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Can Geochemical Regime Shifts and Resilience be identified from Compositional Changes in Riverine Water?

Gozzi C.^{a,*}, Dakos V.^b, Buccianti A.^{a,c}, Vaselli O.^{a,c}

^a*University of Florence, Dept. of Earth Sciences, Via G. La Pira 4, 50121 Firenze, Italy;*

^b*ISEM, CNRS, Université de Montpellier, EPHE, IRD, 34095 Montpellier, France;*

^c*CNR-IGG Institute of Geosciences and Earth Resources, Via G. La Pira 4, 50121 Firenze, Italy*

Abstract

Rivers are dynamic and complex systems that constantly change their composition from sources to deltas. This is due to the influence of a set of variables controlled by hydro-litho-eco-atmospheric processes and anthropo-climate pressures which are, in turn, influenced by the catchment attributes. River water, compared to other environmental media, respond faster to disturbances, which are extensively and immediately reflected by the chemical composition of its waters. The paper explores the possibility to transpose the concept of ecological regime shift to river chemistry, by means of theoretical thoughts and a practical application to the case of the Tiber River (central Italy). Compositional Data Analysis (CoDA), robust Principal Component Analysis (PCA) and score-distance graphs were used to investigate data variability and the interlinks between response and forcing variables. The findings outline mechanisms and factors influencing the river self-restoring ability at a basin-wide scale, providing a better comprehension of the circumstances controlling the water system resilience, one of the major and most urgent challenges for the future of mankind.

Keywords: Regime shift, River chemistry, Environmental Science, Compositional Data Analysis

*Corresponding author, tel: +393394159892

Email address: caterinagozzi@unifi.it (Gozzi C.)

1. Introduction

Natural systems characterized by non-linear dynamics do not always respond smoothly and regularly to changing external conditions, as widely verified across different research fields, e.g. ecology, climate science, medicine and economy (e.g. Andersen et al., 2008; Rodionov, 2004; Dakos et al., 2010; Hirota et al., 2011). An ever-growing research effort on the identification of thresholds and regime shifts has been done especially regarding a broad range of ecological systems, from marine environments to forests and lakes (e.g. Dayton, 1985; Naiman et al., 1988; Lees et al., 2006; Beaugrand, 2004). In ecology, a regime shift is defined as an abrupt status change in the ecosystem caused by passing a threshold where core ecosystem functions, structures and processes are radically changed (Andersen et al., 2008; Scheffer et al., 2012; Dakos et al., 2014). These ecological shifts are generally driven by external perturbations (e.g. climatic fluctuations, overexploitation, eutrophication) or by inner dynamics of the system (Andersen et al., 2008). This subject represents a growing scientific discipline which has not experienced any application to river geochemistry so far. In literature, only few research works are present addressing water system resilience issue, but all of them mainly focused on the hydrologic perspective, i.e. water-table variations and ground-surface water interactions (e.g. H. Fuchsa et al., 2018; de la Hera-Portillo et al., 2020). The basic ingredient for a regime shift is the presence of positive feedback which drives the system toward an alternative state (Angeli et al., 2004). Even though this principle is widely applied for simple isolated systems (Scheffer et al., 2012), its implementation to highly heterogeneous and complex systems represents a challenge to these

26 days. In Earth Science, river catchments are an example of highly complex
 27 systems bearing properties such as self-organization, multi-scale variability,
 28 hydraulic and topographic gradients (Kleidon et al., 2013), patchiness, het-
 29 erogeneity and feedback dynamics. These features together with litho-hydro-
 30 eco-atmospheric processes and anthropo-climate pressures, jointly affect river
 31 water composition at various temporal and spatial scales. The knowledge of
 32 these complex interlinks plays a key role in both river basin management
 33 and water quality preservation from irreversible changes. The consequences
 34 of climate change will be immediately and sharply experienced by water,
 35 through significant modifications in water quantity, quality and distribution
 36 (WWF, 2019). The ever-growing population and its dependence on water
 37 for agriculture, transport, domestic, commercial and industrial activities is
 38 constantly increasing. Additionally, the demand for adequate water quality
 39 for domestic and health purposes will further increase for the prevention and
 40 mitigation of future pandemics (Cooper, 2020). Hence, water is an essential
 41 and defining element, a core variable in human and natural systems. As a
 42 consequence, the requirements for ensuring resilience in water systems should
 43 always guide trajectories and boundaries of human development (Boltz et al.,
 44 2019) and their understanding represents a key element for our future devel-
 45 opment. Since each river basin acts as a unique holistic system in tune with
 46 the climatic, geological and anthropogenic interactions, any study on the
 47 river system should consider river basin dynamics as a whole (Ramkumar
 48 et al., 2015). This implies the necessity to transcend subject barriers and to
 49 conduct interdisciplinary studies focused on basin-scale processes. Numerous
 50 researches suggest that the overall response of complex systems to changing

51 conditions and perturbations depends on properties including heterogeneity
52 of the components and their connectivity (e.g. Scheffer et al., 2012), revealing
53 the importance of an extensive investigation on the nature of these interac-
54 tions for river systems. The purpose of the paper is to verify whether an
55 application of the ecological regime shift theory is possible for water chem-
56 istry. This hypothesis was tested for the surficial waters of the Tiber River
57 (TR) in central Italy. The objective is to open up new avenues of research
58 that might enable an enhanced prediction of the geochemical response of
59 inland waters to environmental changes. The outcomes will be useful to de-
60 fine the critical/threshold limits that are able to guarantee the river system’s
61 self-restoration ability.

62 **2. Material and methods**

63 *2.1. Tiber River Basin overview*

64 The TR represents the seventh major contributing river to the Mediter-
65 ranean Sea according to annual discharge ($240 \text{ m}^3/\text{s}$) and its catchment is
66 the largest of peninsular Italy ($17,375 \text{ km}^2$). TR has its source in the Mt.
67 Fumaiolo at an altitude of 1,268 m and after flowing for 409 km, it enters
68 the Tyrrhenian Sea near Rome. During its course to the sea, five main
69 tributaries (Paglia-Chiani and Treia on the right bank and Chiascio-Topino,
70 Nera-Velino and Aniene on the left bank) flow into it (Fig. 1). The TRB falls
71 within the administrative borders of six different Italian regions, but almost
72 90% of its surface is in Umbria and Lazio, whereas the remaining 10% is in
73 Emilia Romagna, Tuscany, Marche and Abruzzo. The basin is located within
74 the heterogeneous geological-topographical environment of central Italy and

75 is defined by the following geomorphological boundaries: (i) the reliefs of
 76 Tuscan-Emilian Apennines towards N, (ii) the Umbrian-Marchean-Abruzzi
 77 Apennine ridge eastwards, (iii) Mt. Amiata (1,738 m), Sabatini, Vicani,
 78 Vulsini and Cimini mountains towards W and (iv) the Albani hills (956 m)
 79 southwards. The lithology varies from flysch sediments in the upper reaches,
 80 Apennine limestones to south-east and potassic and ultrapotassic volcanics
 81 towards south-west. The mean altitude is 520 m and only 6% of the total area
 82 of the basin exceeds 1,200 m, the highest peak being Mt. Velino (2,487 m),
 83 followed by Mt. Terminillo (2,213 m) and the Sibillini Mountains (Panichi
 84 et al., 2005). Land use in the basin is represented by agricultural areas
 85 (53%), forests (39%), urban areas, lakes and rock outcrops (5%) (Iadanza
 86 and Napolitano, 2006). Lowlands, covering almost 15% of the basin, are
 87 mainly located in the low course of the TR and distributed around the urban
 88 area of Rome and the inter-montane basins (Sansepolcro, Gubbio and Foligno
 89 valleys and the Rieti and Terni depressions). The precipitation regime in the
 90 TRB is defined as sub-coastal (two precipitation minimum values in summer
 91 and winter) to marine (a summer minimum and a winter maximum value).
 92 The mean annual precipitation is about 1,200 mm and ranges from 700 mm
 93 at sea level to 2,000 mm along the central ridge (Bagnini et al., 2005).

94 [Figure 1 about here.]

95 2.2. *The process of detecting regime shifts in river chemistry*

96 The process of identifying the presence of a geochemical regime shift
 97 (GRS) in water chemistry passes through the selection of potential environ-
 98 mental, anthropogenic and climatic drivers able to influence water compo-

99 sition either in time or space. Nevertheless, this first step may be rather
 100 complicated by the large number of factors involved in the analysis and the
 101 high level of interconnection between them. This point gets often more diffi-
 102 cult due to the lack of comprehensive data at an adequate scale. The second
 103 step is to identify the response variables that are to be considered for the
 104 monitoring of the evolution of riverine systems under changing conditions.
 105 From a geochemical point of view, the sentinel of the system state can be
 106 represented by the chemical composition of waters. Since the latter is made
 107 of several constituents (response variables), the state of the river can be mon-
 108 itored from different perspectives and at various scales by considering: (a)
 109 the water chemistry as a whole (e.g. Total Dissolved Solids), (b) major dis-
 110 solves species, (c) nutrients, (d) pollutants or (e) minor and trace elements.
 111 This choice is crucial since environmental drivers can change significantly
 112 depending on the considered response variables. Hence, detecting regime
 113 shifts in a water system requires firstly the identification of the endogenous
 114 and exogenous variables influencing the system function (Boltz et al., 2019).
 115 The third step is to search for potential thresholds and tipping points driven
 116 by the interaction of those variables also considering the possibility of al-
 117 ternative systems states. The flip between different states in networks of
 118 populations, ecosystems or banks, is driven by the level of heterogeneity and
 119 connectivity of the system (Scheffer et al., 2012). Low connectivity coupled
 120 with high heterogeneity might cause the network to change gradually, rather
 121 than abruptly in response to changing conditions. On the contrary, homoge-
 122 neous and highly connected networks try to resist the change until they reach
 123 a critical threshold for a systematic transition (Scheffer et al., 2012; Dakos

et al., 2014, 2010). A stream network is made of nested structures characterized by a fractal geometry resulting in an apparently highly connected system, in which each branch converges in a greater one through a cascade process until reaching the river mouth (Rinaldo et al., 1993; Tarboton et al., 1988), as represented in the scheme of Figure 4. However, drainage divides separating each watershed provide a certain level of structural independence, a feature that can help to ensure a higher system resilience. In fact, feedback loops and connectivity through the river network are possible only following the flow direction and adjacent watersheds cannot affect each other due to the presence of geomorphological boundaries. By contrast, in ecological systems interactions between neighbors are often possible in multiple directions, a feature that can lead to a domino effect and potentially critical transitions. Nevertheless, the inherent structure of the drainage network guarantees a certain grade of inner resilience mainly for the areas further upstream. Going downstream, the progressive mixing of heterogeneous waters having different geochemical origins and suffering multiple pressures is a complex factor that can trigger an abrupt compositional shift or provide a buffering effect through dilution processes.

An additional issue to be considered when determining a GRS in river chemistry is that most environmental pressures influencing river systems cannot be removed or altered to probe the system response. This technique is often used in laboratory tests to verify the answer of organisms to changing environmental conditions in order to predict critical limits for their survival (e.g. Griffiths and Philippot, 2013). This method is not directly applicable when considering complex river basins, nevertheless, an analogous approach

could be used by comparing similar catchments with a great difference on the level of a single driver (e.g. mono-genetic vs geologically heterogeneous, natural- vs anthropic-dominated) or by likening geochemical data for the same basin at different spatial or temporal scales during which a variation of a certain external parameter is expected. In this research, we focused on possible basin-wide chemical variations induced by the spatial changes of some potential environmental drivers considering the intrinsically complex TRB catchment.

2.3. River water dataset and drivers selection

The geochemical dataset used in this work is part of the Ph.D. research conduct by Gozzi (2020), which involved a comprehensive survey on 222 surface waters within the TRB. As a first attempt, the possibility of a spatial Geochemical Regime Shift (GRS) was tested on the chemical composition of the main course of the Tiber River. Overall 38 water samples were considered for the analysis and were collected as follows: 19 during 2017 (13 in the High-Medium Tiber (HMT) during the winter time and 6 in the Low Tiber (LT) during summer) and 19 sampled during 2018 (6 in the LT during winter and 13 from the HMT during the summer). All samples were collected at a distance of about 20 km from one another, starting from the source area (Fig. 1). With the purpose of getting an overview on the hydrological conditions during the sampling time, TR hydrographs at the Ripetta flow gauge during 2017 and 2018 are shown in Figure 2a and 2b, respectively. Discharge data were kindly supplied by Regional Functional Centre - Lazio Region (2020). Mean daily discharges are highlighted in the graphs corresponding to spring and summer sampling days. The hydrographs show that samples

174 refer, with a good approximation, to different flow conditions (high and low),
 175 although spread over two years (2017-2018). For each sample, major cations
 176 (Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+), anions (Cl^- , SO_4^{2-} , F^- , HCO_3^- and NO_3^-)
 177 and minor and trace species (Mn, Fe, SiO_2 , Sr, Rb, Ba and B), were consid-
 178 ered for the GRS analysis. Br^- and PO_4^{3-} species as well as Ni, Co, Cu and
 179 Zn were not included in the analysis because the percentage of values below
 180 the lower detection limit (LDL) was higher than 40 % of the total number of
 181 observations. The few remaining values below the LDL were replaced by 2/3
 182 of the detection limit (Martín-Fernández et al., 2003). Major species enable
 183 the identification of the main hydrochemical facies of the water, revealing the
 184 origin of solutes and evolutionary processes. Conversely, the concentration of
 185 trace elements in surface water more often depends on changing geochemical
 186 conditions, such as pH and redox conditions, which influence their presence
 187 or removal from the water column. Therefore, it is important to evaluate the
 188 response of water chemistry considering both the hierarchical levels of the
 189 composition. Further details regarding sampling and analytical methods are
 190 given in Gozzi (2020).

191 The drainage area was estimated from the Digital Elevation Model (DEM)
 192 and was therefore used as a core variable for the evaluation of the selected
 193 forcing parameters. For each watershed, sampling sites define the outlets of
 194 each contributing area, which is expected to influence the chemical composi-
 195 tion of the respective water sample along the main course (Fig. 1). The DEM
 196 was obtained from Copernicus Land Monitoring Service (2019b) (EU-DEM
 197 version 1.1, zone E40N20; 25 m resolution) and then resampled to a lower
 198 resolution of 100 m for better handling and faster processing. The hydrologic

analysis was performed using the Spatial Analyst and the Hydrology Tool present in ArcGIS. Once delineated the 19 watersheds and their drainage divides, the following landscape properties were estimated: drainage area (ha), mean elevation (m) and slope ($^{\circ}$). The latter were obtained considering not only the calculated basins but all the nested watersheds contributing to the selected outlets. For the estimation of the human impact for each basin, the Global Human Influence Index Dataset of the Last Wild Project, Version 2, 2005 (LWP-2) was used. The index produced by Wildlife Conservation Society and Center for International Earth Science Information Network - Columbia University (2005) is a global dataset of 1-kilometer grid cells, created from nine global data layers covering human population pressure (population density), human land use and infrastructure (built-up areas, nighttime lights, land use/land cover), and human access (coastlines, roads, railroads, navigable rivers). Precipitation data were downloaded from WorldClim 2.0 Beta version 1 (June 2016), where average monthly climate data are available as GeoTiff files for the period 1970-2000 (Fick and Hijmans, 2017). Mean rainfall was estimated for each area using ArcGIS considering the month corresponding to each sampling campaign. Land cover and main lithotypes layers were derived from Copernicus Land Monitoring Service (2019a) and ISPRA Ambiente (2017), respectively. Due to the high number of classes representing different lithotypes and soil use compared to the number of water samples, only the most relevant variables were considered for the GRS analysis. The latter were chosen based on their importance with reference to the total drainage area. In accordance with the stream-graphs represented in Figure 3, sand-silicatic sequences and carbonatic rocks were considered as

224 main geological drivers while forests and arable lands as land use ones.

225 [Figure 2 about here.]

226 [Figure 3 about here.]

227 2.4. *Compositional methods: the solution for an holistic approach*

228 In Geosciences, problems involving compositional data, such as spurious
229 correlations, negative bias, subcompositional incoherence and constrained
230 sample space are well known in literature starting from Aitchison (1982).
231 A reliable analysis of geochemical data should take into consideration their
232 compositional nature. The Compositional Data Analysis Approach (CoDA)
233 starts from the assumption that it is the relative variation of chemical compo-
234 nents the matter of interest, rather than the absolute one (Pawlowsky-Glahn
235 and Egozcue, 2006; Buccianti et al., 2006). Relative behavior means that
236 the information lies in the ratios between the components, not in the abso-
237 lute values (Pawlowsky-Glahn and Egozcue, 2020). Besides, as highlighted
238 by Gozzi et al. (2019, 2020), the CoDA approach provides the possibility
239 to study a chemical composition as a whole leaving aside the investigation
240 of single variables. This holistic aspect is fundamental for the detection of
241 possible regime shifts in riverine chemistry since it enables to investigate
242 simultaneous interactions among water constituents and the complex sur-
243 rounding environment. A solution to deal with CoDa is expressed by the
244 principle of *working on coordinates* (Pawlowsky-Glahn and Buccianti, 2011).
245 Compositional data can be transformed into new real coordinates by means

of transformations, thus allowing the use of classical statistical and geostatistical methods without any further issue. In this research, the centered log-ratio (clr) transformation was applied. It consists of dividing each component x_i by the geometric mean $g(\mathbf{x})$ of all the considered parts, represented, in our case, by the chemical species. The related complete formula is shown in Equation (1):

$$\text{clr}(\mathbf{x}) = \left(\ln \frac{x_i}{g(\mathbf{x})} \right)_{i=1, \dots, D} \quad \text{with} \quad g(\mathbf{x}) = \sqrt[p]{x_1 \cdot x_2 \cdots x_D}. \quad (1)$$

As a result, the obtained clr-coordinates contain within themselves the information about the interlinks between each element and the barycentre of the entire composition.

2.4.1. Robust PCA and analysis of PCs spatial series

Clr-transformed data were used to create robust compositional biplots investigating TR data variability for the different sampling periods. The R package Robcompositions (Templ et al., 2011) was used to perform a robust PCA in a compositional context. The obtained scores and loadings were then used as input factors within the R package Factoextra (Kassambara and Mundt, 2019) which provides more effective graphical tools to display the PCA results. Among these, particularly effective is the possibility to color PCs scores according to the value of an additional variable. This was used to perform a first exploratory analysis to verify potential associations between water chemistry variability and the magnitude of different environmental drivers. Successively, to better evaluate the linkages between water compositions and forcing factors the following steps were performed. First, PCA

268 was run for major, trace elements and drivers separately (Martín-Fernández
 269 et al., 2018). Secondly, chemical PCs scores were plotted together with driver
 270 scores versus the distance from the source area. All scores were normalized
 271 to have mean 0 and standard deviation (sd) 1 using the scale function in R
 272 for an easier comparison. Before performing the PCA, the driver dataset was
 273 also rescaled to make data comparable with each other. The target is to ver-
 274 ify the presence and spacing of a potential GRS along the TR and define the
 275 main chemical response variables (crl-coordinates) and environmental pres-
 276 sures characterizing each regime. This approach is similar to that used by
 277 Mollmann et al. (2009) in time series of ecological parameters for the Central
 278 Baltic Sea. Nevertheless, herein it is implemented for spatial data with new
 279 graphical-numerical tools which includes a compositional approach.

280 [Figure 4 about here.]

281 **3. Results**

282 *3.1. Response variables: major and trace species variability*

283 In this Section the results of the robust compositional PCA for the TR
 284 waters are described. In Figure 5 the resulting clr-biplot for major elements
 285 is shown, together with the loading plots of the first two components. Scores
 286 are colored according to the sampling time, while symbols mark the different
 287 location (HMT or LT). The variable labels (e.g. Cl^- , SO_4^{2-}) in the plot
 288 represent the clr transformed data of the corresponding species. Most of
 289 the clr-variance is accounted by the first dimension with 71% of the total
 290 variability, the second dimension explaining only 14%.

[Figure 5 about here.]

In the covariance biplots, rays length is proportional to the variability of the clr-variable and the attention is mainly focused on the links between the vertices of the rays (Daunis-I-Estadella et al., 2006). On the first component, NO_3^- , NH_4^+ , K^+ , and Cl^- , Na^+ , SO_4^{2-} log-ratios, having positive and negative loadings, respectively, are well represented in the projection and their rays are almost collinear. These variables are the ones showing the highest variability. On the second dimension, the largest contribution is provided by F^- log-ratio, while Ca^{2+} , Mg^{2+} , HCO_3^- exhibit shorter rays and tight links, showing a similar pattern of variability. On the clr-biplot, links between the rays Na^+ - F^- and F^- - NO_3^- are orthogonal, thus indicating a low correlation for the corresponding clr-variables. The biplot highlights the different log-ratio associations characterizing the composition of the river stretches (HMT and LT) under varying hydrologic conditions. In particular, it may be observed that the importance of N-bearing species in relation to the compositional barycenter increases in the HMT and especially during the drought period. On the other hand, the association of Cl^- , Na^+ , SO_4^{2-} clr-variables mark the lower reaches of the river, with higher relative increments during the dry season. The obtained PCs scores were then colored according to the magnitude of the main drivers, also including the drainage area. The outcomes for morphological, land use and geo-climatic parameters are displayed in Appendix 1 as supplementary materials (Figs. A.1, A.2, A.3, respectively). The outcomes reveal interesting patterns and possible environmental-chemical correlations, which deserve to be further investigated by means of a joint analysis. The robust clr-biplot for minor and trace (s.l. trace) elements jointly with

the corresponding loading plots is shown in Figure 6. It accounts for the 85% of the overall variability, 54% on the first and 31% on the second dimension, respectively.

[Figure 6 about here.]

The PCs projection well represents the Fe, Rb and Ba log-ratios which show the longest rays and higher variability, while Sr and SiO₂ are not properly rendered. Even in this case, all groups seem to stand out, with B and Rb log-ratios mainly dominating in LT while those of Fe, Mn and B characterizes the upper reaches.

3.2. Forcing variables: environmental drivers variability

The robust biplot for the selected drivers jointly with the corresponding loading plots is shown in Figure 7. In this case, the interpretation of the biplot follows classical rules, since we deal with non-compositional variables. The plot explains about 88% of the total variability, the first and the second dimension accounting for 70% and 18%, respectively.

[Figure 7 about here.]

Drivers' variability on the first component is mainly guided by geo-climatic factors: sand-silicatic sequences and rainfall are predominant in HTM (negative scores), while carbonatic lithotypes characterize the LT area (positive scores). The right shift of PC scores during drought conditions reflects the difference in precipitations values since other parameters do not change depending on the season. Considering the second component, arable lands and

338 HII on positive loadings oppose to forests, slope and elevation factors on neg-
 339 ative ones, thus highlighting the different dominating features for the upper
 340 (nos. 1-8, 20-27) and medium (nos. 9-13, 28-32) TR.

341 3.3. *Linking response and forcing variables: distance-PCs graphs*

342 In this section, PCs scores for response and forcing variables are plotted
 343 together versus the distance from the TR source to detect the presence and
 344 spacing of a potential GRS. Hereinafter, for the sake of clarity, chemical PC1
 345 scores of major species are called Chemical Index 1 (Ch1) while those of
 346 minor and trace elements, Trace Chemical Index 1 (TCh1) and likewise PC2
 347 scores (Ch2 and TCh2). Similarly, drivers PC1 and PC2 scores are named
 348 Forcing Index 1 (Fc1) and Forcing Index 2 (Fc2), respectively.
 349 In Figure 8(a,c) distance-PCs graphs are shown for major compounds in the
 350 two different hydrological conditions.

351 [Figure 8 about here.]

352 The Wald-Wolfowitz Runs Test (Wald and Wolfowitz, 1940) performed
 353 for all indexes reveals that the data are not random (p-value < 0.05), and
 354 the Augmented Dickey-Fuller test (Fuller, 1996) indicates that the sequences
 355 are not stationary (p-value > 0.05, null hypothesis accepted). Along the
 356 HMT, Ch1 generally show positive scores, indicating the relative dominance
 357 of NO_3^- , NH_4^+ , K^+ species. In this area, only a couple of negative values are
 358 detected just after the river source during flood conditions, thus suggesting a
 359 greater contribution of Cl^- and Na^+ . Downstream, an abrupt negative com-
 360 positional shift (predominance of Cl^- , Na^+ and SO_4^{2-}) is detected at 248 km,
 361 once Nera waters enter the main course, as also shown by Gozzi et al. (2019)

362 by means of the robust pairwise Mahalanobis distance. Successively, values
 363 seem to slightly increase for the next sampling point, in particular during
 364 high flow periods, stabilizing afterwards. After a remarkable change next to
 365 the source, Fc1 exhibits an overall ascending trend featured by a step-wise
 366 behavior with three different steps in both cases (Fig. 8 a, c). The pattern of
 367 Fc1 mainly represents the gradual change geo-climatic drivers, starting from
 368 a dominance of sand-silicatic and rainfall in the HMT (negative scores) to
 369 carbonate rocks in the LT (positive scores) (see also Fig. 7). In the lower
 370 plots (Fig. 8 b, d), deviations from median values of the indexes along the
 371 river course are represented, as a robust measure of change from the barycen-
 372 ter. The two bar-plots help to more easily identify potential bonds between
 373 response and forcing variables. Looking at deviations on the HMT, no clear
 374 interlink between the two indexes can be noticed, even if both of them gen-
 375 erally increase going downstream. On the contrary, in the LT, the change
 376 from positive to negative deviations of Ch1 exactly matches the variation
 377 from negative to positive ones of Fc1, and this association is kept up to the
 378 river mouth.
 379 Since even small changes of external parameters can yield non-linear response
 380 of the system, analogous distance-PCs graphs were also created which com-
 381 pare Ch1 to Fc2 (Fig. 9 a-c).

382 [Figure 9 about here.]

383 Fc2 also shows a step-like behavior changing from a major influence of slope,
 384 forests and elevation parameters (negative scores) in the upper reaches, to
 385 dominance of HII and arable lands in the Medium Tiber (positive scores) and

386 to values close to the median on the last river stretch (see also Fig. 7). In the
 387 early course, during flood conditions Ch1 and Fc2 exhibit a similar behavior,
 388 suggesting a possible mutual interlink (Fig. 9a). Conversely, during summer,
 389 Ch1 is more stable near the source, but then it also increases (dominance of
 390 NO_3^- , NH_4^+ and K^+) when the pressure of HII and arable land rises relatively
 391 to forest and morphological parameters (Fig. 9c). In the LT, deviations of
 392 Fc2 from the median are low compared to the remarkable changes monitored
 393 by Ch1 (Fig. 9b-c), which means a poor interconnection. Herein, we mainly
 394 focus on Ch1, since it accounts for the majority of the chemical variability,
 395 but additional distance-PCs graphs for Ch2 are illustrated in Figures S.4-
 396 S.5 (Supplementary Materials). Once explored the river chemistry from the
 397 perspective of its major compounds, we then looked into the composition
 398 in terms of its minor and trace elements, which represent one of the main
 399 sources of pollution in the aquatic environment. TCh1 and Fc1 are compared
 400 versus the distance from the source in Figure 10, jointly with the bar-plots
 401 indicating the respective deviations from their median values.

402 [Figure 10 about here.]

403 Similarly, statistical tests reveal that data sequences are neither random nor
 404 stationary, but characterized by spatial trends along the river path. TCh1
 405 exhibits negative scores (dominance of Fe, Ba and Mn) in the upper-course
 406 followed by a transition period with values close to the medians and then
 407 positive scores in its lower part (dominance of Rb and B). TCh1 behavior is
 408 overall cumulative with some small fluctuations, especially when moving to
 409 the LT (Fig. 10a,c). The pattern appears to be gradual never showing sudden

410 changes. Nevertheless, a possible turning point can be placed at 203 km, in
 411 correspondence of the transition between HMT and LT, which also matches
 412 the occurrence of volcanic formations (Fig. 3). Comparing the two hydro-
 413 logic conditions, TCh1 shows bigger deviations from the median in the HMT
 414 during high discharge periods (Fig. 10b) with respect to the corresponding
 415 plot for the dry season (Fig. 10d). Geo-climatic drivers (Fc1) seem to reflect
 416 fairly well the global evolution at basin-scale of the composition in terms of
 417 the higher trace elements variability with only a few differences. Considering
 418 the lower variability, TCh2 displays a stable trend with only some chemi-
 419 cal changes approaching the river mouth and poor interconnections with the
 420 considered forcing factors (Fig. S6, Supplementary Materials). For further
 421 details regarding other combinations of indexes for trace elements refer to
 422 Supplementary Materials.

423 4. Discussion

424 4.1. Geochemical response of TR waters to environmental changes

425 The robust PCA enabled to pull out the most relevant chemical and forc-
 426 ing variables dominating TR variability, also considering the river chemistry
 427 from an holistic point of view by means of the CoDA approach. Figure 5
 428 gives prominence, on the first dimension, to two different associations of clr-
 429 variables (NO_3^- , NH_4^+ , K^+ vs Cl^- , Na^+ , SO_4^{2-}) that describe a great amount
 430 of variability (about 70%). Considering PC1, the barycenter of the biplot
 431 separates HMT waters dominated by N-bearing species from those from LT
 432 having a major sodium-chlorinated contribution. The analysis of the joint
 433 behavior of Ch1 and Fc1 (geo-climatic drivers) (Fig. 8a-d), reveals a match

434 between the abrupt shift towards a sodium-chlorinated feature of Ch1 and
 435 the variation of Fc1 from a dominance of sand-silicatic sequences and rainfall
 436 to that of carbonate rocks. Hence, the increasing portion of the watershed
 437 covered by carbonatic lithotypes belonging to the Appennine Ridge (Nera
 438 sub-basin) seems to determine the relative increase of Cl^- , Na^+ and SO_4^{2-}
 439 in TR waters. From a geochemical perspective, this interlink is apparently
 440 unclear since the interaction with carbonatic rocks is expected to provide a
 441 major relative contribution of Ca^{2+} , HCO_3^- ions. Nevertheless, the knowl-
 442 edge of the underlying geological substratum associated with the carbonate
 443 domain and the predominance in the area of infiltration over run-off processes
 444 (Boni et al., 1986), help to explain the reason for the obtained association.
 445 In fact, the chemical change can be understood by considering the role of
 446 groundwater circulation and more specifically the important input of the
 447 high- pCO_2 , high-salinity springs such as those of Stifone-Montoro (e.g. Boni
 448 et al., 1986) located by the Nera river gorge. These high flow rate springs
 449 ($15 \text{ m}^3/\text{s}$) are fed by water circulating in the Narni-Amelia regional aquifer
 450 system and reacting with the hosting rocks, mainly consisting of dolostones,
 451 limestones and evaporites (Frondini et al., 2012). This sub-surface water-rock
 452 interaction sharply increases the salinity of Nera waters and determine the
 453 shift towards a sodium-chlorinated composition of TR after the confluence
 454 with the tributary. As a result, it is possible to assume that the Ch1-Fc1
 455 association defines LT chemistry as mainly guided by a natural geochemical
 456 process induced by the changing pressure of geo-climatic drivers. Instead,
 457 these drivers seem to play a more marginal role in conditioning the compo-
 458 sition of HMT river waters. The analysis of the joint behavior of Ch1 and

459 Fc2 (Fig. 10) explore the influence of the lower part of the drivers' variability
 460 (holding both morphological and land use pressures) on the higher part of the
 461 chemical one. In the early the TR course, there is a slight relative increase
 462 of Cl^- , Na^+ which appear to be linked with a higher impact of slope, forests,
 463 and elevation pattern (Fig. 10a) as well as with sand-silicatic sequences and
 464 rainfall according to Fc1. This behavior might be due to the major con-
 465 tribution of rainfall to the river flow in the steep mountainous area during
 466 winter-spring, leading to a higher relative amount of Cl^- Na^+ derived from
 467 marine inputs in rainwater. This hypothesis is supported by the different
 468 response of Ch1 in the upper reaches during flood and drought conditions
 469 (Fig. 10a,c), the latter being more stable and thus less influenced by mor-
 470 phological and climatic drivers described by Fc1 and Fc2.

471 Going downstream, N-bearing species dominates the HTM composition, until
 472 the above-mentioned tipping point occurring at 248 km, after the confluence
 473 with the Nera river. Ch1 and Fc2 exhibit a similar behavior, suggesting a
 474 potential linkage with the increasing pressure, on the corresponding drainage
 475 area, of arable lands and HII. The dominance of the association of NO_3^- , NH_4^+ ,
 476 and K^+ clr-variables can be the result of diffuse inputs from urban and agri-
 477 cultural areas or animal husbandry practices (Meybeck, 1982; Peierls et al.,
 478 1991; Deutsch et al., 2006; Harrison et al., 2019). Therefore, the Ch1-Fc2 as-
 479 sociation enabled to define two main geochemical-environmental interaction
 480 processes characterizing the HTM: a first one of natural origin mainly guided
 481 by morphological features and dependent on seasonal variations, and a sec-
 482 ond one, largely influenced by the pressure of anthropic activities on TRB
 483 territory. Differently, Fc2 is not able to explain the shift of Ch1 in the LT

484 which is mainly related to Fc1 (geo-climatic drivers). In fact, Figure 10b,d)
 485 highlights that Fc2 deviations from the medians are almost null both at the
 486 beginning and for the entire spacing of the compositional change.
 487 Turning to consider trace elements, we evaluate a response variable that rep-
 488 resents a different hierarchical level of the water composition. TCh1 smoothly
 489 reflects the variations of the Fc1 and consequently the changing proportion
 490 of lithotypes in the drained area. Fe, Mn, and Ba log-ratios dominance in
 491 the HMT can be the result of weathering processes of terrigenous deposits.
 492 Differently, LT is mainly typified by Rb and B log-ratios stemming from
 493 water-rock interaction processes with potassic and ultra-potassic volcanic
 494 complexes of the Vulsini, Cimini and Sabatini districts and by a possible in-
 495 fluence of the hydrothermal springs located by the Aniene river course (e.g.
 496 Acque Albule and Salone-Acqua Vergine).

497 *4.1.1. What is that makes a common chemical change a GRS?*

498 Once marked out the geochemical response to the spatial variation of the
 499 selected external agents, the target was to understand if a GRS can be con-
 500 sidered as a possible feature for the TR or more broadly for water systems.
 501 Among the observed variations the abrupt change detected by Ch1 could
 502 represent a possible GRS since it meets the following requirements: i) it rep-
 503 represents a relevant and sudden chemical change; ii) the new chemical state
 504 is maintained in space and time (different seasons); iii) the shift is driven
 505 by the change of an environmental pressure; iv) the new condition appears
 506 irreversible and affect the self-healing function of TR waters. One of the key
 507 issues is to explain why after the geologically-induced shift, the composition
 508 is not able to restore itself to previous conditions. From the geochemical

509 perspective the ratio between the discharges of the TR before and after the
 510 confluence with the Nera river, drastically influences the concentrations of
 511 Cl^- , Na^+ , SO_4^{2-} measured after the mixing point. This factor determines
 512 the magnitude of the shift compared to the compositional barycenter. Nev-
 513 ertheless, once the composition is shifted to the new state, the system shows
 514 a small level of restoration capacity, which appears to be slightly influenced
 515 by the different flood conditions (Fig. 8). This can be linked to the catch-
 516 ment properties and particularly to the lower connectivity during summer
 517 due to less water supply from the surrounding areas. Moreover, it is impor-
 518 tant to consider that the upper reaches of the TR are characterized by a
 519 torrential and turbulent regime, whereas the end course, after the confluence
 520 with the Nera river, is featured by a slow and meandering flow as a result
 521 of the decreasing elevation. These features can also influence the restoring
 522 capacity of the river after the change. In fact, in low flow rate zones, sed-
 523 imentation prevails upon erosional processes generating lower connectivity
 524 and weaker ground-surface water interchanges with respect to the upstream
 525 areas. Nevertheless, the absence of pressures from positive buffering drivers
 526 for the water quality such as rainfall and forested lands can also have a role in
 527 the observed pattern. The conservative nature of Cl^- and Na^+ elements and
 528 the presence of geochemical barriers avoiding precipitation also contribute
 529 maintaining the new chemical state to the river mouth. From this perspec-
 530 tive, it is possible to state that a GRS exists along the Tiber river course.
 531 The latter represents not just an important geochemical change monitored
 532 by a shift in dominant solutes with respect to the compositional barycenter
 533 of the waters, but also a change that is spatially conserved by means of the

joint effect of several endogenous and exogenous environmental factors and catchment attributes. These influencing agents consist of geochemical properties of the solutes, least rainfalls, changed land use from forest- to human impact- dominated, lower connectivity, surficial-ground water interchanges and seasonal effects. Trace elements pattern show modularity gradually adjusting themselves to changes, thus indicating a higher adaptive capacity of the system to perturbations. This behavior could be linked to the greater trace elements affinity to the solid phase. In fact, they can easily precipitate under varying Eh-pH conditions and can therefore be removed from the aqueous phase and get sequestered in stream sediments (Kabata-Pendias, 2015). The results obtained by the practical example of the TR flow highlighted the concept that considering a change in a single external agent is often not sufficient to explain the water chemistry variations which are the results of a complex environment acting in tune. Nevertheless, the proposed approach could represent a starting point for the analysis of the water chemistry from a new holistic perspective.

5. Conclusions

Due to the extreme importance of river water for human and natural systems, transcending subject barriers and analyzing rivers from a holistic and interaction-based point view is crucial to understand the complexity of basin-wide processes. This work, even though considering a limited amount of data, attempted to understand the connections between the TR composition and the spatial changes of some potential environmental pressures. The robust PCA investigated relevant compositional and forcing variables while

558 distance-PCs graphs highlighted their potential interlinks, thus providing an
559 enhanced prediction of the geochemical response of the TR waters to en-
560 vironmental changes (e.g. pollution or climatic extremes events) The main
561 conclusions of the research are summarized in the following points:

- 562 • HMT is the river stretch more resilient to changes. Its lower chemical
563 variability in the early course is mainly associated with morphological
564 drivers (i.e. forests, slope and elevation), and in the middle course
565 the increasing pressures of arable lands and HII are not able to affect
566 significantly the composition of its water.

- 567 • Differently, a GRS was detected in LT waters as a result of an impor-
568 tant geochemical change in its main species with reference to the com-
569 positional barycenter. The new chemical state is spatially maintained
570 thanks to the joint effect of different drivers and catchment properties,
571 revealing a low resilience of the LT to external perturbations. In this
572 case, the abrupt change in the water system is triggered by a single
573 driver, but the subsequent interactions with the surrounding environ-
574 ment (land use, morphology, climate and HII) are those that actually
575 defined the change as a GRS.

- 576 • Drought conditions generally increase TR water variability in the LT
577 and are able to influence the restoration capacity of the system. This
578 implies that the greater severity of droughts periods induced by climate
579 change represents a threatening factor for TR water self-restoring abil-
580 ity. On the contrary, rainy periods appear to have a major influence
581 on the chemical variability of the early TR course.

582 • The outcomes also revealed that major and trace dissolved species re-
583 spond in a different way to external changes, representing, for the aque-
584 ous phase, the lesser and the major resilient portion of the composition,
585 respectively.

586 The natural extension of this research will be focused not only on the main
587 TR course but on the entire catchment, considering the entire dataset of 222
588 river waters which includes major, minor tributaries and streams. This will
589 enable to encompass a larger number of drivers (e.g. morphometric indexes,
590 run-off, discharge, connectivity) for a more comprehensive assessment of the
591 mutual relationships between river chemistry and environmental pressures.
592 Under this condition, further investigations will be possible on the interlinks
593 between the river basin structure and its energy through the evaluation of
594 its thermodynamic properties. In fact, river systems have an inherent supply
595 of potential energy driven by topographic gradients which is expressed and
596 dissipated in many different ways, such as the creation of complex tree-like
597 drainage networks (Kleidon et al., 2012, 2013).

598 In conclusion, this research represents the first effort in literature to under-
599 stand and transpose the ecological approach of regime shift detection to river
600 geochemistry. Even if with some differences and difficulties, an application
601 to river chemistry is possible and represents an interesting path of research.
602 The recent COVID-19 pandemic highlighted the importance of using holistic
603 methods for an enhanced knowledge of the resilience of the natural environ-
604 ment. Deterioration of riverine water quality due to natural/anthropogenic
605 impacts is linked to ecosystem degradation, loss of biodiversity and therefore
606 human health. As a result, one of the most urgent challenges for the future of

607 mankind is to find out, despite the uniqueness of each river basin, universal
608 mechanisms and natural laws able to preserve water system resilience.

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Figure 6: Robust compositional biplot for clr-transformed minor and trace species data jointly with PCs loading plots. Scores are represented in different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively.

Figure 7: Robust biplot for drivers data jointly with PCs loading plots. Scores are represented in different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively. The considered drivers are the following: arable lands (AL), Human Impact Index (HII), carbonate rocks (Carb.), sand-silicatic successions (Sand-Silic.), forests, slope and elevation (Elev.).

Figure 8: Chemical Index 1 and Forcing index 1 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and (b) bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS, while the colored areas in (b) and (d) highlight the distance for which the new state is preserved.

Figure 9: Chemical Index 1 and Forcing index 2 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and (b) bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS.

Figure 10: Trace Chemical Index 1 and Forcing index 1 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS.