DISCUSSION

The electrical conductivity of the analyzed river waters ranges between 262 and 5,190 µS/cm, measured at the TR source and mouth, respectively. The pH is around a median of 8.2 considering the whole catchment, with higher values measured within the Nera sub-basin. The water temperature ranges from 0.5°C to 25°C and rises moving to the southern part of the basin, as a result of decreasing elevation and different sampling seasons.

Both tributaries and the main river display a prevalent Ca^{2+}-HCO_3^- composition with few cases showing different hydrochemical facies. In the Gibbs diagram, TRB waters are located in the central sector of the plot, where water-rock interaction dominates as controlling factor of river chemistry, only a few of them being more affected by evaporation-precipitation processes and mixing with seawater.

However, the research was not supposed to be a classical study about the TRB chemistry but aimed to explore basin-scale processes from a multidisciplinary point of view and within the perspective of complex systems. To reach this purpose alternative statistical methods based on compositional data analysis were used for studying the geochemistry of surface waters and sediments.

Cascade through the TRB waters variability

In order to probe the structure and origin of the data variability, the *clr*-biplot approach has proved to be extremely effective, playing a fundamental role in the analysis of the relative behavior of chemical components compared to their compositional center (Gozzi *et al*., 2019). The cascade application of robust compositional biplots led to unveil different scales in the variability structure of the data, particularly in terms of major dissolved species. The higher part of the variability, dominated by N- species, appears to be closely associated with human activities diffused through the basin, resulting in a non-informative spatial analysis. On the contrary, the lower part of the variability well explains water-rock interaction processes within the different geological settings of the basin, showing a clear spatial dependence and enabling a geochemical characterization of TRB waters (Gozzi *et al*., 2019). In accordance with the biplot approach, the results of the application of PBs method also suggest the presence of a hierarchy in the variability of the water composition. Balances with high variability seem to be linked to multiple sources of solutes with a close relationship to human activities (Fig. 2a). By contrast, *ilr* coordinates characterized by low variability, *i.e.* $Cl^- \mid Na^+$ (2%) and $HCO_3^- \mid Ca^{2+}$ (1%), seem most likely related purely to water-rock interaction processes, such as weathering and dissolution reactions of limestones, silicates or evaporitic rocks. The symbol “|” separates variables at numerator and denominator in the log-ratios.

RMD as an early warning parameter

The results of the first RMD application to major elements revealed an increasing trend of compositional distances going downstream. This behavior could be explained by a cumulative effect due to the progressive mixing of waters with heterogeneous compositions and draining different types of watersheds in terms of lithology and landscape properties (Gozzi *et al.*, 2019). This pattern is typical of natural systems governed by interaction-dominant dynamics (multiplicative or interdependent systems) (van Rooij *et al.*, 2013).

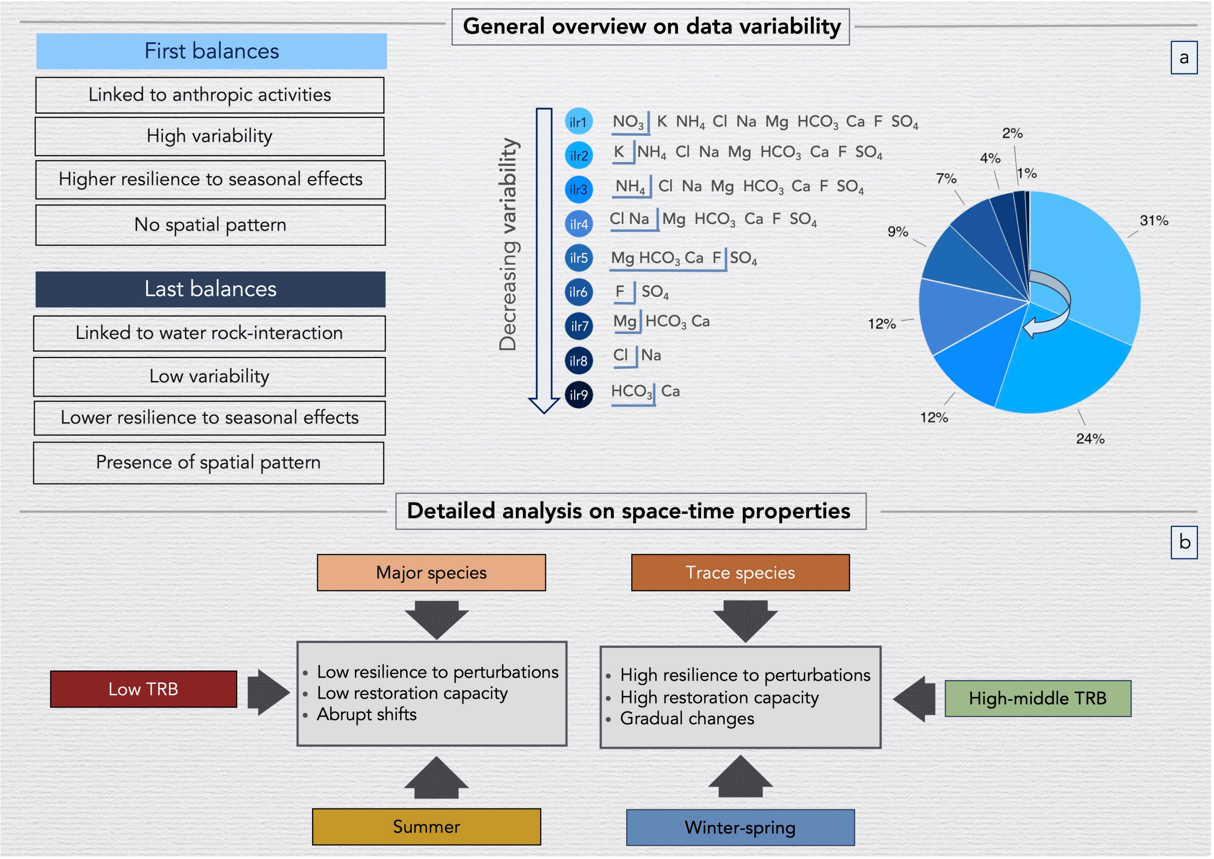

Fig. 2 - Comprehensive outline of the observations made regarding the dynamics characterising the Tiber River system: a) overview on data variability structure and b) analysis on space-time properties and resilience to compositional changes.

Each drainage basin contributes with multiple lithological signals, leading to multiplicative compositional changes with respect to the first pristine water composition. In the upper-medium reaches the main river is able to reduce the compositionally different inputs from the Topino-Marroggia River system due to the geological transition towards the carbonatic domain. Then, TR composition starts to significantly change, firstly after the relative inflow of the SO_4^{2-} contribution (Paglia-Chiani tributaries), and secondly with an abrupt shift after the Nera confluence. In fact, Nera waters dramatically affect TR composition producing an increase in terms of Cl^-, Na^+ and SO_4^{2-} solutes, due to the presence of the high flow rate Montoro-Stifone springs (Frondini *et al.*, 2012). The results of the iterative application of RMD, suggest that TR presents a high resilience to changes in its early to medium course, with a high capacity to restore and maintain its chemical composition after perturbations (Gozzi *et al.*, 2019). By contrast, a low resilience characterizes its low course which displays, after the Nera confluence, a critical shift towards an alternative state (composition) and a weak restoration capacity (Fig. 2b).

Seasonal shift in TRB waters

The *ilr* balances reveal a higher variability and smoother density distributions in summer with respect to those related to the winter-spring season. As a consequence, the respective basins of attraction are generally deeper during winter-spring time indicating a stronger resistance to changes (Fig. 2a, b). In fact, the deeper is the hole the greater energy is required to move the system out of the basin, preventing potential transition to alternative states (Dakos *et al*., 2010, 2014). Differently, during summertime, lower saddles can more easily favor the creation of possible alternative conditions, indicating weaker predictability and a high vulnerability of the river chemistry to potential perturbations. In fact, during droughts periods, TB is less able to absorb and dilute the disturbances caused by the Nera confluence, resulting in an abrupt and systematic shift of the TR composition towards an alternative state. By contrast, during winter-spring, subsidiary inputs from the surrounding watersheds are able to respond to the sudden change with a buffering action.

Stream sediments as a product of chemical-physical weathering and magnetic susceptibility

When exploring the dynamics of complex and heterogeneous river basins, such as the TRB, a joined-up approach encompassing both the geochemical composition of surface waters and stream sediments represents a valid aid. The results of the RFA for stream sediment data, performed in the framework of the CoDA approach, allowed the identification of five factors accounting for the majority of the data variability. The factors well explain different weathering processes linked to the heterogeneous geological setting of the catchment and possible pollution sources.

MS for TRB stream sediments has a median value of 42×10^{-8} m^3kg^{-1} and covers a wide range varying from a minimum of 7.0×10^{-8} m^3kg^{-1}, measured at the Tiber River source, to a maximum of $8{,}637\times10^{-8}$ m^3kg^{-1} at the Treia River in the volcanic area of the Mts. Sabatini. High values of susceptibility were detected especially in the LT basin linked to the different lithology of the area. However, the observations made by digital microscopy highlighted the presence of perfectly spherical particles that could derive from possible anthropic sources of pollution coming from the urban area of Rome. Anthropic activities might also be responsible for the high MC values measured in the carbonatic domain, which cannot be explained by the bedrock geology of this area.

Impact of landscape attributes

Understanding the complex interlinks and feedback dynamics between the different riverine media and the geo-environmental forcing agents is crucial to develop water system resilience. Nevertheless, the high number of possible drivers, the unique combination of attributes characterizing each catchment, and the lack of data at an adequate scale make this type of investigation rather difficult (Lutz *et al*., 2016). In this study, a first attempt has been done to relate the landscape attributes of each watershed with the TDS of the river waters. The results showed a clear influence of mean elevation and slope on the TDS measured at the outlets, especially for HT, MT and NE sub-basins. Instead, some samples show a completely independent behavior, thus indicating that surface-runoff and water-rock interaction processes are not able to explain the resulting TDS values. These outcomes proved to be particularly useful to discriminate between water chemistry mainly influenced by superficial processes and that affected by groundwater circulation.

CONCLUSIONS

The extensive field and analytical work carried out during this three-year project has led to achieve a general overview of the catchment from different perspectives, providing new data for a river basin which has driven very little attention so far. Data processing by means of the CoDA approach provided a double advantage, firstly it solved the mathematical issue concerning the compositional nature of geochemical data and secondly it enabled the study of TRB waters composition as a whole. This holistic aspect is crucial for a better understanding of riverine chemistry and its interlinks with the surrounding environment. From the research thesis, the following conclusions can be made.

i) The geochemical landscapes of the TRB were characterized in terms of river water, stream sediment composition and magnetic susceptibility, within the different geological and topographical settings of the basin.

ii) The geochemical landscapes are mainly the result of water-rock interaction and denudation processes within the corresponding catchment. Nevertheless, the research also highlighted a significant role of the diffuse anthropic activities in governing the water chemistry which reveals a high level of structural complexity characterized by a multi-scale variability.

iii) New methods and graphical numerical elaborations (*e.g.*, cascade approach of *clr*-biplots, PBs, RMD and application of ecological concepts) were proposed with the intention of opening completely new perspectives for the study of complex river systems from a multidisciplinary point of view.

iv) The methods provided an enhanced comprehension of the adaptive capacity and the resilience of TRB to changing conditions (*e.g.*, seasonal effects, compositional shifts), improving system predictability in face of potential pollution events or climatic variations.

v) In addition, this research also attempted to understand the relations between landscape properties of the watersheds and the chemical composition of surface waters, revealing, for TRB, a pivotal role of elevation and slope pattern.

An extension of this research is in progress in the light of the recently acquired discharge data and analytical results of the isotopic signature of TRB waters. Further developments will concern the analysis of the system from a thermodynamic perspective (Kleidon *et al.*, 2013) and the comparison of the results obtained for the TRB with data from other catchments in Italy and worldwide. The target is to find out possible universal behavior and natural laws useful to achieve a better comprehension of the factors controlling water system resilience.

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