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

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## 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

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## 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

124 et al., 2014, 2010). A stream network is made of nested structures charac-  
125 terized by a fractal geometry resulting in an apparently highly connected  
126 system, in which each branch converges in a grater one through a cascade  
127 process until reaching the river mouth (Rinaldo et al., 1993; Tarboton et al.,  
128 1988), as represented in the scheme of Figure 4. However, drainage divides  
129 separating each watershed provide a certain level of structural independence,  
130 a feature that can help to ensure a higher system resilience. In fact, feedback  
131 loops and connectivity trough the river network are possible only following  
132 the flow direction and adjacent watersheds cannot affect each other due to  
133 the presence of geomorphological boundaries. By contrast, in ecological sys-  
134 tems interactions between neighbors are often possible in multiple directions,  
135 a feature that can lead to a domino effect and potentially critical transitions.  
136 Nevertheless, the inherent structure of the drainage network guarantees a cer-  
137 tain grade of inner resilience mainly for the areas further upstream. Going  
138 downstream, the progressive mixing of heterogeneous waters having differ-  
139 ent geochemical origins and suffering multiple pressures is a complex factor  
140 that can trigger an abrupt compositional shift or provide a buffering effect  
141 through dilution processes.

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

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

### 157 *2.3. River water dataset and drivers selection*

158 The geochemical dataset used in this work is part of the Ph.D. research  
159 conduct by Gozzi (2020), which involved a comprehensive survey on 222 sur-  
160 face waters within the TRB. As a first attempt, the possibility of a spatial  
161 Geochemical Regime Shift (GRS) was tested on the chemical composition of  
162 the main course of the Tiber River. Overall 38 water samples were consid-  
163 ered for the analysis and were collected as follows: 19 during 2017 (13 in the  
164 High-Medium Tiber (HMT) during the winter time and 6 in the Low Tiber  
165 (LT) during summer) and 19 sampled during 2018 (6 in the LT during winter  
166 and 13 from the HMT during the summer). All samples were collected at  
167 a distance of about 20 km from one another, starting from the source area  
168 (Fig. 1). With the purpose of getting an overview on the hydrological condi-  
169 tions during the sampling time, TR hydrographs at the Ripetta flow gauge  
170 during 2017 and 2018 are shown in Figure 2a and 2b, respectively. Discharge  
171 data were kindly supplied by Regional Functional Centre - Lazio Region  
172 (2020). Mean daily discharges are highlighted in the graphs corresponding  
173 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 ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ ), anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ )  
177 and minor and trace species (Mn, Fe,  $\text{SiO}_2$ , Sr, Rb, Ba and B), were consid-  
178 ered for the GRS analysis.  $\text{Br}^-$  and  $\text{PO}_4^{3-}$  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

199 analysis was performed using the Spatial Analyst and the Hydrology Tool  
200 present in ArcGIS. Once delineated the 19 watersheds and their drainage di-  
201 vides, the following landscape properties were estimated: drainage area (ha),  
202 mean elevation (m) and slope ( $^{\circ}$ ). The latter were obtained considering not  
203 only the calculated basins but all the nested watersheds contributing to the  
204 selected outlets. For the estimation of the human impact for each basin, the  
205 Global Human Influence Index Dataset of the Last Wild Project, Version  
206 2, 2005 (LWP-2) was used. The index produced by Wildlife Conservation  
207 Society and Center for International Earth Science Information Network -  
208 Columbia University (2005) is a global dataset of 1-kilometer grid cells, cre-  
209 ated from nine global data layers covering human population pressure (popu-  
210 lation density), human land use and infrastructure (built-up areas, nighttime  
211 lights, land use/land cover), and human access (coastlines, roads, railroads,  
212 navigable rivers). Precipitation data were downloaded from WorldClim 2.0  
213 Beta version 1 (June 2016), where average monthly climate data are available  
214 as GeoTiff files for the period 1970-2000 (Fick and Hijmans, 2017). Mean  
215 rainfall was estimated for each area using ArcGIS considering the month  
216 corresponding to each sampling campaign. Land cover and main lithotypes  
217 layers were derived from Copernicus Land Monitoring Service (2019a) and  
218 ISPRA Ambiente (2017), respectively. Due to the high number of classes  
219 representing different lithotypes and soil use compared to the number of wa-  
220 ter samples, only the most relevant variables were considered for the GRS  
221 analysis. The latter were chosen based on their importance with reference to  
222 the total drainage area. In accordance with the stream-graphs represented  
223 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 (Pawłowsky-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 (Pawłowsky-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* (Pawłowsky-Glahn and Buccianti, 2011).  
245 Compositional data can be transformed into new real coordinates by means



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

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

252 As a result, the obtained clr-coordinates contain within themselves the in-  
253 formation about the interlinks between each element and the barycentre of  
254 the entire composition.

#### 255 *2.4.1. Robust PCA and analysis of PCs spatial series*

256 Clr-transformed data were used to create robust compositional biplots  
257 investigating TR data variability for the different sampling periods. The R  
258 package Robcompositions (Templ et al., 2011) was used to perform a robust  
259 PCA in a compositional context. The obtained scores and loadings were  
260 then used as input factors within the R package Factoextra (Kassambara  
261 and Mundt, 2019) which provides more effective graphical tools to display  
262 the PCA results. Among these, particularly effective is the possibility to color  
263 PCs scores according to the value of an additional variable. This was used to  
264 perform a first exploratory analysis to verify potential associations between  
265 water chemistry variability and the magnitude of different environmental  
266 drivers. Successively, to better evaluate the linkages between water compo-  
267 sitions 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 (clr-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.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) 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%.

291 [Figure 5 about here.]

292 In the covariance biplots, rays length is proportional to the variability of  
293 the clr-variable and the attention is mainly focused on the links between the  
294 vertices of the rays (Daunis-I-Estadella et al., 2006). On the first component,  
295  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  log-ratios, having positive and negative  
296 loadings, respectively, are well represented in the projection and their rays  
297 are almost collinear. These variables are the ones showing the highest vari-  
298 ability. On the second dimension, the largest contribution is provided by  $\text{F}^-$   
299 log-ratio, while  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  exhibit shorter rays and tight links, show-  
300 ing a similar pattern of variability. On the clr-biplot, links between the rays  
301  $\text{Na}^+$ - $\text{F}^-$  and  $\text{F}^-$ - $\text{NO}_3^-$  are orthogonal, thus indicating a low correlation for the  
302 corresponding clr-variables. The biplot highlights the different log-ratio asso-  
303 ciations characterizing the composition of the river stretches (HMT and LT)  
304 under varying hydrologic conditions. In particular, it may be observed that  
305 the importance of N-bearing species in relation to the compositional barycen-  
306 ter increases in the HMT and especially during the drought period. On the  
307 other hand, the association of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  clr-variables mark the lower  
308 reaches of the river, with higher relative increments during the dry season.  
309 The obtained PCs scores were then colored according to the magnitude of the  
310 main drivers, also including the drainage area. The outcomes for morpho-  
311 logical, land use and geo-climatic parameters are displayed in Appendix 1 as  
312 supplementary materials (Figs. A.1, A.2, A.3, respectively). The outcomes  
313 reveal interesting patterns and possible environmental-chemical correlations,  
314 which deserve to be further investigated by means of a joint analysis.  
315 The robust clr-biplot for minor and trace (s.l. trace) elements jointly with

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

319 [Figure 6 about here.]

320 The PCs projection well represents the Fe, Rb and Ba log-ratios which  
321 show the longest rays and higher variability, while Sr and SiO<sub>2</sub> are not prop-  
322 erly rendered. Even in this case, all groups seem to stand out, with B and Rb  
323 log-ratios mainly dominating in LT while those of Fe, Mn and B characterizes  
324 the upper reaches.

### 325 *3.2. Forcing variables: environmental drivers variability*

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

331 [Figure 7 about here.]

332 Drivers' variability on the first component is mainly guided by geo-climatic  
333 factors: sand-silicatic sequences and rainfall are predominant in HTM (neg-  
334 ative scores), while carbonatic lithotypes characterize the LT area (positive  
335 scores). The right shift of PC scores during drought conditions reflects the  
336 difference in precipitations values since other parameters do not change de-  
337 pending 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  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  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  $\text{Cl}^-$  and  $\text{Na}^+$ . Downstream, an abrupt negative com-  
360 positional shift (predominance of  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ ) 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  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ) 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 chr-  
429 variables (  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  vs  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  ) 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  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$   
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  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  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<sub>2</sub>, 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 m<sup>3</sup>/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 (Froncini 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  $\text{Cl}^-$ ,  $\text{Na}^+$  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  $\text{Cl}^-$   $\text{Na}^+$  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  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  
476 and  $\text{K}^+$  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  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  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  $\text{Cl}^-$  and  $\text{Na}^+$  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

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

## 550 **5. Conclusions**

551 Due to the extreme importance of river water for human and natural  
552 systems, transcending subject barriers and analyzing rivers from a holistic  
553 and interaction-based point view is crucial to understand the complexity of  
554 basin-wide processes. This work, even though considering a limited amount  
555 of data, attempted to understand the connections between the TR composi-  
556 tion and the spatial changes of some potential environmental pressures. The  
557 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 reveling 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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### 615 **References**

- 616 Aitchison, J., 1982. The Statistical Analysis of Compositional Data. *Journal of*  
617 *the Royal Statistical Society Series B* 44(2), 139–177.
- 618 Andersen, T., Carstensen, J., Hernandez-Garcia, E., Duarte, C., 2008. Ecological  
619 thresholds and regime shifts: approaches to identification. *Trends in Ecology*  
620 *and Evolution* 24, 49–57.
- 621 Angeli, D., Ferrell Jr., E., Sontag, E., 2004. Detection of multistability, bifurca-  
622 tions, and hysteresis in a large class of biological positive-feedback systems, in:  
623 *Proc. Natl. Acad. Sci. U.S.A.*, p. 1822.
- 624 Bagnini, S., Bruschi, S., Castellano, F., Colatosti, G., Gatta, L., Malvati, P.,  
625 Moretti, D., Ruisi, M., Terranova, I., Traversa, P., Vitale, V., Villani Conti, C.,  
626 Verga, V., 2005. Tevere Pilot River Basin Article 5 Report: pursuant to the  
627 water framework directive. Gangemi Editore spa, Roma, 175pp.



628 Beaugrand, G., 2004. The North Sea regime shift: evidence, causes,  
629 mechanisms and consequences. *Progress in Oceanography* , 245–  
630 262doi:10.1016/j.pocean.2004.02.018.

631 Boltz, F., Poff, N., Folke, C., Kete, N., Brown, C., Freeman, S., Matthews, J.,  
632 Martinez, A., Rockström, J., 2019. Water is a mater variable: Solving for  
633 resilience in the modern era. *Water Security* 8.

634 Boni, C., Bono, P., Capelli, G., 1986. Hydrogeological scheme of central Italy.  
635 *Memories of the Italian Geological Society* 35, 991–1012. [in Italian].

636 Buccianti, A., Mateu-Figueras, G., Pawlowsky-Glahn, V., 2006. Compositional  
637 Data Analysis in the Geosciences: From Theory to Practice. volume 264(1-10).  
638 Geological Society, London, Special Publications, 207pp.

639 Cooper, R., 2020. Water Security beyond Covid-19. Technical Report. Brighton,  
640 UK: Institute of Development Studies.

641 Copernicus Land Monitoring Service, 2019a. Corine land cover. URL:  
642 <https://land.copernicus.eu/pan-european/corine-land-cover/clc2018>.

643 Copernicus Land Monitoring Service, 2019b. EUDEM Digital Surface Model.  
644 URL: <https://land.copernicus.eu/imagery-in-situ/eu-dem/eu-dem-v1.1>.

645 Dakos, V., Carpenter, S., van Nes, E., Scheffer, M., 2014. Resilience indicators:  
646 prospects and limitations for early warnings of regime shifts. *Philosophical*  
647 *Transactions of the Royal Society B* 370(20130263), 1–10.

648 Dakos, V., van Nes, E.H., Donangelo, R., Fort, H., Scheffer, M., 2010. Spatial cor-  
649 relation as leading indicator of catastrophic shifts. *Theoretical Ecology* 177(3),  
650 163–174.

- 651 Daunis-I-Estadella, J., Barceló-Vidal, C., Buccianti, A., 2006. Exploratory compo-  
652 sitional data analysis. Geological Society, London, Special Publications 264(1),  
653 161–174.
- 654 Dayton, P., 1985. Ecology of kelp communities. *Annu.Rev.Ecol.Syst.* 16, 215–245.
- 655 Deutsch, B., Mewes, M., Liskow, I., Voss, M., 2006. Quantification of dif-  
656 fuse nitrate inputs into a small river system using stable isotopes of oxy-  
657 gen and nitrogen in nitrate. *Organic Geochemistry* 37, 1333 – 1342.  
658 doi:<https://doi.org/10.1016/j.orggeochem.2006.04.012>.
- 659 Fick, S., Hijmans, R., 2017. Worldclim 2: New 1-km spatial resolution climate  
660 surfaces for global land areas. *International Journal of Climatology* .
- 661 Frondini, F., Cardellini, C., Caliro, S., G. Chiodini, G., Morgantini, N., 2012. Re-  
662 gional groundwater flow and interactions with deep fluids in western Apennine:  
663 the case of Narni-Amelia chain (Central Italy). *Geofluids* 12, 182–196.
- 664 Fuller, W.A., 1996. *Introduction to Statistical Time Series*. second ed. ed., New  
665 York: John Wiley and Sons.
- 666 Gozzi, C., 2020. Weathering and transport processes investigated through the  
667 statistical properties of the geochemical landscapes: the case study of the Tiber  
668 river basin (Central Italy). Ph.D. thesis. University of Pisa, Department of  
669 Earth Sciences.
- 670 Gozzi, C., Filzmoser, P., Buccianti, A., Vaselli, O., Nisi, B., 2019. Statistical  
671 methods for the geochemical characterisation of surface waters: The case study  
672 of the Tiber River basin (Central Italy). *Computers and Geosciences* 131, 80–88.

- 673 Gozzi, C., Sauro Graziano, R., Bucciante, A., 2020. Part–Whole Relations: New  
674 Insights about the Dynamics of Complex Geochemical Riverine Systems. *Min-*  
675 *erals* 10. doi:doi:10.3390/min10060501.
- 676 Griffiths, B.S., Philippot, L., 2013. Insights into the resistance and resilience  
677 of the soil microbial community. *FEMS Microbiology Reviews* 37, 112–129.  
678 doi:10.1111/j.1574-6976.2012.00343.x.
- 679 H. Fuchsa, E., C. Carrollb, K., P. King, J., 2018. Quantifying groundwater re-  
680 siliance through conjunctive use for irrigated agriculture in a constrained aquifer  
681 system. *Journal of Hydrology* 565, 747–759.
- 682 Harrison, S., McAree, C., Mulville, W., Sullivan, T., 2019. The problem of agricul-  
683 tural ‘diffuse’ pollution: Getting to the point. *Science of The Total Environment*  
684 677, 700 – 717. doi:https://doi.org/10.1016/j.scitotenv.2019.04.169.
- 685 de la Hera-Portillo, A., López-Gutiérrez, J., Zorrilla-Miras, P., Mayor, B., López-  
686 Gunn, E., 2020. The Ecosystem Resilience Concept Applied to Hydrogeological  
687 Systems: A General Approach. *Water* 12. doi:doi:10.3390/w12061824.
- 688 Hirota, M., Holmgren, M., H. Van Nes, E., Scheffer, M., 2011. Global Resilience  
689 of Tropical Forest and Savanna to Critical Transitions. *Science* 334, 232–235.  
690 doi:10.1126/science.1210657.
- 691 Iadanza, C., Napolitano, F., 2006. Sediment transport time series in the Tiber  
692 River. *Physics and Chemistry of the Earth* 31, 1212–1227.
- 693 ISPRA Ambiente, 2017. Geoportale Ispra Ambiente. URL:  
694 <http://geoportale.isprambiente.it/sfoglia-il-catalogo/?lang=en>.
- 695 Kabata-Pendias, A., 2015. Trace Elements in Abiotic and Biotic Environments.  
696 CRC Press, Taylor and Francis Group, 458 pp.

- 697 Kassambara, A., Mundt, F., 2019. factoextra: Extract and Vi-  
698 sualize the Results of Multivariate Data Analyses. URL:  
699 <https://CRAN.R-project.org/package=factoextra>. R package version  
700 1.0.6.
- 701 Kleidon, A., Zehe, E., Ehret, U., Scherer, U., 2012. Thermodynamics, maximum  
702 power, and the dynamics of preferential river flow structures on continents.  
703 *Hydrol. Earth Syst. Sci. Discuss.* 9. doi:doi:10.5194/hessd-9-7317-2012.
- 704 Kleidon, A., Zehe, E., Ehret, U., Scherer, U., 2013. Thermodynamics, maximum  
705 power, and the dynamics of preferential river flow structures at the continental  
706 scale. *Hydrology and Earth System Sciences* 17, 225–251.
- 707 Lees, K., Pitois, S., Scott, C., Frid, C., Mackinson, S., 2006. Characterizing regime  
708 shifts in the marine environment. *Fish Fish.* 7, 104–127.
- 709 Martín-Fernández, J., Barceló-Vidal, C., Pawlowsky-Glahn, V., 2003. Dealing with  
710 Zeros and Missing Values in Compositional Data Sets. *Mathematical Geology*  
711 35(3), 253–278.
- 712 Martín-Fernández, J.A., Olea, R.A., Ruppert, L.F., 2018. Compositional Data  
713 Analysis of Coal Combustion Products with an Application to a Wyoming Power  
714 Plant. *Mathematical Geosciences* 50, 639–657.
- 715 Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers.  
716 *American Journal of Science* 282, 401–450. doi:10.2475/ajs.282.4.401.
- 717 Mollmann, C., Diekmann, R., Muller-Karulis, B., Kornilovs, G., Plikshs, M. Axe,  
718 P., 2009. Reorganization of a large marine ecosystem due to atmospheric and  
719 anthropogenic pressure: a discontinuous regime shift in the Central Baltic Sea.  
720 *Global Change Biology* 15, 1377–1393.

- 721 Naiman, R., Johnston, C., Kelley, J., 1988. Alteration of North-American streams  
722 by beaver. *Bioscience* 38, 753–762.
- 723 Panichi, C., Giuliano, G., Preziosi, E., Gherardi, F., Droghieri, E., 2005. Hydro-  
724 chemical and Isotopic Characterisation of the Base Flow in the Tiber Basin.  
725 Relations between Surface Waters and Groundwaters. volume 124. Romana  
726 Editrice, 113pp.
- 727 Pawlowsky-Glahn, V., Buccianti, A., 2011. *Compositional Data Analysis: Theory*  
728 *and Applications*. John Wiley & Sons Ltd., 400pp.
- 729 Pawlowsky-Glahn, V., Egozcue, J., 2006. Compositional data and their analysis:  
730 an introduction, in: *Compositional Data Analysis in the Geosciences: From*  
731 *Theory to Practice*. Geological Society, London, Special Publications. volume  
732 264, pp. 1–10.
- 733 Pawlowsky-Glahn, V., Egozcue, J., 2020. *Compositional Data in Geostatistics:*  
734 *A Log-Ratio Based Framework to Analyze Regionalized Compositions*. *Math*  
735 *Geosci* doi:<https://doi.org/10.1007/s11004-020-09873-2>.
- 736 Peierls, B., N. Caraco, M.P., Cole., J.J., 1991. Human influence on river nitrogen.  
737 *Nature* 350, 386–387.
- 738 Ramkumar, M., Muthuvairavasamy, K., Kumaraswamy, K., Mohanraj, R., 2015.  
739 *Environmental Management of River Basin Ecosystems*. Springer Earth System  
740 Sciences, pp.761.
- 741 Regional Functional Centre - Lazio Region, 2020. URL:  
742 <http://www.idrografico.regione.lazio.it/>.

743 Rinaldo, A., Rodriguez-Iturbe, I., Rigon, R., Ijjasz-Vasquez, E., Bras, R.L.,  
744 1993. Self-organized fractal river networks. *Phys. Rev. Lett.* 70, 822–825.  
745 doi:10.1103/PhysRevLett.70.822.

746 Rodionov, S., 2004. A sequential algorithm for testing climate regime shifts. *Geo-*  
747 *phys. Res. Lett.* 31. doi:10.1029/2004GL019448.

748 Scheffer, M., Carpenter, S., Lenton, T., Bascompte, J., Brock, W., Dakos, V.,  
749 van de Koppel, J., van de Leemput, I., Levin, S., van Nes, E., Pascual, M.,  
750 Vandermeer, J., 2012. Anticipating critical transitions. *Science* 338, 344–348.

751 Tarboton, D.G., Bras, R.L., Rodriguez-Iturbe, I., 1988. The fractal  
752 nature of river networks. *Water Resources Research* 24, 1317–1322.  
753 doi:10.1029/WR024i008p01317.

754 Templ, M., Hron, K., Filzmoser, P., 2011. *robCompositions: an R-package for*  
755 *robust statistical analysis of compositional data.* John Wiley & Sons Ltd.

756 Wald, A., Wolfowitz, J., 1940. On a test whether two samples are  
757 from the same population. *The Annals of Mathematical Statistics* 11.  
758 doi:http://projecteuclid.org/euclid.aoms/1177731909.

759 Wildlife Conservation Society and Center for International Earth Science Infor-  
760 mation Network - Columbia University, 2005. Last of the Wild Project, Version  
761 2, 2005 (LWP-2): Global Human Influence Index (HII) Dataset (Geographic)  
762 URL: <https://doi.org/10.7927/H4BP00QC>.

763 WWF, 2019. Climate change and water, why valuing rivers is critical to adaptation.  
764 Technical Report. WWF.

## List of Figures

- 1 Map of the TRB showing the drainage network and the sampling locations along the TR, which also represents the outlets of the calculated watersheds. Each colored surface represents the new contributing area which adds up to the ones upstream for the watershed delineation of the selected outlet. . . . . 37
- 2 Mean daily discharge in  $\text{m}^3/\text{s}$  measured during 2017 (a) and 2018 (b) at the Ripetta flow gauge on the Tiber river. River discharge during spring and summer sampling days are highlighted in the hydrograph in blue and red color, respectively. . 38
- 3 Streamgraph of the lithotypes and land use characterizing the different drainage areas along the Tiber river course. Lithotypes from top to bottom (not in stratigraphic sequence): sand-silicatic sequences, karstic carbonate rock, carbonate rocks, marls and clays, riverine deposits, volcanic rocks. Land use from top to bottom: water bodies, shrub-herbaceous vegetation association, permanent crops, open spaces with little or no vegetation, heterogeneous agricultural areas, forests, artificial areas, arable lands. . . . . 39
- 4 a) Scheme of the main catchment properties influencing the response to forcing agents; b) Flowchart summarizing the GRS delineation process. . . . . 40

5	Robust compositional biplot for clr-transformed major species data jointly with PCs loading plots. Scores are represented with different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively. . . . .	41
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. . . . .	42
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.). . . . .	43
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. . . . .	44



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. . . . . 45
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. . . . . 46

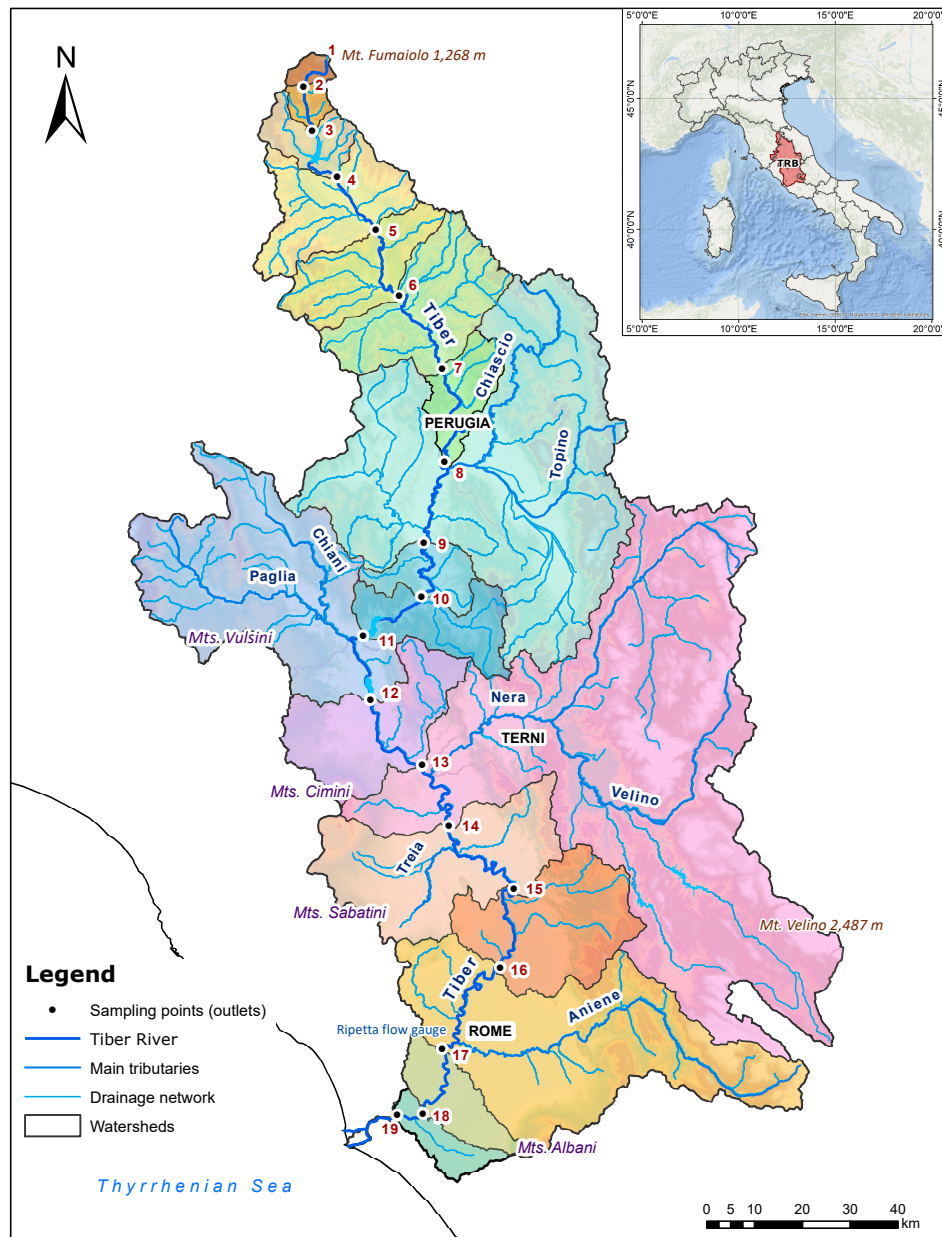


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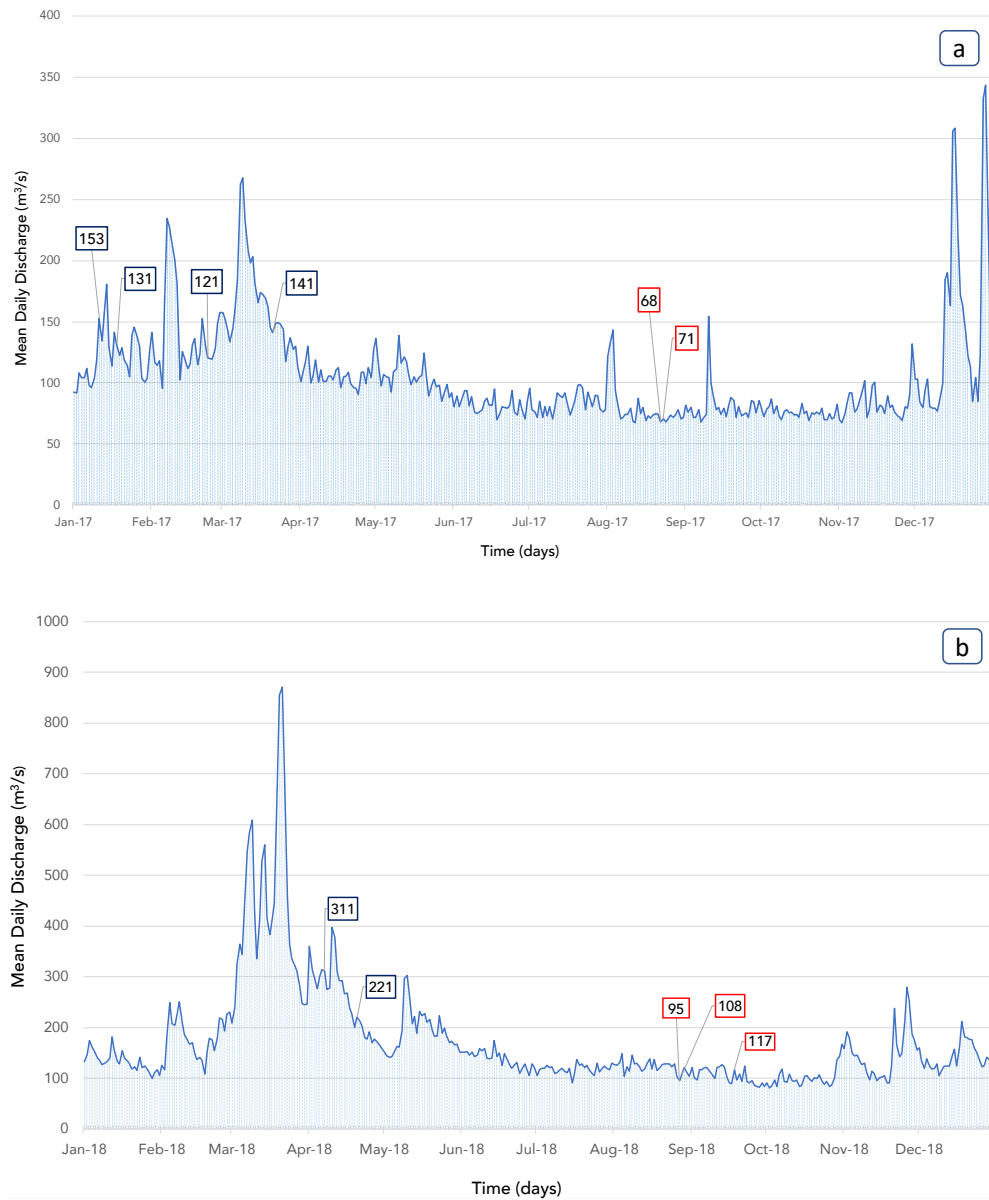


Figure 2: Mean daily discharge in  $m^3/s$  measured during 2017 (a) and 2018 (b) at the Ripetta flow gauge on the Tiber river. River discharge during spring and summer sampling days are highlighted in the hydrograph in blue and red color, respectively.

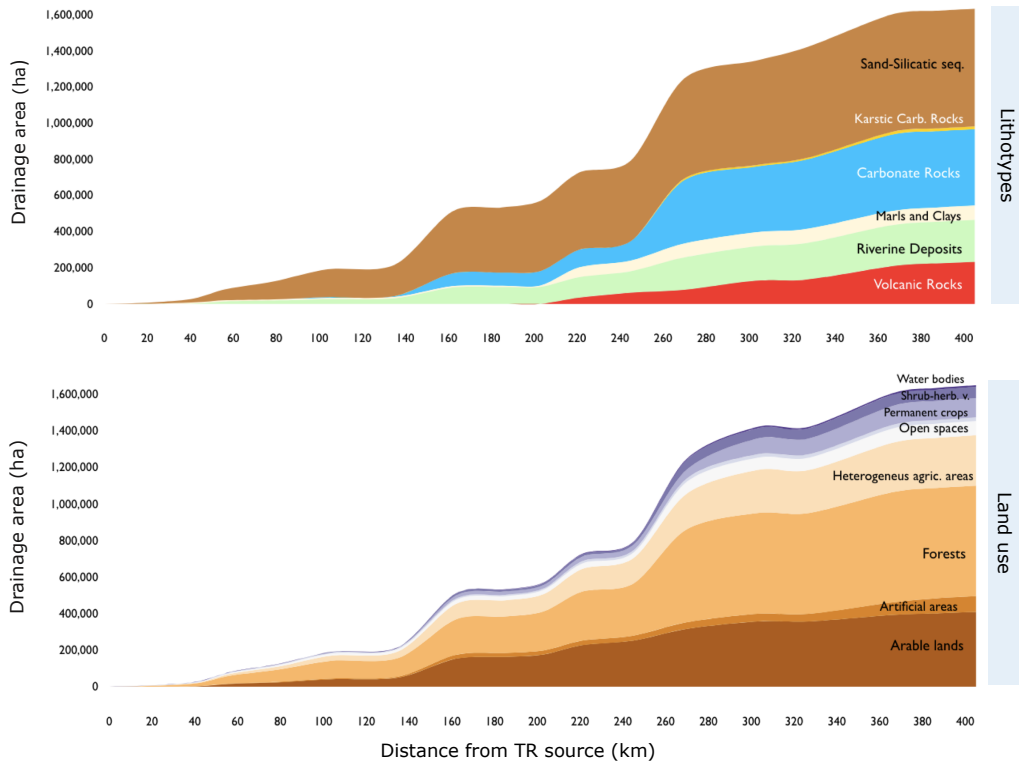


Figure 3: Streamgraph of the lithotypes and land use characterizing the different drainage areas along the Tiber river course. Lithotypes from top to bottom (not in stratigraphic sequence): sand-silicatic sequences, karstic carbonate rock, carbonate rocks, marls and clays, riverine deposits, volcanic rocks. Land use from top to bottom: water bodies, shrub-herbaceous vegetation association, permanent crops, open spaces with little or no vegetation, heterogeneous agricultural areas, forests, artificial areas, arable lands.

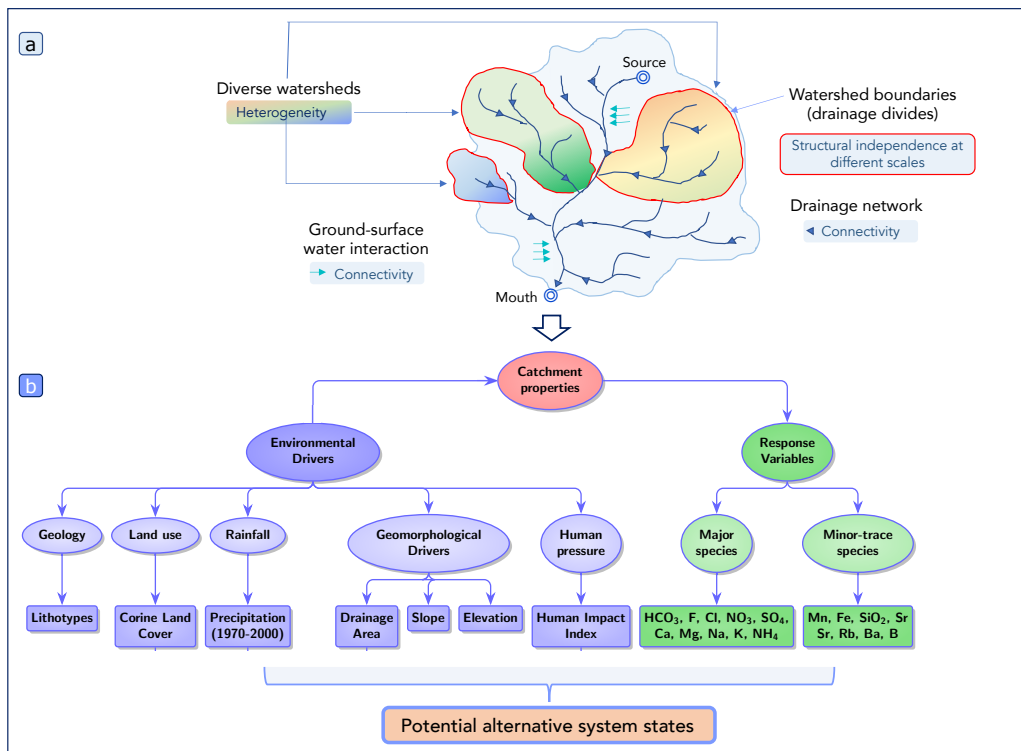


Figure 4: a) Scheme of the main catchment properties influencing the response to forcing agents; b) Flowchart summarizing the GRS delineation process.

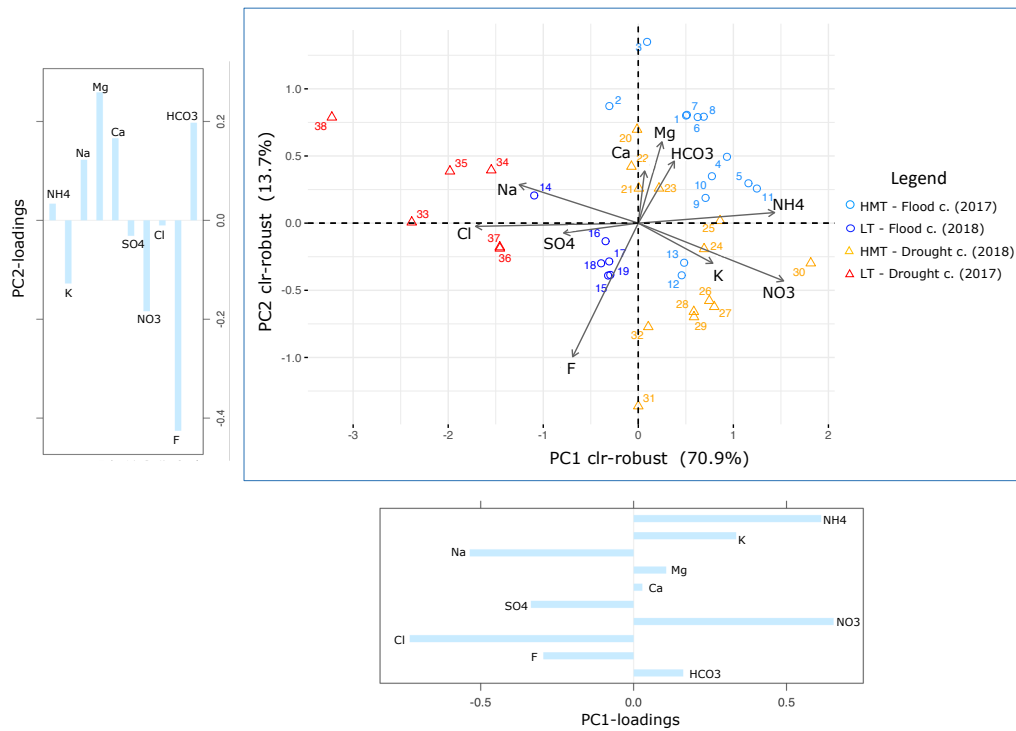


Figure 5: Robust compositional biplot for clr-transformed major species data jointly with PCs loading plots. Scores are represented with different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively.

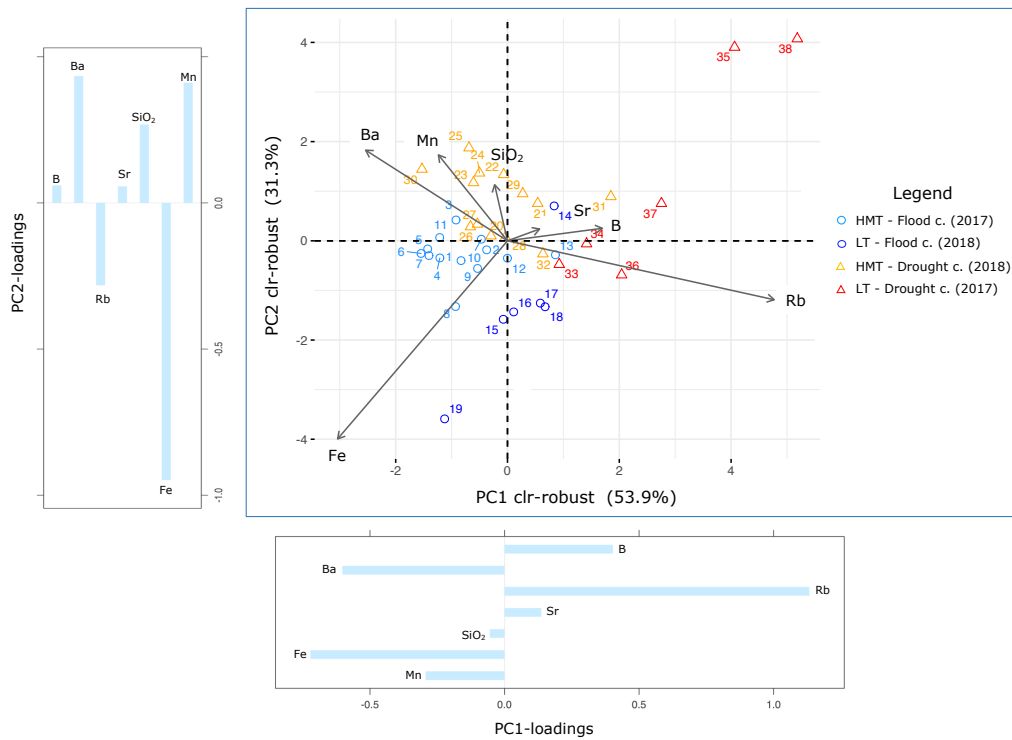


Figure 6: Robust compositional biplot for clr-transformed minor and trace species data jointly with PCs loading plots. Scores are represented in different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively.

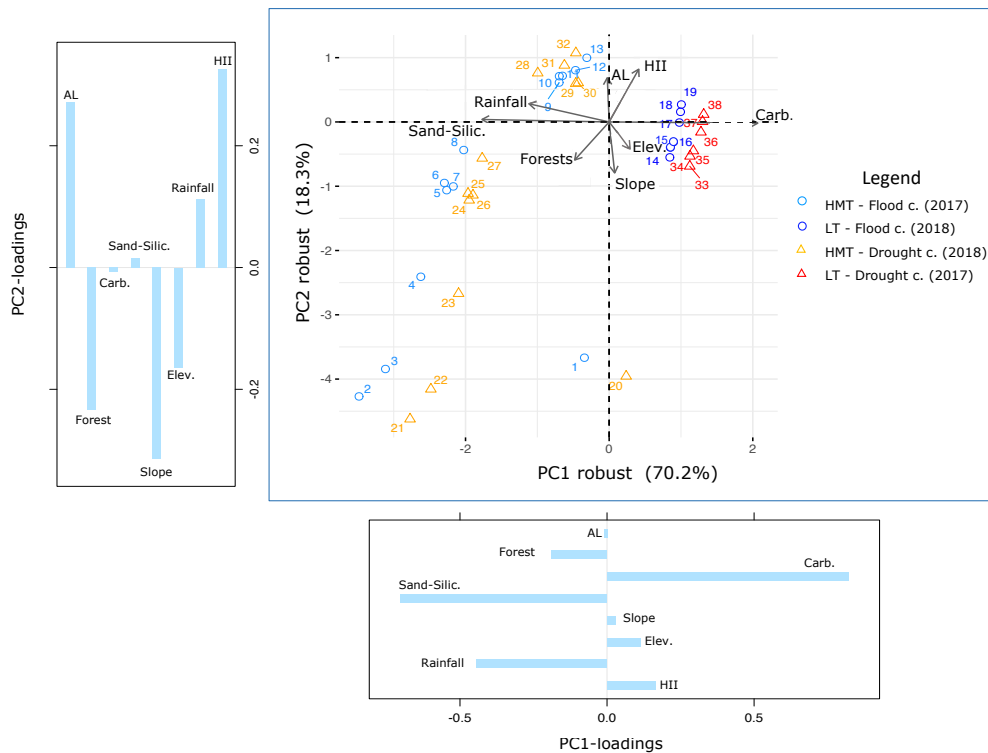


Figure 7: Robust biplot for drivers data jointly with PCs loading plots. Scores are represented in different symbols and colors according to the sampling location (High-Middle Tiber (HMT) or Low Tiber(LT)) and season (flood or drought conditions), respectively. The considered drivers are the following: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



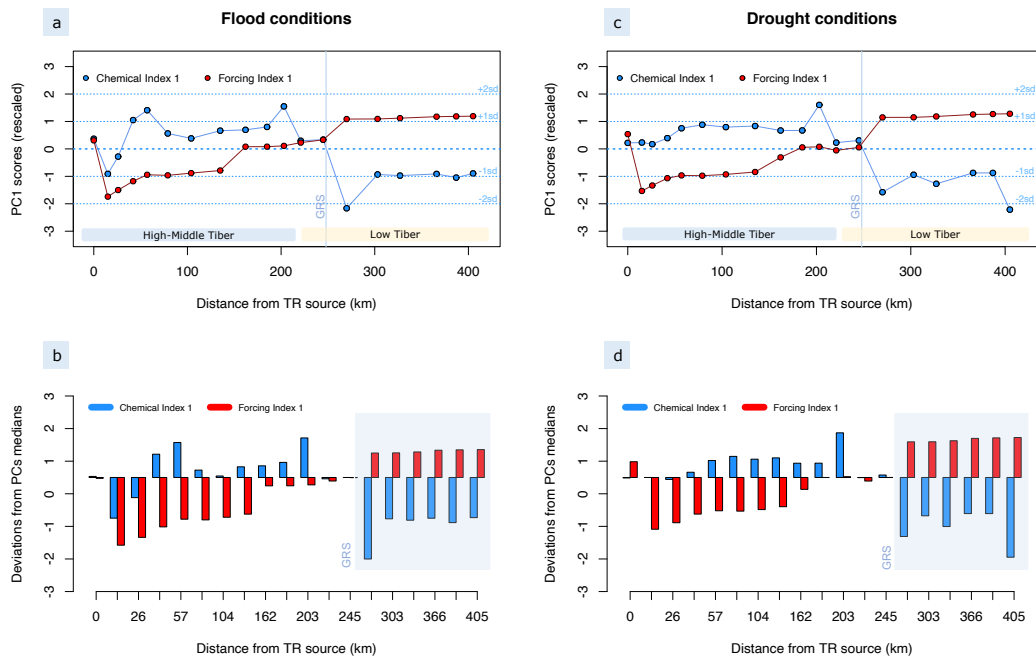


Figure 8: Chemical Index 1 and Forcing index 1 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and (b) bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS, while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

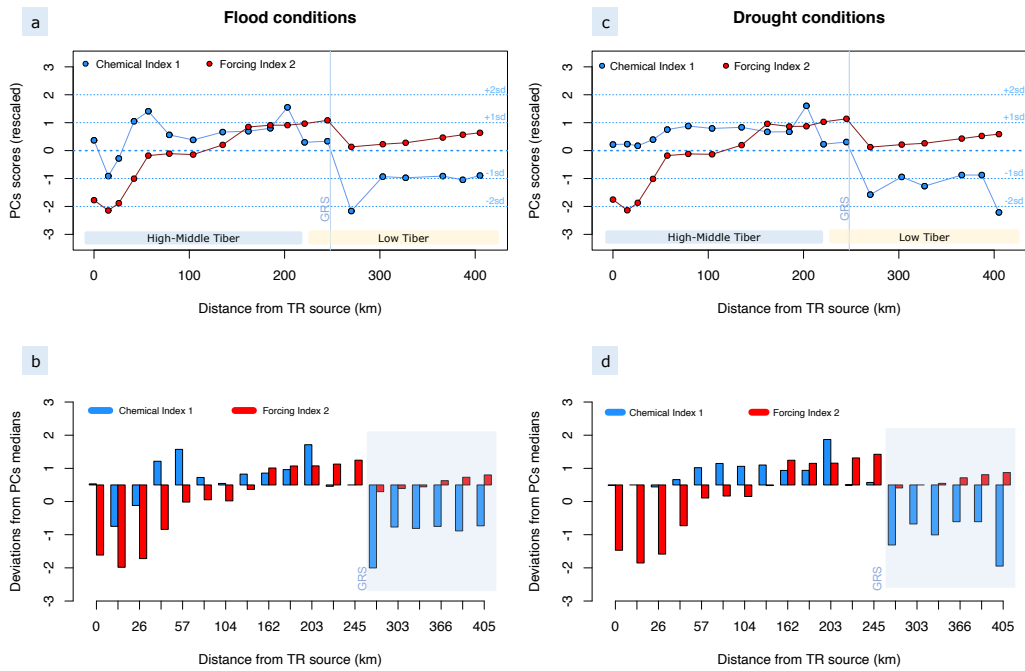


Figure 9: Chemical Index 1 and Forcing index 2 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and (b) bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS.

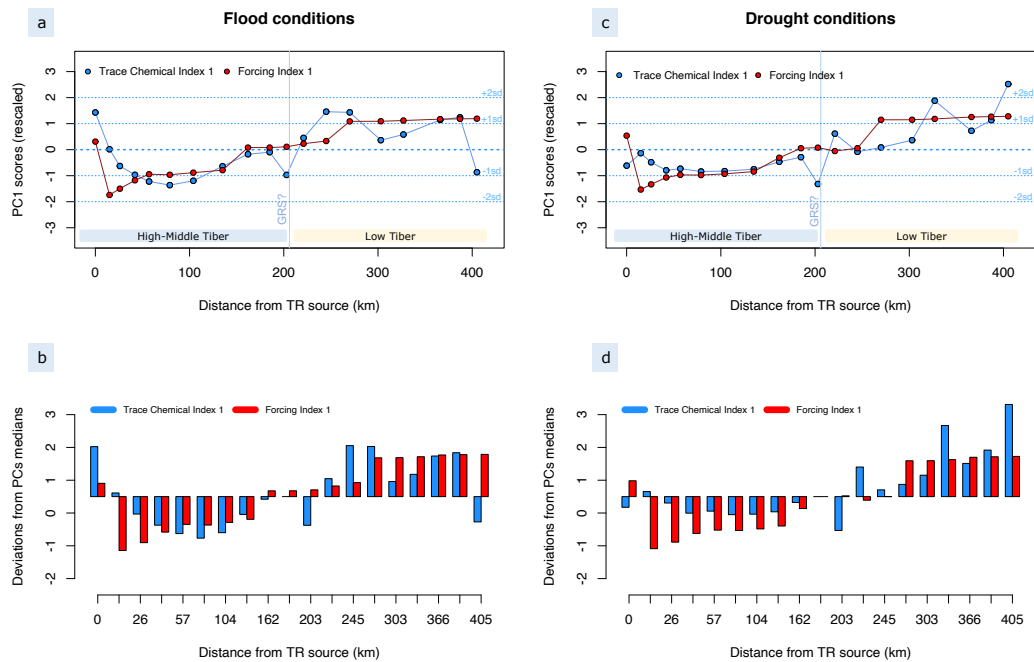


Figure 10: Trace Chemical Index 1 and Forcing index 1 for flood (a) and drought (c) hydrological conditions plotted versus the distance from the TR source and bar plots showing deviations from their respective medians (b and c). Vertical lines in (a) and (c) indicate the spacing of a potential GRS.